NO OXIDATION REACTION MECHANISMS OVER ZEOLITE CATALYSTS

by

Jason A. Loiland

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

Fall 2015

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by

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ACKNOWLEDGMENTS

There are many people I would like to acknowledge for helping me to complete this dissertation. First, with the deepest gratitude I would like to thank my advisor, Dr. Raul Lobo, for bringing me into his group and giving me the opportunity to conduct research under his guidance. He has taught me so much in the areas of catalysis and kinetics. I enjoyed taking his kinetics class during my first semester at the University of Delaware, and could tell from his teaching style that he would be a great advisor to work with. Raul has a wonderful personality and truly cares about the well-being of everyone in his group. I am especially fond of his great management style, as he allows his students space to independently work but makes himself immediately available whenever questions arise or a discussion is needed. He was always very interested in my career intentions after graduating, and wanted to make sure that my time at UD prepared me for meeting those goals as best as possible. Since I was interested in pursuing a career in industry after graduating, Raul nominated me for the Air Products Fellowship, which allowed me to do an internship during the summer of 2014. While at Air Products, I had the opportunity to work under Mr. Mike Popule in the Performance Materials Process R&D group. I very much enjoyed my time working there and learned a lot about how research is conducted in industry. Raul also encouraged me to attend many conferences and symposiums at which I could present my work to the scientific community. These were great opportunities for me to receive feedback on my work, meet many researchers, and learn about other important research topics. I would also like to thank Dr. Michael Klein, Dr. Bingjun Xu, and Dr.

Klaus Theopold for kindly agreeing to be on my Ph.D. committee and helping to improve this thesis.

I would also like to thank all members of Dr. Lobo's research group who have been at the University of Delaware during my time here: Dr. Andrew Foster, Dr. Jang Ho Yun, Dr. Adriana Aristizabal, Dr. Phuong Do, Dr. Qingling Liu, Dr. Ji Na, Dr. Takahito Moteki, Dr. Shewanigan Forsido, Dr. Matthew Wulfers, Dr. Jelvehnaz Mirzababaei, Dr. Trong Pham, Edward Schreiner, Jacob Weiner, Bahar Ipek, Eyas Mahmoud, Huibo Sheng, Molly Koehle, and Chen-Yu Chou. You have all taught me so much related to different aspects of chemical engineering and life in general, and it has been a pleasure working with you in the laboratory. In particular, I would like to thank Trong for helping me out with zeolite synthesis and different characterization methods (SEM, BET, XRD), offering me advice for job interviews, and also being a great friend to play tennis, racquetball, and volleyball with.

I also want to thank those who I have had the opportunity to collaborate with on various projects. Dr. Nagesh Peela was of immense assistance in teaching me how to use the high-throughput microreactor for catalyst screening tests (results presented in Chapter 6), and Dr. Matthew Wulfers was a great collaborator to work with on the investigation of the reverse water-gas shift reaction (results presented in Chapter 7). I would like to thank Dr. Nebojsa Marinkovic from Brookhaven National Laboratory, who was very helpful during our trip to the National Synchrotron Light Source (NSLS) and assisted with the analysis of the XANES data presented in Chapter 7 of this thesis (thank you also to Ed Schreiner and Huibo Sheng for coming along on the trip to BNL and taking shifts at the beamline!). Finally, I would like to acknowledge Dylan Shea, an undergraduate researcher in our group, for contributing to the results presented in Chapter 5; it was a pleasure to mentor you, and I am grateful for all of the experiments you planned and carried out. I hope you enjoyed working in our group, and I wish you the best of luck during your senior year and beyond!

I would also like to acknowledge the Department of Energy, Air Products, and the U.S. Army at Aberdeen Proving Ground for funding the various projects that I worked on during my time at the University of Delaware.

Most importantly, I would like to thank my family and close friends for all of your support over the years. To my parents, Randy and Bernadette, my sister, Julie, my Grandma, Geneva, my Aunt, Ann, and the rest of my family, I have tried to use all of the valuable things you have taught me through my life, and I thank you for all of your love over the years.

Finally, I dedicate this work to my fiancé, Stephanie: You are my best friend and biggest supporter, and have always been by my side to sustain me through this difficult and long process. I could not have completed this work without your constant love and encouragement, and I am grateful for the sacrifices and commitment you have made. You mean everything to me, and I am excited for our new life together in Texas and wherever else life may take us.

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ABSTRACT

"Lean-burn" engines such as diesel-powered vehicles and newer internal combustion engines operate at high air/fuel ratios to increase fuel efficiency and decrease CO and hydrocarbon emissions. However, the highly oxidizing environment leads to increased nitrogen oxide (NO_x) emissions, which cannot be effectively reduced to N₂ with conventional three-way catalytic converters. Over the past 30 years, the selective catalytic reduction of NOx with ammonia (NH3-SCR) using Fe- or Cu-exchanged zeolite catalysts has been developed to address the "lean-NO_x" problem. This technology has since been commercialized and is currently one of the most effective means of abating NO_x emissions released from mobile or stationary power sources. Small pore zeolites such as chabazite (CHA) are the state-of-the-art materials because of their very high NO_x conversion and exceptional hydrothermal stability. Much of the research on NH₃-SCR has focused on identifying the reaction mechanism and kinetics, and although great progress has been made, many details remain unknown or are widely debated. Numerous investigations have identified the oxidation of NO to NO₂ to be an important reaction in the mechanism, but the precise kinetic role of the reaction remains unclear. The primary goal of the research described in Part I of this dissertation (Chapters 1-5) has been to identify the mechanism of the NO oxidation reaction over zeolites and other microporous materials to better understand the catalytic sites responsible for activity, which will hopefully aid in understanding the role of NO oxidation in NH₃-SCR.

At temperatures between 298 K and 423 K, it is shown that NO oxidation is catalyzed by CHA zeolites in the proton (H+), sodium (Na+), and siliceous forms. Additionally, microporous carbons and the metal-organic framework (MOF) material Basolite A100 also showed substantial catalytic activity. Catalytic rates decreased with increasing temperature to yield negative apparent activation energies between -24.9 kJ mol⁻¹ and -37.5 kJ mol⁻¹. Reaction orders on all microporous materials at low conversion were measured to be second order with respect to NO concentration and first order with respect to O₂ concentration; the same reaction orders are observed for the gas-phase reaction. The catalytic properties of the samples are attributed to their ability to stabilize a $[N_2O_4]^{\ddagger}$ transition state within the micropores through van der Waals forces. Na-SSZ-13 samples exhibited faster catalytic rates than siliceous chabazite due to the additional presence of electrostatic forces stabilizing the transition state. An enhancement of catalytic rates on H-SSZ-13 was also observed and is the result of more complex interactions due to the formation of NO⁺ and NO₃⁻ in the zeolite pores, which can also stabilize the $[N_2O_4]^{\ddagger}$ transition state.

Different reactivity for the zeolite samples was observed at temperatures greater than 423 K. Reaction rates on H-SSZ-13 and Na-SSZ-13 now increased with increasing temperature, a clear indication that a different reaction mechanism occurs in this temperature regime. The reaction rates on siliceous CHA were low and unaffected by temperature above 423 K, indicating that the material has minimal catalytic activity in this temperature window and that framework aluminum atoms with exchanged cations are necessary to observe significant activity. For all samples, rates were proportional to NO and O₂ concentrations, in contrast to the low-temperature catalytic rates (second order in NO and first order in O₂). *In-situ* FTIR

studies revealed that NO⁺ coordinated at framework sites in the zeolite pores (Si–O⁻ (NO⁺)–Al) plays a direct role in the catalysis. Furthermore, it was found that NO⁺ is in equilibrium with gas-phase NO and that desorption of NO⁺ (as NO) yields an oxidized acid site (Si–O⁻–Al). No evidence of NO⁺ formation was observed over the siliceous zeolite samples. A working model of the NO oxidation reaction at high temperatures is proposed for acidic zeolites that is consistent with the observed form of the rate equation and the observed NO⁺ reaction intermediate.

Incorporation of copper into the zeolite framework resulted in substantially higher activity (by ~1-2 orders of magnitude) compared to the acid zeolites. A number of factors were observed to influence the activity of these samples, including zeolite framework, Cu loading, and pretreatment conditions. Cu-ZSM-5 exhibited superior NO oxidation activity compared to Cu-SSZ-13 and Cu-BEA. On Cu-SSZ-13, an investigation of Cu loading on reaction rates showed that rates normalized per gram of catalyst increased substantially with increasing Cu loading up to ~1 wt%. Cu loadings beyond 1 wt% resulted in only slight increases in the rate. Meanwhile, rates normalized per mol of Cu (turnover frequencies) decreased considerably with increased Cu loading up to ~1 wt%, and were relatively independent of Cu loading at higher levels. Samples reduced in a flow of 1% CO/He exhibited higher activity compared to samples pretreated in 5% O₂/He. Rates on Cu-zeolite samples pretreated in 5% O₂/He were observed to be first order with respect to NO and O₂ concentrations. For pre-reduced samples, the rate dependency on O₂ concentration changed to half order. DRIFTS spectra collected under *in-situ* conditions showed that different $N_x O_y$ surface species formed based on the Cu loading of the zeolite. A mechanism for the reaction on Cu-zeolites pretreated in 1% CO/He is presented and discussed.

Part II of this thesis (Chapters 6 and 7) investigates the chemistry of the reverse water-gas shift (RWGS) reaction, which is an important reaction for the conversion of CO_2 to value-added products. Specifically, the reaction mechanism of the RWGS reaction is examined on Fe/ γ -Al₂O₃ and Fe-K/ γ -Al₂O₃ catalysts at temperatures between 723 K and 753 K and atmospheric pressure. It is shown that both materials are excellent catalysts for the selective hydrogenation of CO₂ to CO, with selectivities in excess of 99%. Potassium had a remarkable effect on activity, as it increased rates by a factor of \sim 3, changed the rate-determining step of the reaction as verified by a change in the kinetic isotope effect using H_2/D_2 , and changed the rate orders with respect to CO_2 and H_2 . Iron, on both catalysts, was found to reduce to the +2 oxidation state under H_2 flow, and oxidize to the +3 oxidation state under CO_2 flow based on *in-situ* XANES. Iron is mostly in the +2 oxidation state under continuous equimolar flow of CO₂ and H₂. The catalysts were stable under excess H₂ but deactivated slowly under an equimolar mixture of CO_2 and H_2 (1-2%/h of the overall reaction rate). Gas-switching experiments (CO_2 or H_2 only) and DRIFTS spectra collected *in-situ* showed that stable intermediates formed on Fe-K/ γ -Al₂O₃ but not on Fe/γ -Al₂O₃. This suggests, but does not conclusively prove, that a redox mechanism is the only reaction pathway on the Fe/ γ -Al₂O₃ catalyst and is the predominant pathway on the Fe-K/ γ -Al₂O₃ catalyst. A detailed mechanistic analysis of the simpler Fe/ γ -Al₂O₃ showed that the redox mechanism is the main reaction channel for CO₂ hydrogenation, but that there is a hydrogen pool on the surface of the catalyst that provides or consumes hydrogen as needed to reform the sites that capture the oxygen of CO₂. We conclude that Fe/Al₂O₃ is a promising catalyst for practical applications of the RWGS reaction at the conditions investigated.

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Chapter 1

INTRODUCTION

1.1 Sources and Effects of Nitrogen Oxide (NO_x) Emissions

Anthropogenic nitrogen oxides (NO_x) are some of the most toxic and abundant air pollutants produced by combustion processes in automotive internal combustion engines, power plants, and other industrial processes [1]. Approximately 30 million tons of NO_x are emitted into the earth's atmosphere on an annual basis [2]. As Figure 1.1 shows, mobile sources and fuel combustion processes generate the majority of NO_x emissions in the United States. NO_x emissions lead to the greenhouse effect, stratospheric ozone depletion, tropospheric ozone formation, smog, and acid rain, all of which have significant negative impacts on both the environment and human health [3]. In the presence of air and ultraviolet (UV) light, nitrogen dioxide (NO₂) reacts to form ozone (O₃) and nitric oxide (NO), leading to unhealthy levels of ozone in the air. NO can then react with free radicals in the atmosphere (commonly generated by volatile organic compounds), leading to additional NO₂ creation and even higher ozone levels [4]. With regards to human health, the small size of NO_x molecules (~3.2 Å) allows them to penetrate deeply into the human lungs and react with other compounds, leading to respiratory problems (emphysema, bronchitis, asthma) or aggravation of existing heart diseases [5].



Figure 1.1. National nitrogen oxide (NO_x) emissions in the United States by source in 2011 (data taken from the EPA's website).

Although NO_x pollutants are still emitted in substantial amounts into the atmosphere on a global scale, the U.S. national average of NO₂ concentration in the atmosphere has decreased by 60% from 1980 to 2013 (Figure 1.2). This considerable decrease in emissions is largely a result of increased awareness of the numerous problems associated with NO_x, creation of more stringent emissions legislation, and the development of improved methods for reducing or eliminating NO_x emissions. Japan and nations of Western Europe are other countries in addition to the U.S. that have imposed similarly stringent legislation over the past several decades. However, as NO_x emissions decrease in the developed nations, emissions in developing nations

in Asia and South America are dramatically increasing due to rapid industrialization and limited emissions standards [6].



Figure 1.2. NO₂ air quality in the United States from 1980-2013 (figure taken from the EPA's website).

Awareness of the environmental and health problems associated with large emissions of anthropogenic NO_x, carbon monoxide (CO), sulfur dioxide (SO₂), particulate matter (PM), and hydrocarbons (HC) into the atmosphere began in the 1900s, and led to the creation and passage of the U.S. Clean Air Act (CAA) in 1955, which was the first attempt by the U.S. to control pollution on a national scale. However, it was not until 1970 that regulations for NO_x were added and enforced [7]. Since then, amendments have been passed every several years to decrease the maximum allowable NO_x emissions, and many other industrialized nations have followed suit and implemented NO_x emissions regulations [7]. Figure 1.3 shows the decreasing NO_x emissions standards in the U.S. for heavy-duty diesel engines from 1994-2010, as mandated by the Environmental Protection Agency (EPA). Most recently, regulations for diesel vehicles require another 5-fold reduction in the allowable NO_x concentration present in the exhaust stream [2].



Figure 1.3. EPA NO_x emissions standards for heavy-duty diesel engines from 1994-2010.

1.2 NO_x Emission Control Technologies

The decrease in NO_x emissions standards over the years has required the development of more efficient emission control technologies and catalysts. NO_x controls were introduced on a commercial level in the 1970s with the development of combustion modification technologies. These methods aimed at limiting NO_x formation, and consisted of reducing the flame temperature near burners, delaying

mixing, recirculating the flue gas, and controlling the air-to-fuel ratio to ensure fuel rich environments [7]. These early technologies were effective in decreasing the NO_x emissions by 25-45% [7]. For gasoline engine vehicle exhaust emissions, the threeway catalyst (TWC) was developed in the 1970s to simultaneously abate carbon monoxide (CO), unburned hydrocarbon (HC), and NO_x air pollutants [8]. The TWCs are typically platinum (Pt), palladium (Pd), and rhodium (Rh) used in some combination, and work by oxidizing CO to CO_2 , oxidizing hydrocarbons to CO_2 and H_2O_1 , and reducing NO_x to N₂. They are very effective and continue to be improved and used in the majority of today's vehicles, despite the significant cost associated with the precious metal catalysts. Diesel engines, however, have oxygen rich exhausts, and so while TWCs can easily oxidize CO and HC emissions under such conditions, the reduction of NO_x becomes very difficult [9]. Thus, alternative technologies were needed for diesel engines. Additionally, as most gasoline engines are now operated under lean-burn conditions (air-to-fuel ratio ~65:1) in order to increase fuel efficiency and minimize carbon emissions, specialized NO_x exhaust aftertreatment systems must be added for these systems as well.

Direct NO_x decomposition to N₂ and O₂ (2 NO \rightarrow N₂ + O₂) is an attractive method of NO_x reduction, as it represents a straightforward approach and is thermodynamically favored at temperatures below 1,173 K [10]. Most exhaust temperatures are well below 1,173 K, and direct decomposition would be especially attractive for low-temperature applications (T < 423 K) where other catalytic processes for NO_x removal are less effective. However, the reaction suffers from extreme kinetic limitations due to a high activation energy, and to date no effective catalysts have been identified. Additionally, the highly oxidizing environment of

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diesel and lean-burn gasoline engines adds to the difficulty of this approach. Cu-ZSM-5, one of the most effective NO_x decomposition catalysts, only showed conversion levels of ~10% across a narrow temperature operation window [11].

The initial attempts of using selective catalytic reduction (SCR) to decrease NO_x emissions started in the 1970s [7]. In this technology, urea (NH₂-CO-NH₂) is injected into the post-combustion stream at temperatures between 420 K and 1,000 K. The urea decomposes to ammonia (NH_3) and isocyanic acid (HNCO), and the HNCO is hydrolyzed to form additional NH₃ and CO_2 . The ammonia reacts with the NO_x over a catalyst to form N₂ and H₂O (Eqs. 1.1-1.3), and only a stoichiometric amount of NH₃ is required for complete NO_x conversion. In some instances, the NH_3 reducing agent is replaced with hydrocarbons such as methane (CH_4) or ethane (C_2H_6), which may be present in the diesel fuel; this process is referred to as HC-SCR [12]. The SCR activity depends on the composition of the NO_x stream. Standard NH₃-SCR is illustrated by Eq. 1.1, and is most common because the NO_x produced in diesel engines is typically in the form of NO, with only a minor fraction existing as NO_2 [12]. This reaction is a 12 electron redox process, in which eight electrons go to NO and four go to O_2 . Fast SCR (Eq. 1.2) results in significantly higher reaction rates, and occurs when the feed gas contains a 1:1 mixture of NO and NO₂ [12]. Finally, a feed consisting of mostly NO₂ leads to NO₂ SCR (Eq. 1.3). In this scenario, the SCR activity is reduced slightly compared to fast SCR, and also results in significant production of unwanted N₂O [13].

$$4NH_3 + 4NO + O_2 \to 4N_2 + 6H_2O \tag{1.1}$$

$$4NH_3 + 2NO + 2NO_2 \to 4N_2 + 6H_2O \tag{1.2}$$
$$4NH_3 + 3NO_2 \to \frac{7}{2}N_2 + 6H_2O \tag{1.3}$$

Vanadia promoted with tungsta over titania ($V_2O_5/WO_3/TiO_2$) was one of the initial SCR catalysts used for stationary sources of NO_x, and it is still widely used throughout industry [14]. Several problems still remain with the $V_2O_5/WO_3/TiO_2$ catalyst, though, which include its high activity for oxidizing SO₂ to SO₃, its rapid decrease in activity and selectivity at temperatures above 823 K due to its low thermal stability, and its toxicity [9]. As a result, many other catalysts have been investigated for both low-temperature and high-temperature SCR applications, including transition metal oxides (Fe, V, Cr, Cu, Co, Mn) [15-18], supported metal oxide catalysts [19-21], metal oxides supported on carbon [22], and zeolites [23, 24]. The large volume of research into these materials has resulted in NH₃-SCR becoming the predominant industrial technology employed for reducing NO_x emissions from both mobile and stationary sources [25].

Zeolites have emerged as very promising candidates to replace the standard $V_2O_5/WO_3/TiO_2$ SCR catalyst. In 1986, Iwamoto et al. [26] discovered that Cu-ZSM-5 (MFI) zeolite exhibited very high NH₃-SCR activity. This work initiated a wave of SCR research on this material and many other Cu- and Fe-zeolites, and sparked intense efforts over the past several decades to elucidate the SCR mechanism, identify the active sites, understand the causes and mechanisms of deactivation, and develop improved catalysts [27-30]. Figure 1.4 illustrates the superior SCR activity that commercial Cu- and Fe-zeolites exhibit relative to vanadium-based catalysts [9].



Figure 1.4. NO_x conversion profiles for Cu-zeolite, Fe-zeolite, and vanadium based SCR catalysts in gas mixtures containing 350 ppm NO, 350 ppm NH₃, 14% O₂, 5% CO₂, and 5% H₂O [9]. Reproduced with permission from *Catalysis Today* (Elsevier).

ZSM-5 (MFI), mordenite (MOR), beta (BEA), and more recently the chabazite (CHA) zeolite SSZ-13 have been the primary zeolites investigated for their abilities to catalyze SCR. Despite their thermal stability and overall effectiveness across a wide range of temperatures, zeolites do suffer from several problems. Most notably, these shortcomings include low activity in the presence of water vapor, susceptibility to dealumination at higher temperatures, and propensity to adsorbing hydrocarbons at low temperatures, which generate heat (by combustion) as the temperature is raised and damage the zeolite structure [31]. SSZ-13 and other small-pore zeolites (i.e., SSZ-62), however, have shown superior SCR activity and remarkable improvements with regards to the aforementioned weaknesses associated with other zeolite frameworks, and thus have garnered increased attention in recent years from both academia and industry [32, 33]. Figure 1.5 shows NO_x conversion profiles as a function of temperature for Cu-SSZ-13, Cu-ZSM-5, and Cu-BEA as measured by Kwak et al.

[29]. At low temperatures (150°C < T < 300°C), all three zeolites show similar NO_x conversion. At higher temperatures (T > 300°C) and in the presence of water vapor, the superior hydrothermal stability of Cu-SSZ-13 enables it to maintain NO_x conversion levels greater than 80%, while Cu-ZSM-5 and Cu-BEA show significant drop-offs in catalytic activity.



Figure 1.5. NO_x conversion profiles for Cu-SSZ-13, Cu-beta, and Cu-ZSM-5 in gas mixtures containing 350 ppm NO, 350 ppm NH₃, 14% O₂, and 2% H₂O [29]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

 NO_x storage and reduction (NSR) is another emerging technology for the control of NO_x emissions [34]. This concept was developed by researchers at Toyota in 1995, and involves continuous cycling of the engine between short periods of leanburn and rich-burn conditions [35]. First, during the lean-burn conditions, NO is oxidized to NO_2 , usually over a Pt catalyst, and then stored as nitrate on an alkaline

earth compound (typically BaCO₃ or BaO) [34]. Subsequently, during the rich-burn period (air-to-fuel ratio < 14.6), the stored NO_x is released and reduced to N₂ by reductants present in the rich conditions. NSR technology is a very practical approach for reducing NO_x emissions, although much uncertainty remains regarding the NSR mechanism. Additionally, despite their promise, NSR catalysts are still prone to sulfur poisoning and thermal degradation [36]. NO oxidation over Pt catalysts has been investigated in great detail because of its relevance in NSR technology, and it has been discovered that larger Pt particle sizes with lower dispersion significantly increase the NO oxidation rates [37, 38]. The storage and reduction cycles of the NSR approach are illustrated in Figure 1.6.



Figure 1.6. NSR mechanism scheme over $Pt/Ba/Al_2O_3$ catalyst and NO_x concentration profiles at the exit during lean and rich burns [39].

1.3 NH₃-SCR Reaction Mechanism and the Importance of NO Oxidation

The NH₃-SCR reaction mechanism has proven to be very complex, and many issues remain unresolved after several decades of research. Key factors that contribute to the difficulty of identifying the reaction mechanism are the multitude of metal

species that form in Fe- or Cu-zeolites, the differences between fast SCR (NO/NO₂ ratio of 1) and standard SCR, which do not appear to follow the same reaction pathways, the occurrence of side reactions (N₂O formation, NH₃ oxidation to NO_x), and the presence of Brønsted acid sites. Brønsted acid sites are typically present in the zeolite, either because the sample was not completely exchanged to its metal form or because new sites are generated upon reduction of the metal sites, but their exact role in the mechanism remains unclear. Figure 1.7 summarizes the current understanding of SCR reaction schemes over metal-exchanged zeolites.



Figure 1.7. SCR reaction pathways over metal-exchanged zeolites [12]. Reproduced with permission from *Catalysis Reviews: Science and Engineering* (Taylor & Francis LLC).

The mechanism begins with NO oxidation to generate NO₂. The NO₂ can then go in one of two different pathways to form the products N₂ and H₂O. In the first pathway, NO₂ adsorbs onto the catalyst and forms reactive surface species such as nitrate (NO₃⁻) and nitrosonium (NO⁺) ions. The formation of these species constitutes the primary reaction pathway towards the production of N₂ and H₂O. After the formation of NO⁺ at a Brønsted acid site, nitrates interact with the released proton to form nitric acid (HNO₃), which subsequently reacts with NO to form nitrous acid (HNO₂) and NO₂. The NO⁺, meanwhile, can react with H₂O to form HNO₂ and regenerate the Brønsted acid site. HNO₂ formed from the NO₃⁻ and NO⁺ pathways then interacts with NH₃ to form ammonium nitrite (NH₄NO₂), which quickly decomposes at temperatures above 373 K to yield N₂ and H₂O. In the second pathway, NO₂ reacts with NO to form N₂O₃. In the presence of NH₃ and H₂O, N₂O₃ forms NH₄NO₂, which yields the products.

Although the pathway illustrated in Figure 1.7 begins with an NO oxidation step, recent evidence suggests that the reaction is not always kinetically important in NH₃-SCR, specifically when the reaction is catalyzed over Cu-SSZ-13 [40]. NO oxidation rates on Cu-SSZ-13 were shown to be much slower compared to NH₃-SCR rates [40]. Additionally, water significantly inhibits NO oxidation on Cu-SSZ-13 but has minimal impact on the NH₃-SCR reaction. These results indicate that NO oxidation is not the rate-determining step (RDS), as the rates and effects of water on the reactions would be expected to be similar if it were the RDS.

Determining the roles of metal sites and Brønsted acid sites in the SCR mechanism has also been the subject of many investigations. It was previously thought that the Cu or Fe ions oxidize NO to NO₂, while the SCR reaction takes place on ammonia adsorbed on the Brønsted acid sites. However, it has been shown that the

SCR activity does not depend on the number of Brønsted acid sites over Cu-MFI, Cu-CHA, and Fe-MFI [27, 41-43], and thus it seems that the SCR reaction actually occurs entirely on the metal sites. The Brønsted sites may influence the distribution and proximity of metal sites, which in turn determines the formation of dimer species. Over Fe-ZSM-5, most authors assert that isolated Fe³⁺ sites catalyze standard SCR [44-46], while others consider that oligomeric Fe-oxo structures may be active as well [47, 48]. Over Cu-SSZ-13, Gao et al. [28] have shown that the active site for SCR seems to depend on the catalyst composition and reaction temperature. Their investigation showed that standard SCR on Cu-SSZ-13 is catalyzed by transient Cudimers at low Cu loadings (Cu/Al 0.016) and low temperatures (T < 523 K). These dimers dissociate at temperatures between 523 K and 623 K, causing rates to decrease. At higher temperatures (T > 623 K), Cu^{2+} monomers form in the faces of the sixmembered rings (6MR) and become the active sites, causing rates to increase. At intermediate Cu loadings, Cu²⁺ ions existing as [Cu(OH)]⁺ within the CHA cages near the 8-memerbered rings (8MR) are also active in low-temperature SCR. At high Cu loadings, stable Cu-dimers form, which do not dissociate at temperatures above 623 K; instead, they block pore openings, decrease the catalytic ability of the material, and decrease the catalyst selectivity by causing higher rates of NH₃ oxidation.

The redox cycle of metal cations is another key aspect of the NH₃-SCR reaction mechanism that remains uncertain. The reduction part, which is better understood, is thought to involve the adsorption of NH₃ and NO onto Cu^{2+} (or Fe³⁺) sites to form NH₄NO₂, which decomposes to N₂ and H₂O and reduces Cu^{2+} to Cu^+ (or Fe³⁺ to Fe²⁺). The oxidation part of the redox cycle, which reoxidizes the metal site and involves the activation of NO, is less understood. It is thought that NO oxidation

may accompany the oxidation of the catalyst, but it has not yet been established. Janssens et al. [49] have recently proposed a comprehensive redox reaction pathway that describes both standard and fast SCR on Cu-SSZ-13. The proposed mechanism is shown in Figure 1.8. The mechanism begins with NO and O₂ reacting in the presence of a Cu^+ atom; the Cu^+ atom is oxidized to Cu^{2+} and an adsorbed NO_3^- species forms (step 1). NO from the gas phase then reacts with the adsorbed NO_3^- to form nitrite (NO_2^-) on Cu^{2+} (step 2). Cu^+ can also be directly oxidized by NO₂, which forms a nitrite (NO_2) species (step 8). These steps constitute the oxidation part of the redox cycle. Subsequently, the nitrites react with NH_3 to release H_2O and N_2 (steps 3 and 4). Cu^{2+} -OH⁻ forms, and undergoes further reaction with NO and NH₃. Cu^{2+} -OH⁻ is reduced to Cu^+ in the process and additional H₂O and N₂ are released (steps 5-7). Steps 5-7 represent the reduction part of the redox cycle. Note that the proposed mechanism only involves isolated Cu sites, excluding any role for Cu-dimers or Brønsted acid sites. Cu-dimers may play a role in the mechanism at higher Cu loadings, while Brønsted acid sites have a limited effect on SCR activity and serve as adsorption sites for NH₃.



Figure 1.8. Proposed reaction mechanism for the standard and fast SCR reactions over Cu-zeolite [49].

1.4 Gas-phase and Catalytic NO Oxidation

The homogeneous gas phase nitric oxide (NO) oxidation by O₂ is peculiar in the sense that the reaction rate constant decreases with increasing temperature, resulting in irregular Arrhenius behavior and yielding a negative apparent activation energy (~ -4.4 kJ mol⁻¹) [50]. The reaction is second order in NO and first order in O₂, a dependency that has been verified at total pressures between 25 mbar and 1 bar. NO oxidation is reversible and is highly exothermic ($\Delta H^{\circ} = -114$ kJ mol⁻¹) [51], and thus conversion to NO₂ is favored at lower temperatures. Despite its low activation energy, significant entropic barriers associated with forming a termolecular transition state prevent the reaction from occurring rapidly at ambient temperatures. Several reaction routes have been proposed for homogeneous NO oxidation. The first is truly termolecular, and involves two molecules of NO and one molecule of O_2 simultaneously colliding to form a complex, which then dissociates in a single step to form two molecules of NO₂. More recently, though, researchers have preferred to describe the reaction by a two-step mechanism involving the formation of an intermediate, as this is more probable to occur compared to a termolecular reaction involving three-body collisions [50]. Two such pathways have been proposed in the literature. The first mechanism (Scheme 1.1) begins with two molecules of NO reacting to form an NO dimer (ONNO), as illustrated by Step 1. This step is reversible and reaches equilibrium. Step 2 is then the kinetically relevant step, and involves the reaction between ONNO and O₂, which proceeds through a termolecular transition state with a composition of $[N_2O_4]^{\ddagger}$ to form two molecules of NO₂.

Scheme 1.1 Proposed two-step reaction pathway for homogeneous NO oxidation involving the reaction between two NO molecules in Step (1), followed by the reaction between an NO dimer (ONNO) and O_2 in Step (2).

(1) NO + NO \implies ONNO (2) ONNO + O₂ \implies 2NO₂

Eq. 1.4 shows the rate equation for the reaction pathway depicted in Scheme 1.1, under the assumption that Step 1 is quasi-equilibrated so that the rate constants associated with Step 1 (k_1 and k_{-1}) are much greater than that associated with Step 2 (k_2). Additionally, note that the denominator term becomes negligible when $k_2 \ll k_{-1}$. This rate equation is consistent with the experimentally observed reaction orders of 2 for NO and 1 for O₂ for homogenous NO oxidation.

$$r = \frac{k_2 K_1 [NO]^2 [O_2]}{1 + \frac{k_2}{k_{-1}} [O_2]} \tag{1.4}$$

The second two-step mechanism (Scheme 1.2) begins with a pre-equilibrated reaction between NO and O₂ to form an NO₃ (ONOO) intermediate (Step 1). The second step is kinetically limiting and involves the reaction between the NO₃ intermediate and another molecule of NO to form two molecules of NO₂, again proceeding through an $[N_2O_4]^{\ddagger}$ transition state.

Scheme 1.2. Proposed two-step reaction pathway for homogeneous NO oxidation involving the reaction between NO and O_2 molecules in Step (1), followed by the reaction between ONOO and NO in Step (2).



The rate equation for the reaction pathway illustrated in Scheme 1.2 is shown in Eq. 1.5, under the assumption that Step 1 is quasi-equilibrated. As a result, the rate constants k_1 and k_{-1} are much greater than k_2 , and the denominator term becomes negligible. As was the case for the two-step reaction pathway shown in Scheme 1.1, the rate equation for Scheme 1.2 is consistent with the experimentally observed reaction orders of 2 for NO and 1 for O₂. These rate equations (Eqs. 1.4, 1.5) clearly show that both two-step mechanisms (Schemes 1.1, 1.2) are possible pathways for homogeneous NO oxidation, although it remains undetermined as to the occurrence or relative contributions of each pathway.

$$r = \frac{k_2 K_1 [NO]^2 [O_2]}{1 + \frac{k_2}{k_{-1}} [NO]}$$
(1.5)

The two-step molecular processes illustrated in Schemes 1.1 and 1.2 can be used to explain the negative apparent activation energy of -4.4 kJ mol⁻¹ observed for homogeneous NO oxidation [52]. The apparent rate constants in Eqs. 1.5 and 1.6 are actually products of the equilibrium constants (K_1) and the intrinsic rate constants (k_2) associated with elementary steps (1) and (2), respectively, in the reaction pathways. The formation of a stable intermediate (ONNO in Scheme 1.1 and ONOO in Scheme 1.2) in Step (1) is an exothermic process, and thus K_1 decreases with increasing temperature according to the van't Hoff relation (Eq. 1.6). K_1 must be much larger than k_2 so that it dominates the temperature dependence of the apparent rate constant and gives rise to falling reaction rates with rising temperatures.

$$\frac{dlnK}{dT} = \frac{-\Delta H}{RT^2} \tag{1.6}$$

Figure 1.9 illustrates a qualitative energy diagram of the reaction pathway described in Scheme 1.2.



Reaction Coordinate

Figure 1.9. Qualitative energy diagram of the homogeneous NO oxidation reaction pathway from Scheme 1.2.

The *catalytic* NO oxidation is an important reaction in a number of chemical processes, with applications ranging from environmental chemistry (NO_x reduction) to the production of valuable chemical products such as nitric acid and aromatic nitrates [53]. The reaction is currently investigated in the context of diesel emissions control technologies to abate the release of NO_x. As mentioned in Section 1.3, evidence from various reports suggests that the role of NO oxidation in the NH₃-SCR mechanism is different depending on the type and composition of the zeolite catalyst used. For instance, previous investigations [54-59] have implicated NO oxidation as the rate-determining step (RDS) of standard SCR over H-ZSM-5 and certain Fe- or Cu-

zeolites. However, other reports [14, 40] have shown that NO oxidation is clearly not the RDS. Over Cu-SSZ-13, currently the state-of-the-art material for NH₃-SCR, there is growing consensus that NO oxidation is not the RDS, although the precise role of NO oxidation in the reaction mechanism remains unresolved [28, 40].

Catalytic NO oxidation has been investigated over various materials. Richter [60] established in an early investigation that activated carbon materials could effectively catalyze the reaction at temperatures between 298 K and 393 K. Later Richter et al. [61] reported NO conversions over NH₄-mordenite (MOR) and NH₄-Y at 373 K of up to 98% and 92%, respectively, revealing that acid sites were not necessary to achieve high conversion levels. Halasz et al. [62] suggested that Brønsted acid sites in H-ZSM-5 samples are important for catalyzing NO oxidation, and Schmeisser et al. [63] established that NO oxidation increases with decreasing temperature from room temperature to 373 K over a commercial Cu-zeolite, resulting in a negative apparent activation energy. Järås and coworkers [59, 64, 65] studied NO oxidation and NH₃-SCR over MOR zeolites with different compositions and ranked the materials based on the observed reaction rates in the order of H-MOR > Fe-MOR > Cu-MOR for NO oxidation, but in the reverse order for NH₃-SCR. The NO oxidation rate was dependent on the aluminum content for the H-MOR catalyst, and the authors suggested that surface NO⁺ is involved in the catalytic cycle [65]. Yogo and coworkers [66-68] observed that the NO oxidation rate on Na-H-ZSM-5 increased with increasing proton exchange level. From this observation, they deduced that acid sites in ZSM-5 were responsible for the activity. They also noted a strong inhibition of the reaction by water. Stakheev et al. [69] found that H-ZSM-5 was in fact more active than Co/H-ZSM-5 catalysts with low levels of Co exchange (< ~30%) and suggested

that the Co ions only become catalytically active at increased loadings when cobalt oxide particles form. Lonyi et al. [70] recently observed NO oxidation activity over H-ZSM-5 at temperatures between 573 K and 823 K, though it was substantially lower compared to Co-H-ZSM-5; the activity of H-ZSM-5 was assigned to the Brønsted acid sites, though the authors did not propose a reaction mechanism. Miller et al. [71] observed acid forms of ZSM-5 and MOR to be effective for NO oxidation at 573 K, while USY and silica-alumina exhibited poor activity.

Several groups have shown that Cu-SSZ-13 is capable of catalyzing NO oxidation, but typically only at higher Cu loadings (Cu/Al > 0.3) [28, 30]. Cu-dimers (Cu_xO_y) form at higher Cu loadings, and the amount formed directly correlates to an observed increase in NO oxidation activity. At lower loadings, on the other hand, copper only exists as isolated Cu²⁺ species within the SSZ-13 framework; these isolated sites are active for NH₃-SCR but are ineffective in catalyzing NO oxidation, at least at temperatures below 773 K. Fe-zeolites, particularly Fe-ZSM-5, have been shown to be much more effective NO oxidation catalysts than Cu-zeolites. Metkar et al. [54], for example, observed a maximum NO conversion of 53% on Fe-ZSM-5 at 623 K compared to only a maximum conversion of 36% on Cu-CHA at 673 K. Ellmers et al. [72] showed that NO oxidation rates on Fe-ZSM-5 decreased with increasing Fe content, which suggested that a small minority of isolated Fe sites catalyze the reaction in this material. It remains unresolved as to why Cu-SSZ-13 is such an effective catalyst for NH₃-SCR but a relatively poor catalyst for NO oxidation [49].

In addition to the relevance of NO oxidation to SCR chemistry, the reaction plays a significant role in NO_x-mediated homogeneous pathways of CH₄ oxidation to

produce formaldehyde (HCHO). Iglesia and coworkers [73] have shown that CH_4-O_2 mixtures in the presence of NO_x , particularly NO_2 , exhibit significant reaction rate increases and HCHO yield. Lastly, NO oxidation is part of nitric acid synthesis via the Ostwald process (Eqs. 1.7-1.9). An effective high-temperature catalyst for NO oxidation in this process would enable the gas to be directly converted without the need for a cooling stage in the process.

$$4NH_3 + 50_2 \to 4NO + 6H_2O \tag{1.7}$$

$$2NO + O_2 \rightarrow 2NO_2 \tag{1.8}$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \tag{1.9}$$

1.5 Scope of Dissertation

The work presented in this dissertation is divided into two parts. Part I (Chapters 1-5) is focused on the chemistry of catalytic NO oxidation on zeolites and microporous materials. Part II (Chapters 6-7) addresses the chemistry of the reverse water-gas shift (RWGS) reaction on metal catalysts, with a particular focus on identifying the reaction mechanisms on Fe/Al₂O₃ and Fe-K/Al₂O₃. Chapter 8 presents the overall conclusions that were drawn from each investigation, and also provides recommendations for future research directions.

Despite the significant number of investigations that have been conducted by researchers regarding the NO oxidation reaction, a detailed knowledge of the reaction mechanism was still undetermined prior to this thesis. This dissertation focuses on developing a fundamental understanding of the NO oxidation reaction mechanisms at low and high temperatures on zeolites and other microporous materials. Specifically, the roles that the framework, acid sites, and copper sites play in the mechanisms are investigated. The identification of important surface intermediates with mechanistic roles and the effects of gas composition on the reaction have also been thoroughly examined.

Chapter 2 provides background information on the catalytic materials, the analytical techniques used for sample characterization, and the collection of the experimental data presented in this dissertation. The catalysts used for these investigations of NO oxidation include zeolites, microporous carbons, and metal-organic frameworks (MOFs). Additionally, a description is provided of the reactor setup used to measure reaction rates and perform kinetic experiments.

Chapter 3 presents the low-temperature NO oxidation reaction mechanism on microporous materials (zeolites, microporous carbons, MOFs). The investigation shows that the reaction is catalyzed by chabazite (CHA) zeolites in the proton (H⁺), sodium (Na⁺), and siliceous forms, by the MOF Basolite A100, and by microporous carbons at temperatures between 298 K and 423 K. Transition state theory calculations show strong enthalpic benefits associated with confinement, benefits that lead to high reaction rates despite significant entropic losses.

Chapter 4 presents the high-temperature NO oxidation reaction mechanism on H-zeolites. Reaction kinetics over three zeolite structures (SSZ-13, ZSM-5, BEA) are investigated at temperatures above 423 K using a plug-flow microreactor and *in-situ* FTIR spectroscopy. *In-situ* FTIR studies reveal that NO⁺ coordinated at framework sites in the zeolite pores (Si–O⁻(NO⁺)–Al) play a direct role in the catalysis, and they also reveal that the NO oxidation rate is proportional to the amount of NO⁺ present in the sample. A working model of the reaction mechanism for the high-temperature NO

oxidation reaction is proposed for acidic zeolites that is consistent with the observed form of the rate equation and the observed NO⁺ reaction intermediate.

Chapter 5 discusses the NO oxidation reaction catalyzed by Cu-zeolites. Specifically, the effects of zeolite framework (SSZ-13, ZSM-5, BEA), Cu loading, and pretreatment conditions on reactivity are investigated for the NO oxidation reaction. Rate measurements showed that pretreatment of the Cu-zeolites in 1% CO/He resulted in substantially higher catalytic activity compared to pretreatment in 5% O₂/He, which indicates that Cu⁺ cations are more active than Cu²⁺ cations in catalyzing the reaction. UV-vis spectra are presented showing the Cu species present after different gas treatments, and diffuse reflectance infrared Fourier transform (DRIFT) spectra are presented showing the N_xO_y surface intermediates that form under *in-situ* conditions. Finally, a proposed reaction model for the reaction on reduced Cu-zeolites is discussed.

The focus of the thesis shifts to the chemistry of the reverse water-gas shift (RWGS) reaction in Chapters 6 and 7. This project came about during my third year at the University of Delaware with a collaboration between Dr. Lobo's research group and the U.S. Army Research Development and Engineering Command located at Aberdeen Proving Ground in Aberdeen, Maryland. The aim of this research collaboration was to develop effective and stable heterogeneous catalysts for the hydrogenation of carbon dioxide (CO₂), with the ultimate goal being to form methanol (CH₃OH) with high selectivity through a two-step reaction process. In the first step, the RWGS reaction takes place to produce CO and H₂O from a reactant mixture of CO₂ and H₂. In the second step, methanol production occurs from the CO/CO₂/H₂ gas mixture exiting the RWGS reactor, with the yield depending primarily on the CO

concentration in the gas stream. As part of my thesis work, my objective was to investigate the first step in the CO₂ hydrogenation process and identify an effective and cheap RWGS catalyst. Chapter 6 presents an overview of CO₂ hydrogenation and the RWGS reaction, and includes a discussion regarding the catalysts that have been investigated in the literature or used industrially. Additionally, the chapter presents the materials we identified as promising RWGS catalysts and includes details of their synthesis procedures. The materials were screened for their RWGS activities and selectivities using a high-throughput microreactor (HTM), and the results showed that platinum (Pt) materials (Pt/CeO₂, Pt-Ce/ZrO₂) exhibited the highest CO₂ conversion levels. Additionally, Fe/ γ -Al₂O₃ and Fe-K/ γ -Al₂O₃ showed reasonably good activity (~15-35% lower activity than Pt materials) and very high CO selectivity (> 99%). The Fe-based materials are significantly cheaper alternatives to Pt-based catalysts, and thus were selected for further kinetic and mechanistic investigations.

Chapter 7 presents the study of the RWGS reaction on the Fe/ γ -Al₂O₃ and Fe-K/ γ -Al₂O₃ catalysts. Both materials exhibit fast catalytic CO formation rates and high CO selectivity (>99%) at temperatures between 723 K and 753 K. Addition of potassium to the Fe/ γ -Al₂O₃ material (Fe/K mass ratio = 1.24) led to a threefold increase in reaction rate, but also resulted in a higher rate of deactivation. Gasswitching experiments suggest that a redox mechanism is the only reaction pathway on the Fe/Al₂O₃ catalyst, and is the predominant pathway on the Fe-K/Al₂O₃ catalyst. The potassium promoter activates a secondary pathway for CO formation, which is probably the so-called associative pathway.

Chapter 8 concludes the thesis with an overview of the major findings and accomplishments. Additionally, several proposed ideas for future research are

presented on topics directly or closely related to the thesis work. Proposed areas of research that are discussed include catalysts for low-temperature SCR, materials for NO_x capture, methods to improve the stability of Fe-K/Al₂O₃ for the RWGS reaction, and further mechanistic studies of both reactions.

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Chapter 2

EXPERIMENTAL: MATERIALS AND METHODS

This chapter provides essential information on the foundations of the experimental techniques used to characterize the materials and collect the data reported in this dissertation related to studying the NO oxidation reaction. The chapter begins with an overview of the microporous materials that were investigated, and additionally includes a description of the reactor setup that was used for catalytic testing. Specific details on how reaction rates were measured are presented in subsequent chapters. Finally, I introduce the characterization techniques that were used to analyze materials as related to crystallinity, surface area, pore size, and elemental composition. Further details on the synthesis of these materials and how the characterization experiments were performed are provided in subsequent chapters.

2.1 Microporous Catalysts for NO Oxidation

Three types of high surface area microporous catalysts were investigated for their ability to catalyze the NO oxidation reaction: (1) zeolites, (2) carbon molecular sieves, and (3) metal-organic frameworks (MOFs).

2.1.1 Zeolite Catalysts

Zeolites are microporous, crystalline materials comprised of TO₄ tetrahedra (T = any tetrahedral species, commonly Si, Al, B, or P) that link through apical oxygen atoms to form three-dimensional lattice structures [1]. The open frameworks consist of pores, channels, windows, rings, cages, and cavities which allow for molecules to

diffuse in and out as well as adsorb or undergo reactions within the structure. Typical T atoms include Si^{IV}, Al^{III}, B^{III}, Fe^{III}, Ga^{III}, or P^V. Zeolites composed entirely of [SiO₄] are referred to as siliceous zeolites, and are unattractive for most catalytic applications because they possess no active sites [2]. As a result, other heteroatoms, such as those mentioned previously, are often substituted into the framework during the material synthesis. Incorporation of trivalent Al^{III} atoms into a siliceous zeolite results in a charge deficiency that must be compensated by the presence of a positively charged cation in the porous system. Commonly, zeolites contain Brønsted acid sites, which are hydroxide groups bridged between aluminum and silicon atoms within the framework (Si-OH-Al) that give rise to the acidic strength of the zeolite [3]. The Si/Al ratio of the zeolite is controlled during the synthesis procedure, and can range from 1 to ∞ . Higher Si/Al ratios increase the hydrothermal stability and hydrophobicity of the zeolite, as the structure is less prone to dealumination or attacks from water. According to Lowenstein's rule, Si/Al ratios less than 1 cannot be obtained because of the unfavorable electrostatic repulsions between the negative charges of adjoining $[AlO_4]^-$ [4]. Therefore, Al-O-Al bonds are not present within zeolite frameworks. Post-synthesis ion exchange methods can be used to replace acid sites with other interstitial cations (Na⁺, K⁺, Ca²⁺, Cu²⁺, ...) and control cation loadings. The presence of these charge-compensating cations inside the zeolite pores leads to catalysts with different properties, adsorption, or ion exchange characteristics. Additionally, cations with the ability to change oxidation states, such as Cu and Fe, can be incorporated to facilitate redox catalysis.

Zeolites possess broad applications in catalysis, adsorption, and ion exchange due to their numerous framework types (small-, medium-, and large-pore) and varied

compositions [5]. These physical and chemical properties are controlled through synthesis methods and tailored for specific applications. To date, more than 200 different zeolite frameworks have been synthesized, although only a few have found widespread industrial application. These include beta (BEA), faujasite (FAU), ZSM-5 (MFI), mordenite (MOR), chabazite (SAPO-34), zeolite P (GIS), zeolite A, zeolite L, MCM-22, and SAPO-11 [1]. Main catalytic uses of zeolites in industry include catalytic cracking and reforming [6], methanol-to-gasoline (MTG) processes [7], xylene isomerization [8], benzene oxidation to phenol [9], NO_x emissions control [10], and methanol-to-olefin (MTO) processes [11]. Table 2.1 lists the physical properties of several common zeolites [12].

Common Name	3-Letter Code	Channels	Window or Channel Diameter (nm)	Pore Volume (mL g ⁻¹)	Si/Al
Zeolite A	LTA	3D, cages connected by windows, cubic	0.45	0.30	1
Zeolite X	FAU	3D, cages connected by windows, tetragonal	0.75	0.35	1-1.5
Zeolite Y	FAU	3D, cages connected by windows, tetragonal	0.75	0.35	≥ 2.5
Mordenite	MOR	1D, two straight, parallel channels	0.70; 0.65	0.20	≥ 5
Zeolite L	LTI	1D, one straight channel			
ZSM-5	MFI	2D, one straight, one sinusoidal, mutually perpendicular channels	0.55	0.15	≥ 10
Beta	BEA	3D, two straight, one sinusoidal, perpendicular channels	0.76; 0.64	0.25	≥5

 Table 2.1. Physical properties of common zeolite frameworks.

SSZ-13 (CHA), ZSM-5, and BEA are the zeolites investigated in this thesis for their ability to catalyze NO oxidation. Figure 2.1 provides illustrations of these zeolite frameworks and information on their pore sizes. CHA zeolites have the R3m space group, and a hexagonal setting with unit cell dimensions of $a_{\rm H} = 13.85$ Å, $c_{\rm H} = 14.94$ Å. The basic building units of CHA zeolites are double 6-membered rings (D6MR) which are stacked in an ABCABC... sequence to make up the tetrahedral framework, and create a three-dimensional pore system with 8-ring pore windows of diameters of ~3.8 Å [13]. Because of the small pore size, molecules such as argon (3.84 Å) and methane (3.8 Å) can rapidly diffuse into and be adsorbed by CHA, while larger molecules such as propane (4.3 Å), n-butane (4.3 Å), or iso-butane (4.9 Å) slowly adsorb or are completely excluded. The surface area (S.A.) and microporous volume of a good sample of SSZ-13 are ~ 650 m² g⁻¹ and 0.27 cm³ g⁻¹, respectively. SSZ-13 is favored over other zeolites for SCR processes because of its small-pore structure, enabling it to resist dealumination from hydrothermal aging (in acid) and avoid structure collapse due to hydrocarbon adsorption and combustion [13]. ZSM-5 zeolites have the *Pnma* space group and an orthorhombic crystal system with unit cell dimensions of a = 20.07 Å, b = 19.92 Å, c = 13.42 Å. The framework contains straight and sinusoidal 10-ring channels with openings of ~5.6 Å that run along only two crystallographic directions. Nonetheless, molecules may move along all three crystallographic directions within ZSM-5. ZSM-5 can be synthesized with Si/Al ratios ranging from ~8 to ∞ , and has a S.A. of ~400-425 m² g⁻¹ and microporous volume of $0.14 \text{ cm}^3 \text{ g}^{-1}$. Zeolite BEA has the $P4_122$ space group, and a tetragonal crystal system with unit cell dimensions of a = 12.66 Å, c = 26.41 Å. BEA has a 3D channel system

with 12- and 6-membered rings. BEA zeolites have a S.A. of ~680-700 m² g⁻¹ and microporous volume of 0.17 cm³ g⁻¹.



Figure 2.1. Pore size (Å) and framework illustration for SSZ-13, ZSM-5, and BEA zeolites.

2.1.2 Carbon Molecular Sieves

Carbon molecular sieves are disordered forms of graphitic carbon produced from the pyrolysis and activation of organic materials at high temperatures [14]. These materials have important applications in gas adsorption, catalysis, and phase separation [15]. Their porous structures typically contain combinations of micropores (< 20 Å), mesopores (20-500 Å), and macropores (> 500 Å) [14]. The pores are generally slitlike in shape, and taper from macro- to meso- to micropores, which results in excellent thermodynamic and kinetic properties. These materials exhibit adsorption volumes and surface areas up to 0.5-0.8 cm³ g⁻¹ and 700-1,800 m² g⁻¹, respectively [16]. Three commercial carbon molecular sieves (Supelco) were used in this thesis: Carboxen 569, Carboxen 1000, and Carboxen 1003. Carboxen 569 has the lowest surface area of the three samples (~485 m² g⁻¹), has a closed-pore structure, and is highly hydrophobic. Carboxen 1000 has a through-pore structure, meaning that the pores pass entirely through the particles. As such, the material has a very high surface area (~1200 m² g⁻¹). Carboxen 1003 is hydrophobic, has a through-pore structure, and has a large surface area (~1000 m² g⁻¹). These materials are stable up to temperatures of ~673 K. Figure 2.2 provides an illustration of nanoporous carbon materials.



Figure 2.2. Images of nanoporous carbon models.

2.1.3 Metal-Organic Frameworks

Metal-organic frameworks (MOFs) are a class of porous, crystalline materials with well-defined geometric structures formed by the coordination of metal cations to electron-donating organic linking units [17]. Their combination of organic and inorganic components makes them unique when compared to zeolites or other microporous materials, and allows the pore size and chemical environment to be modified for specific applications [18]. MOFs have a number of distinct properties, which include their high surface areas, large internal volumes, and variety in metal and functional groups [19]. In recent years, MOFs have emerged as promising candidate materials for numerous applications in heterogeneous catalysis and gas adsorption, and have been the subject of many recent experimental investigations [20]. Specifically, considerable research has focused on using MOFs as part of CO_2 capture technologies [21]. Several drawbacks of MOFs that have prevented them from gaining increased use in industry are their low chemical stability and thermal stability (only up to ~300°C) [22].

The specific MOF investigated in this thesis is Basolite A100, which is produced commercially by BASF Catalysts. Basolite A100 is a hydrophilic material that exhibits a very high surface area (1,100-1,500 m² g⁻¹) and an open framework structure. The framework is identical to the MOF-MIL-53-Al and consists of octahedral AlO₄(OH)₂ units coordinated to terephthalic acid (1,4benzenedicarboxylate) organic linking units [23]. MOF-MIL-53 has a onedimensional framework and a typical pore size of 8.5 Å. The structure of MOF-MIL-53-Al is illustrated in Figure 2.3.



Figure 2.3. Structure of MOF-MIL-53-Al.

2.2 Flow-reactor with FTIR Spectroscopy

A flow-reactor system was designed and built to measure NO oxidation reaction rates (Figure 2.4). Gases from calibrated mixtures with helium were sent to the reaction chamber by mass flow controllers (Brooks 5850E series). A pressure gauge upstream of the reactor was used to monitor the total pressure at all times. Moisture removal purifiers containing a molecular sieve (Chromatography Research Supplies) were placed directly after the O₂ and helium gas cylinders, and the lines prior to and after the reactor were maintained at 398 K to avoid any condensation. Thermocouples (Omega, K-type) were placed along the gas lines before and after the reactor to monitor the temperature. Powder catalyst samples were placed on a porous quartz frit within a U-shaped quartz reactor (10 mm O.D.). Reactions were carried out isothermally by placing the reactor within a temperature-programmable furnace (ATS Series 3210 split tube furnace with Watlow EZ-Zone PM temperature control). The reactor bed temperature was monitored by the insertion of a thermocouple through the reactor (Omega, K-type, 1/16 in. diameter). The reactor effluent composition was measured using a heated transmission infrared (IR) gas cell (Specac Cylcone C2 fixed long pathlength) within a Fourier transform infrared (FTIR) spectrometer (Nicolet Nexus 470). The spectrometer was equipped with an MCT-A (mercury cadmium telluride) detector and operated at 4 cm⁻¹ resolution. Alternatively, the IR gas cell could be substituted with a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) reaction chamber (Harrick) to monitor the formation of surface intermediates under a controlled temperature and gas atmosphere.



Figure 2.4. Schematic diagram of the steady state reactor set-up [24]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

2.3 Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

DRIFTS is a mid-infrared (IR) spectroscopy technique that allows for *in-situ* measurements of the surface chemistries that occur on powder catalyst samples [25].

The DRIFTS accessory consists of a high-temperature reaction chamber that permits gases to flow over the powder sample under carefully controlled reaction conditions. The powder sample is placed within a sample cup and packed with a level surface to ensure consistency between experiments. The DRIFTS accessory contains a series of mirrors that direct the incident IR beam onto the surface of the powder sample. Then, a focusing mirror collects the scattered (diffusely reflected) radiation and reflects it off of flat mirrors, which subsequently direct the reflected light to the detector in the IR spectrometer. The cartoon in Figure 2.5, adapted from Smith et al. [26], illustrates this process. Minimal sample preparation is required, other than that the particle size should preferably be less than 10 μ m. Prior to *in-situ* measurements, the sample is pretreated within the reaction chamber under a specific gas flow and temperature. Then, a background spectrum is taken under an inert gas flow at the temperature of interest for the experiment. IR spectra are subsequently collected as reactant gases pass into the DRIFTS chamber. A Praying Mantis Diffuse Reflection Accessory (Harrick) with a Praying Mantis High Temperature Reaction Chamber (Harrick) was used to collect the DRIFTS spectra presented in this thesis. The DRIFTS cell was used within the experimental set-up depicted in Figure 2.4. The gas stream bypassed the reactor and was sent directly to the catalyst sample within the DRIFTS cell, which was substituted for the heated gas cell within the FTIR spectrometer.



Figure 2.5. Illustration of reflection of IR light during DRIFTS.

2.4 Powder X-ray Diffraction (XRD)

X-ray diffraction (XRD) is used to identify the structure and position of atoms within a crystalline material, providing both qualitative and quantitative information related to the crystal phases present and the dimensions of the unit cell parameters [27]. X-rays are generated from a stream of high-energy electrons. The electrons are directed towards a metal target, and <<1% of the electrons are excited into higher energy levels after hitting the target. The excited electrons emit electromagnetic radiation in the form of X-rays when they revert back to their original energy level. The resulting X-ray beam then passes through a filter to create a monochromatic beam, which is then shined onto the powder sample. X-ray wavelengths (λ) vary between 10⁻⁵ Å and 100 Å, but the typical wavelengths selected for XRD will be in the range of 0.1 Å to 25 Å in order to be on the same scale as the distance between atomic
planes in the sample (d_{hkl}). The X-ray beam is shined onto the crystal sample at an incident angle θ , and interactions occur between the X-ray radiation and the electrons from the material. Part of the radiation refracts through the sample without a change in direction, while part is reflected by the plane at an angle equal to the incidence angle θ . The diffracted waves leaving the sample will overlap with one another, resulting in constructive and destructive interference. Bragg demonstrated in 1912 that the constructive interference from a set of consecutive parallel planes can only occur for certain angles θ , and that θ is related to the X-ray wavelength and the interplanar spacing of the material (Eq. 2.1). This fundamental equation of diffraction is commonly referred to as the Bragg equation. In Eq. 2.1, d_{hkl} represents the spacing for the planes (*hkl*), θ represents the Bragg angle, *n* is an integer representing the order of the diffraction process, and λ represents the wavelength of the incident X-ray beam.

$$2d_{hkl}\sin\theta = n\lambda \tag{2.1}$$

During the XRD measurement, the X-ray beam is shined onto the sample at an angle ω , and an X-ray detector is positioned above the sample at the opposite end of the equipment, also at an angle ω (Figure 2.6). The incident beam angle is then slowly increased during the course of the measurement, and the X-ray intensity collected by the detector is measured as a function of θ . The resulting diffraction pattern will be unique for a specific structure, and depends on the crystal geometry and composition. The peak positions within the pattern provide information about the size and shape of the unit cell, while the relative intensities of the peaks provide information about the positions of the atoms within the unit cell. In this dissertation, XRD patterns of zeolite

samples were collected and compared to spectra from the International Zeolite Association (IZA) database [28].



Figure 2.6. Schematic of experimental set-up for X-ray powder diffractometer.

2.5 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) Spectroscopy

The scanning electron microscope (SEM) allows for solid materials to be observed and characterized on the nanometer (nm) to micrometer (μ m) scale. The SEM uses a focused beam of electrons to form an image of the sample. Figure 2.7 shows a schematic of an SEM to illustrate how electrons are generated and the path they take to reach the sample. The electrons excite the atoms of the sample and cause the release of backscattered or secondary electrons. Backscattered electrons are electrons from the incoming electron beam that undergo elastic scattering, and thus circle around the nucleus of an atom and are reflected out. Heavier atoms result in increased backscattering compared to lighter atoms. Secondary electrons are k-shell electrons that are ejected from the sample because of inelastic scattering interactions with electrons from the incoming beam. Both the backscattered and secondary electrons are collected by a detector to produce high resolution images of the sample topography.



Figure 2.7. SEM schematic (image provided by Iowa State University, Department of Materials Science and Engineering).

The SEM can also be used to obtain localized chemical characterization of solid samples. SEM can be accompanied by X-ray analysis, a technique known as SEM with energy dispersive X-ray spectroscopy (EDX). X-rays are also emitted from the sample during the bombardment with the electron beam, and can be measured by

an energy-dispersive spectrometer. The X-ray energies are characteristic of specific atoms, and thus quantitative elemental information can be obtained.

2.6 Nitrogen Physisorption

Physisorption of gas adsorbates is commonly employed for studying the textural properties of solid porous materials. Adsorption isotherms can be collected to allow for the determination of specific surface areas, microporous volumes, and pore size distributions. Nitrogen (N₂) is chemically inert, has a near-spherical shape, has a high saturation pressure, and only weakly interacts with solid materials through van der Waals forces, thus making it a suitable adsorbate in most instances. Also, N₂ physisorption does not result in significant changes to the electronic structure of the material since no electrons are exchanged, which allows for the sample to be used for other applications after the measurement. Adsorption within porous materials that occurs near the boiling point of the adsorbate is typically a multilayer process. That is, several layers of adsorbates form on the surfaces within the pores, and attractive interactions between adsorbate molecules cause the gases to condense into a liquid film on top of the molecules from the first monolayer.

During the experiment, the uptake of N_2 is measured as a function of pressure at a constant temperature to generate an adsorption isotherm. Typically, the temperature is held at 77 K during adsorption, by letting liquid N_2 at a pressure of 1 atm boil off from a Dewar flask that contains the sample. Important characteristics of the isotherm include the amount of N_2 uptake at a certain pressure, the slope of the isotherm in certain pressure regions, and the desorption profile. Porous materials are typically classified as microporous (< 2nm), mesoporous (2-50 nm), or macroporous

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(> 50 nm), and their isotherms display different physical shapes, as illustrated in Figure 2.8. Brunauer proposed in 1945 that adsorption of gases onto solid surfaces can be classified into five general forms (type I-V). The materials studied in this dissertation exhibited either type I or type II isotherms. A type I isotherm indicates that the material becomes saturated at low relative pressures, and is characteristic of a material that is entirely microporous with a moderately low external surface area. The micropores are quickly filled at a low relative pressure by a monolayer of gas, and the formation of multilayers at higher relative pressures do not lead to considerable increases in the amount of gas adsorbed. Most zeolites are entirely microporous, and thus exhibit type I isotherms during N₂ physisorption measurements. Type II isotherms do not indicate a saturation limit, and signify the presence of a larger pore size distribution. After the monolayer forms at low relative pressures within the micropores, adsorption occurs in successive layers because of capillary condensation happening in the macropores, resulting in an indefinite increase in gas uptake at higher relative pressures.



Figure 2.8. Five types of adsorption isotherms [29]. Reproduced with permission from John Wiley & Sons.

Several mathematical techniques exist to quantify surface areas, pore volumes, and pore size distributions from the adsorption isotherms. The BET model, which was developed in 1938 by Brunauer, Emmett, and Teller [30], is commonly used to determine the surface area of the materials, and extends the classical Langmuir model to account for multilayer adsorption at higher relative pressures. The BET model is shown in Eq. 2.2, where V_a is the volume of gas adsorbed at standard temperature and pressure (STP), V_m is the volume of gas adsorbed at STP to produce an apparent monolayer on the surface, C is the dimensionless BET constant that is related to the enthalpy of adsorption of the adsorbate gas, P is the partial vapor pressure of adsorbate gas in equilibrium with the surface at 77 K, and P_o is the saturated pressure of the adsorbate gas. V_a is measured for at least three different values of $\frac{P}{P_o}$ during the experiment.

$$\frac{V_a}{V_m} = \frac{CP}{(P_o - P) \left[1 + (C - 1)\frac{P}{P_o}\right]}$$
(2.2)

Linearizing the model and plotting $\frac{1}{V_a} \left(\frac{P_o}{P} - 1\right)^{\text{vs. }P}/P_o$ yields a straight line in the relative pressure $\left(\frac{P}{P_o}\right)$ range of 0.05 to 0.30. The slope and y-intercept are evaluated by linear regression analysis, allowing for the determination of V_m and C. The specific surface area (S.A.) can then be calculated by Eq. 2.3, where N_a is Avogadro's number, m is the mass of the sample, and 22,400 is the volume (in mL) occupied by 1 mol of the adsorbate gas at STP.

$$S.A. = \frac{V_m N_A}{m \times 22,400}$$
(2.3)

Total micropore volume is another important property of porous materials, and can be calculated by the *t*-plot method, which is based on standard N₂ adsorption isotherms. The average thickness (in nm) of the adsorbate layer on the surface is given by $t(P) = N_{ads}{}^{0}(P)/\rho_{0}S$, where $N_{ads}{}^{0}(P)$ is the adsorbed amount at each pressure, ρ_{0} is the bulk liquid density of the adsorbed phase, and *S* is the specific surface area of the surface. The function t(P) is known as the *t*-curve. The *t*-plot is obtained by plotting the volume of gas adsorbed ($N_{ads}{}^{0}(P) \rho_{0}$) against the corresponding value of t(P), as shown in Figure 2.10. For a microporous material, the *t*-plot can be divided into two regimes as a function of pressure. At low *t*-values (and thus low pressure and thickness), adsorption occurs only in the micropores; subsequently adsorption takes place on the external surface of the material. The *t*-plot is linear at larger thicknesses because adsorption only occurs on the external surface. The first point that deviates from this linear regime at lower *t*-values represents the contribution of the adsorbed gas in the micropores, and the microporous volume can be determined by the corresponding value on the y-axis (see the blue dotted line in Figure 2.9).



Figure 2.9. Illustration of *t-plot*. The intercept of the blue dashed line with the y-axis corresponds to the microporous volume ($V_{micro.}$) of the material.

Finally, the pore size distribution of a porous material is important to quantify, and can be determined by the Barrett-Joyner-Halenda (BJH) method. This method is applied to the desorption isotherm, and uses a modified form of the Kelvin equation (Eq. 2.4) to relate the amount of adsorbate removed from the pores of the material, as the relative pressure (P/P_0) is decreased, to the size of the pores.

$$r_K = \frac{-2\gamma V_m}{RT \ln \left(\frac{P}{P_0}\right)} \tag{2.4}$$

In Eq. 2.4, γ is the surface tension of nitrogen at its boiling point, $V_{\rm m}$ is the molar volume of liquid nitrogen, R is the gas constant, T is the boiling point of nitogen, P/P_0 is the relative pressure of nitrogen, and $r_{\rm K}$ is the Kelvin radius of the pore. The actual pore radius ($r_{\rm p}$) is then calculated using Eq. 2.5.

$$r_p = r_k + \left[\frac{13.99}{\log(P/P_0) + 0.034}\right]^{1/2}$$
(2.5)

The pore volume calculated as a function of pore radius is found using the BJH equation (Eq. 2.6), where V_p is the pore volume, Δt is the thickness of the adsorbed layer of nitrogen, and A_c is the area exposed by the pore from which the physically adsorbed gas is desorbed.

$$V_p = \left(\frac{r_p}{r_k + \Delta t/2}\right)^2 \left(\Delta V_n - \Delta t \sum_{j=1}^{n-1} Ac_j\right)$$
(2.6)

2.7 Nuclear Magnetic Resonance (NMR) Spectroscopy

Solid state nuclear magnetic resonance (NMR) spectroscopy provides direct information on the local surroundings of atoms in catalyst samples [31]. NMR techniques are widely used to characterize the structure of zeolite frameworks and extraframework species. Magnetically active nuclei that are often examined in zeolites include ²⁹Si and ²⁷Al. Silicon atoms are coordinated to four oxygen atoms in the zeolite framework, forming SiO₄ tetrahedra. SiO₄ tetrahedra can exist in five different possible environments within the zeolite depending on the number of AlO₄ tetrahedra connected to the silicon via oxygen. The ²⁹Si NMR spectra of aluminosilicate zeolites (Si/Al < 10) differentiate between the non-equivalent crystallographic environments of these SiO₄ tetrahedra by giving a series of peaks which correspond to the different SiO₄ sites [31]. These sites are notated as either Si(*n*Si, 4-*n*Al) where $n \le 4$, or Qⁿ sites where *n* denotes the number of linked SiO₄ tetrahedra (i.e. Si(3Si, 1Al) corresponds to Q³). Si(4Si) sites are predominant in siliceous zeolites or aluminosilicate samples with high Si/Al ratios. The number of peaks present in the NMR spectrum provides information on the types of SiO₄ tetrahedra present, while the intensities of the peaks provide information on their relative populations. The Si/Al ratio of a sample can be estimated from ²⁹Si NMR according to Eq. 2.7, where *I* is the intensity of a particular silicon resonance and *n* is the number of coordinated Al atoms for that resonance.

$$\frac{Si}{Al} = \frac{\sum_{n=0}^{4} I_{Si(nAl)}}{\sum_{n=0}^{4} 0.25 n I_{Si(nAl)}}$$
(2.7)

Figure 2.10 shows the typical chemical shifts of different Si(*n*Al) species.



Figure 2.10. ²⁹Si NMR chemical shifts in zeolites [31].

The distribution of aluminum sites and the presence of extraframework aluminum can be detected and used to characterize aluminum sites in zeolite samples through the use of ²⁷Al NMR spectroscopy. Tetrahedral Al is typically indicated by a chemical shift between 50-65 ppm in the NMR spectrum, while octahedral Al typically shows a shift around 0 ppm [31].

2.8 Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Analysis

Inductively coupled plasma mass spectrometry (ICP-MS) is an analytical technique capable of detecting elemental compositions at concentrations as low as 1 ppq (part per quadrillion). The ICP-MS uses ICP to convert the atoms in the sample into ions, which are subsequently separated and quantified by the MS. For this dissertation, ICP-MS analysis of our zeolite samples was performed by Galbraith Laboratories, Inc. at their facility in Knoxville, TN.

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Chapter 3

LOW TEMPERATURE CATALYIC NO OXIDATION OVER MICROPOROUS MATERIALS

3.1 Introduction

Low-temperature NO oxidation is a unique chemical reaction from a fundamental point of view in that the reaction rate decreases with increasing temperature. The origins of this irregular Arrhenius behavior, which results in negative apparent activation energies, were discussed in detail in Chapter 1, Section 1.4. A limited number of reports have investigated heterogeneously catalyzed NO oxidation at low temperatures (T < 400 K), and even fewer have probed the underlying mechanism. In 1960, Jaffer and Bliss [1] showed that reaction rates over silica gels showed a similar dependence on temperature as the homogeneous reaction at temperatures below 330 K; at temperatures between 355 K and 410 K, rates began to increase with increasing temperature in typical Arrhenius fashion. In contrast, Pt/Al₂O₃ and Pd/Al₂O₃ catalysts, which are common for NO oxidation, only show significant activity at temperatures above ~550 K [2]. Remarkable low-temperature activity such as that by the silica gels remained largely unexplored and unexplained mechanistically until an investigation by Artioli et al. [3], which showed that siliceous zeolites and microporous silica materials also exhibited significant NO oxidation activity at low temperatures. The authors proposed that the catalytic enhancements were brought forth by a confinement effect that stabilized the termolecular transition states. The work presented in this chapter builds upon the investigation by Artioli and

coworkers [3] by examining other microporous materials, such as metal-organic frameworks (MOFs) and porous molecular carbons, for their ability to catalyze this reaction by the confinement effect. It is shown that NO oxidation rates on these materials are ~100-10,000 times larger than rates for the homogeneous phase reaction at temperatures in the range of 298-423 K. The effects that protons and sodium cations exchanged into the zeolite framework have on reactivity and stabilizing the transition state were also investigated. Finally, *in-situ* FTIR studies were conducted to examine the numerous N_xO_y species that occupy the micropores under reaction conditions, and a Langmuir-Hinshelwood kinetic model was used to assess the inhibition effect of NO₂ on reaction rates.

3.2 Materials and Methods

3.2.1 Catalyst Synthesis

A pure-silica SSZ-13 (CHA) sample was synthesized by preparing a solution of 11.78 g of tetraethyl orthosilicate (TEOS, 98%, Sigma Aldrich) and 23.87 g of N,N,N-trimethyl-1-adamantanamine hydroxide (TMAdaOH, 25 wt %, Sachem Inc.) and stirring for 24 h at room temperature [4]. With continued stirring, the mixture was heated to evaporate 13.4 g of water and 10.4 g of ethanol (23.8 g total), resulting in a final H₂O/SiO₂ ratio of 3. 1.18 g of hydrofluoric acid (HF, 48-51%, Acros) was added, and the mixture was transferred to a 23 mL Teflon-lined stainless-steel autoclave (Parr) and heated in a convection oven at 423 K under rotation (40 rpm) for two days. The product was recovered by vacuum filtration, rinsed several times with deionized (DI) water, and dried at 373 K overnight in air. The sample was then calcined in air at 823 K for 8 h using a ramping rate of 180 K h⁻¹ to remove the occluder and remaining impurities.

Alumino-silicate samples of SSZ-13 (CHA) with silica-to-alumina (SiO_2/Al_2O_3) ratios of 12 were prepared using a hydrothermal synthesis protocol described by Fickel et al. [5]. To begin, the N,N,N,-trimethyl-1-adamantanamine iodide structure directing agent (SDA) was synthesized by dissolving 10 g of 1adamantanamine (97%, Sigma Aldrich) in 24.8 g of methanol (Fisher Scientific). Then, 29 g of tributylamine (98.5%, Sigma Aldrich) was added to the mixture. After stirring, the mixture was transferred to an ice bath, and 28.4 g of methyl iodide (99.5%, Sigma Aldrich) was added dropwise. The solution was covered and stirred for 5 days at room temperature. At this point, 100 mL of diethyl ether (Fisher Scientific) was added to the solution and stirred for 30 minutes. The crystalline product was then vacuum-filtered using 0.20 micron filter paper and dried at 373 K overnight in air. To prepare the zeolite, 5 g of sodium silicate (26.5% SiO₂, Sigma Aldrich), 0.16 g of NaOH (>98%, Fisher Scientific), and 12 g of DI water were stirred for 15 minutes at room temperature. 0.5 g of NH₄-Y (SiO₂:Al₂O₃ 5.2:1, Zeolyst CBV500) was added to the solution and stirred for 30 minutes. 0.8 g of N,N,N,-trimethyl-1-adamantanamine iodide was then added to the mixture and stirred for 30 minutes. Following the mixing step, the sample was transferred to a 23 mL Teflon-lined stainless-steel autoclave (Parr) and heated at 413 K under rotation (60 rpm) for six days in a convection oven. The resulting product was recovered by vacuum filtration, rinsed with DI water several times, and dried at 373 K overnight in air. Finally, the sample was calcined in air at 823 K for 8 h using a ramping rate of 180 K h⁻¹ to remove any residual SDA or remaining impurities.

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SSZ-13 (CHA) samples with SiO₂/Al₂O₃ ratios of 24 were prepared using a hydrothermal synthesis protocol reported by Pham et al. [6]. A mixture of 13.02 g of tetraethyl orthosilicate (TEOS, 98%, Sigma Aldrich), 26.375 g of N,N,N-trimethyl-1-adamantanamine hydroxide (TMAdaOH, 25 wt % Sachem Inc.), 2.72 g of DI water, and 0.71 g of aluminum ethoxide (99%, Strem chemical) was prepared to obtain a gel composition of SiO₂/H₂O/TMAdaOH/Al₂O₃ with a ratio of 1:20:0.5:.14. The mixture was covered and stirred for 24 h at room temperature. The solution was then transferred to a 23 mL Teflon-lined stainless-steel autoclave (Parr) and heated in a convection oven at a temperature of 413 K under static conditions for six days. The product was recovered by vacuum filtration, rinsed several times with DI water, and dried at 373 K overnight in air. The sample was then calcined in air at 823 K with a ramping rate of 180 K h^{-1} for 8 h to remove the occluded organic structure director.

Na-SSZ-13 samples were prepared by liquid-phase ion-exchange of calcined SSZ-13 samples. 1 g of SSZ-13 was added to 500 mL of 0.1 M NaCl (> 99.0%, Sigma Aldrich) and stirred for 1 hour at 353 K. Following ion exchange, the sample was vacuum filtered, rinsed several times with DI water, and dried at 373 K overnight in air. The ion-exchange process was repeated two or three times to ensure complete cation exchange.

Porous carbon samples were manufactured by Supelco (Carboxen 569, 1000, 1003 materials) and purchased from Sigma-Aldrich. These highly porous carbon materials possess specially designed frameworks with pores that taper from macro- to meso- to micropores. Additionally, a non-porous carbon material (Carboxen 1016) was used as a control.

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The metal-organic framework (MOF) Basolite A100 is produced commercially by BASF Catalysts. Basolite A100 is a hydrophilic material that exhibits a very high surface area (1100-1500 m² g⁻¹) and an open framework structure. The framework is identical to the MOF-MIL-53-Al and consists of octahedral $AlO_4(OH)_2$ units coordinated to terephthalic acid (1,4-benzenedicarboxylate) organic linking units [7].

3.2.2 Analytical

Powder X-ray diffraction (XRD) patterns were obtained using a Philips X'pert diffractometer with a Cu K α source. The patterns were collected for 2 θ values of 5⁰ to 50⁰ with a step size of 0.02⁰ and 2 s per step. Textural characterization of the samples was determined using N₂ adsorption at 77 K. Isotherms were collected on a Micrometrics ASAP 2020 and analyzed using the t-plot method to calculate microporous volumes. Prior to the adsorption measurements, SSZ-13 samples were degassed at 623 K for 6 h, while Basolite A100 and porous carbon samples were degassed at 473 K for 12 h. Scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDX) spectra were obtained on a JEOL JSM7400F microscope to provide information regarding sample morphology and elemental compositions, respectively.

²⁹Si and ²⁷Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectra of zeolite samples were recorded on a Bruker AVIII-500 solid-state NMR spectrometer. The spectrometer was operated at a Larmor frequency of 500.138 MHz for ¹H and 99.362 MHz for ²⁹Si. A 4 mm HX MAS probe was used for all measurements. All spectra were recorded at a MAS frequency of 10 kHz, controlled to within +/- 2Hz using a Bruker MAS controller. ²⁹Si single pulse and cross polarization (CP) measurements were performed as well. For ²⁹Si single pulse MAS experiments, a

90° pulse with a width of 4.3 μ s was used and the recycle delay was 30 s. For {¹H}-²⁹Si CP MAS experiments, ¹H 90° pulse duration was 2.5 μ s, a linear amplitude ramp (80-100%) on ¹H was used with a contact time of 4.5 ms, and the recycle delay was 5 s. SPINAL64 ¹H decoupling with an rf field strength of 100 kHz was applied during the acquisition period for both SP and CP MAS measurements. For ²⁷Al single pulse MAS experiments, a 90° pulse with a width of 1.25 μ s was used and the recycle delay was 1 s.

Ethane and propane adsorption isotherms were measured for pure-silica CHA at 283 K, 303 K, 323 K, and 343 K at pressures up to 1 atm using a Micrometrics ASAP 2020. Prior to adsorption measurements, samples were degassed at 623 K for 6 h. Temperatures were controlled using a Lauda Alpha RA 12 thermostat. Isosteric heats of adsorption ($\Delta H_{ads.}$) were calculated using the Clausius-Clapeyron equation and are presented along with reported values from literature over other zeolite and MOF materials. The enthalpies of formation of the transition state (ΔH^{\dagger}) for the catalyzed NO oxidation reactions were compared to $\Delta H_{ads.}$ values to compare the stabilization of these alkanes to [N₂O₄][†] activated complexes for the heterogeneously catalyzed and homogeneous phase reactions.

3.2.3 Catalytic Testing

The NO oxidation reaction (Eq. 3.1) is a reversible reaction with low activation barriers, and thus the rate of the reverse reaction can be significant.

$$2NO + O_2 \rightleftharpoons 2NO_2 \tag{3.1}$$

Consequently, measured net reaction rates are transformed into forward reaction rates using Eqs. 3.2-3.4.

$$r_{obs.} = r_{+} - r_{-} = r_{+}(1 - \eta)$$
(3.2)

$$\eta = \frac{[NO_2]}{K_C[NO]^2[O_2]} \tag{3.3}$$

$$K_{C} = \left(\prod_{i} C_{i_{eq}}^{\gamma}\right) \frac{1}{C_{o}}$$
(3.4)

 C_o (Eq. 3.4) represents the standard state (1 mol L⁻¹). Due to the large equilibrium constant (K_c) for this reaction at low temperatures (T < ~450 K), the reverse reaction has a negligible contribution toward the observed rate for all measurements. NO oxidation rates were measured using a differential reactor flow system (schematic shown in Chapter 2, Figure 2.4). Prior to reaction rate measurements, catalyst samples were pre-treated in 10% O₂/He (100 sccm) at 793 K (300 K h⁻¹ ramp rate) for 2 h to remove any adsorbed species. Following the pretreatment, He, NO, NO₂ and O₂, from calibrated mixtures with He, were sent to the reaction chamber by mass flow controllers (Brooks 5850E series) at a total flow rate of 100 sccm to provide a range of inlet partial pressures (0.02-0.10 kPa NO, 1-5 kPa O₂, 0.015-0.030 kPa NO₂). Total pressure was monitored at all times and was within the range of 101.6-104.4 kPa. The reactor effluent composition was measured using a heated transmission infrared (IR) gas cell (Specac Cylcone C2 fixed long pathlength) within a Fourier transform infrared (FTIR) spectrometer (Nicolet Nexus 470). The spectrometer was equipped with an MCT-A (mercury cadmium telluride) detector and was operated at 4 cm⁻¹ resolution. All IR spectra were obtained from the average of 100 collected scans. OMNIC software was used to obtain IR spectra and integrate

peak areas. The reactor system was calibrated by flowing known concentrations of NO and NO₂, measuring peak areas, and generating calibration curves. To obtain rate measurements, NO₂ concentration was monitored during the reaction by its characteristic IR features in the 1660-1550 cm⁻¹ spectral region. For all rate measurements, NO conversion was maintained below ~15%. Reaction rates are reported on the basis of catalyst mass. Homogenous gas phase NO oxidation rates were measured through the empty reactor on a reactor volume basis to evaluate the contribution towards the observed catalytic rates.

3.3 Results and Discussion

3.3.1 Material Characterization

X-ray diffraction patterns confirmed that the calcined SSZ-13 and Basolite A100 samples were highly crystalline with the expected framework structures (Figure 3.1). No indications of amorphous impurities were detected in any case. XRD patterns for SSZ-13 samples with different SiO₂/Al₂O₃ ratios also reveal that the samples are highly crystalline and have no impurities.



Figure 3.1. XRD patterns of calcined H-SSZ-13 (SiO₂/Al₂O₃ = 24), Na-SSZ-13 (SiO₂/Al₂O₃ = 24), and Basolite A100 [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

Nitrogen adsorption isotherms were measured at 77 K for all materials (Figure 3.2). The observed plateaus for the isotherms (Type 1) of the SSZ-13 samples indicate that they are purely microporous materials. The isotherm shapes for the Basolite A100 and porous carbon samples indicate that pores with diameters larger than micropores (> 20 Å) are present.



Figure 3.2. Adsorption isotherms of N₂ at 77 K for a) Carboxen samples and b) Basolite A100, H-SSZ-13 (SiO₂/Al₂O₃ = 24), Na-SSZ-13 (SiO₂/Al₂O₃ = 24), and puresilica CHA [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

Pore size distributions [8] for the carbon samples confirmed the presence of pores with diameters as large as ~600 Å, indicating that the samples taper from macro-to meso- to micropores (Figures 3.3-3.5).



Figure 3.3. Pore size distribution for Carboxen 569 [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).



Figure 3.4. Pore size distribution for Carboxen 1000 [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).



Figure 3.5. Pore size distribution for Carboxen 1003 [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

Microporous volumes were determined using *t*-plot analysis of the adsorption isotherms (Table 3.1). Carboxen 1000, Basolite A100, and the zeolite materials have comparable micropore volumes within the range of 0.22-0.29 cm³ g⁻¹. The low micropore volume for Carboxen 569 (0.06 cm³ g⁻¹) is consistent with its pore size distribution, which reveals only a small fraction of the pores within the microporous region (< 20 Å) and a large contribution from macropores (> 500 Å). This is also evident from the isotherm (Figure 3.2.a), which shows lower uptake within the microporous region compared to the other materials. The isotherm for Carboxen 1003 (Figure 3.2.a) reveals high adsorption capacity within the microporous region compared to all other materials.

Material	Microporous Volume [cm ³ g ⁻¹]	
Pure-silica CHA	0.26	
H-SSZ-13 (SiO ₂ /Al ₂ O ₃ = 24)	0.29	
Na-SSZ-13 (SiO ₂ /Al ₂ O ₃ = 24)	0.27	
Carboxen 569	0.06	
Carboxen 1000	0.24	
Carboxen 1003	0.36	
Basolite A100	0.22	

Table 3.1. Microporous volumes of samples investigated for NO oxidation using *t*-plot method [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

SEM images revealed that SSZ-13 particles with SiO₂/Al₂O₃ ratios of 12 and 24 formed agglomerates comprised of small cube-shaped or spherical crystals approximately 1 μ m in size, respectively (Figure 3.6). EDX chemical analyses of the zeolite samples are consistent with the expected SiO₂/Al₂O₃ ratios of 12 and 24 of the samples.



Figure 3.6. SEM images of a) pure-silica CHA, b) H-SSZ-13 (SiO₂/Al₂O₃ = 24), and c) Na-SSZ-13 (SiO₂/Al₂O₃ = 12) [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

The ²⁹Si NMR spectrum of pure-silica CHA (Figure 3.7.a) shows a peak at a chemical shift δ of -111.5 ppm, assigned to Q⁴ (Si(OSi)₄) species, and a much smaller peak at -102.1 ppm, assigned to Q³ (Si(OSi)₃OH silanol groups) species. The single Q⁴ peak is consistent with the presence of only one T-atom in the asymmetric unit of the chabazite unit cell. The ²⁹Si MAS NMR spectrum of Na-SSZ-13 (SiO₂/Al₂O₃ = 12)

shows peaks at -104.6 ppm (Si₃Al₁) and -99.3 ppm (Si₂Al₂) in addition to the Q⁴ peak at -111.5 ppm (Figure 3.7.b). Minimum and maximum SiO₂/Al₂O₃ ratios of 10.2 and 15.3, respectively, were determined for the material. The ²⁹Si MAS NMR spectrum of Na-SSZ-13 (SiO₂/Al₂O₃ = 24) shows the Q⁴ peak at -111.5 ppm and a peak at -104.6 ppm (Si₃Al₁), but does not display the peak at -99.3 ppm (Si₂Al₂) because of the higher SiO₂/Al₂O₃ ratio of the sample (Figure 3.7.c). This may indicate that the peak at -99.3 ppm is in fact from defects present in the sample with SiO₂/Al₂O₃ = 12. From the spectrum, a SiO₂/Al₂O₃ ratio of 25.1 was determined for the material. The ²⁷Al MAS NMR spectrum of Na-SSZ-13 (SiO₂/Al₂O₃ = 12) confirms the presence of only tetrahedrally coordinated framework aluminum atoms as evidenced by a single peak at 58.7 ppm (Figure 3.7.d). NMR spectra of the other SSZ-13 zeolite samples indicated similar results.



Figure 3.7. a) ²⁹Si MAS NMR spectra of pure-silica CHA. b) ²⁹Si MAS NMR spectra of Na-SSZ-13 (SiO₂/Al₂O₃ = 12). c) ²⁹Si MAS NMR spectra of Na-SSZ-13 (SiO₂/Al₂O₃ = 24). d) ²⁷Al MAS NMR spectra of Na-SSZ-13 (SiO₂/Al₂O₃ = 12) [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

3.3.2 Reaction Rates and Reaction Orders

Artioli et al. [3] reported reaction orders of 2 and 1 with respect to NO and O_2 for the NO oxidation reaction on siliceous samples of silicalite-1 (SIL-1), beta (BEA), and chabazite (CHA) at 305 K and 331 K. We investigated if these reaction orders were also observed on the aluminosilicates H-SSZ-13 and Na-SSZ-13, the porous carbons, and the MOF sample described above. NO oxidation rates were measured at 323 K and 373 K as a function of NO and O_2 pressures (0.02-0.10 kPa NO, 1-5 kPa

 O_2). To establish the reaction rate orders, we analyzed the rate dependency on reactant concentration over the different catalysts using the relation shown in Eq. 3.5.

$$r_{NO_2} = k[NO]^{\alpha} [O_2]^{\beta}$$
(3.5)

Reaction orders α and β with respect to NO and O₂ were obtained by fitting the NO oxidation rate vs. the reactant concentration for each reactant, which on logarithmic plots produced linear relationships with slopes equal to the reaction orders if a suitable rate law was proposed. Figure 3.8 displays the plots for NO and O₂ reaction orders at 373 K on H-SSZ-13 (SiO₂/Al₂O₃ = 12). At these conditions, the reaction rate dependencies over H-SSZ-13 closely match the stoichiometry of the reaction and correspond to the rate law for the homogeneous oxidation reaction (Eq. 3.6).

$$r_{NO_2 \, gas} = k_{gas} [NO]^2 [O_2] \tag{3.6}$$



Figure 3.8. a) Log-log plot of reaction rate vs. NO concentration at 373 K on H-SSZ-13 ($SiO_2/Al_2O_3 = 12$) (20-100 Pa NO + 5 kPa O₂, 100 sccm, 0.1 g catalyst). b) Log-log plot of reaction rate vs. O₂ concentration at 373 K on H-SSZ-13 ($SiO_2/Al_2O_3 = 12$) (100 Pa NO + 1-5 kPa O₂, 100 sccm, 0.1 g catalyst) [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

Residual errors of the data fit in Figure 3.8 were inspected graphically to verify that no apparent trends existed in the data and that the estimated reaction orders were reliable (Figure 3.9). Ideally, the variation of the residuals should be random and departure from such behavior indicates inadequacies of the model. Examination of the residuals for the data to determine the NO reaction order on H-SSZ-13 at 373 K reveals a discernible pattern, with residuals clearly increasing and then decreasing (Figure 3.9.a). The trend suggests that the reaction rate model (Eq. 3.5) is not entirely adequate (see section 3.3.5) and that at high concentrations there is another factor that decreases (slightly) the reaction rate. The residual plot for the O₂ reaction order determination shows no evident deviation from a random distribution (Figure 3.9.b).



Figure 3.9. Residual errors for NO oxidation rates on H-SSZ-13 ($SiO_2/Al_2O_3 = 12$) at 373 K for a) NO reaction order determination and b) O₂ reaction order determination [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

The same reaction orders for NO and O_2 (Eq. 3.6) were observed on all materials at 323 K and 373 K (Table 3.2). In all cases, the difference from the integers 2 and 1 is within experimental error. Similarly, an analysis of the residuals was carried

out for all samples to identify any inadequacies of the model (Eq. 3.5). For NO reaction orders on pure-silica CHA (323 K), Carboxen 569 (323 K), Carboxen 569 (373 K), and Na-SSZ-13 (SiO₂/Al₂O₃ = 12, 373 K), and for O₂ reaction orders on pure-silica CHA (323 K), Carboxen 1003 (323 K), and Basolite A100 (373 K), we also observed discernible trends in the residuals, again indicating that the model may be incomplete despite its apparent good fit.

Table 3.2. Reaction orders with respect to NO (20-100 Pa NO + 5 kPa O₂) and O₂ (100 Pa NO + 1-5 kPa O₂) [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

Material	α NO Reaction Order	βO2 Reaction Order	α NO Reaction Order	βO2 Reaction Order
	323 K	3 K	373 K	
Pure-silica CHA	2.04 ± .06	$1.02 \pm .04$	$2.02 \pm .06$	1.05 ± .05
H-SSZ-13	$1.98\pm.02$	$1.03 \pm .04$	$2.04 \pm .05$	$1.03 \pm .06$
Na-SSZ-13	$2.05\pm.05$	$1.04 \pm .06$	$2.02 \pm .07$	$1.01 \pm .04$
Carboxen 569	$1.99 \pm .04$	$1.04 \pm .05$	$1.98 \pm .07$	$1.01 \pm .04$
Carboxen 1000	$2.02\pm.07$	$0.97 \pm .06$	$2.05 \pm .06$	$0.99 \pm .05$
Carboxen 1003	$2.03\pm.07$	$1.05 \pm .05$	$2.01 \pm .08$	$1.04 \pm .03$
Basolite A100	$1.96\pm.06$	$0.98\pm.05$	$2.03\pm.03$	$1.02\pm.07$

The observation of similar reaction orders for the homogeneous and heterogeneously catalyzed reactions strongly indicates that the reactions proceed through similar reaction mechanisms [3]. The homogenous phase reaction proceeds through a two-step reaction mechanism with a slight negative activation energy (-4.4 kJ mol⁻¹) in the temperature range of 270-600 K [9]. The activated complex in this mechanism has been suggested to be a *cis-cis-* [ON-O-O-NO][‡] species [10]. Artioli et al. [3] proposed that the catalyzed reactions on siliceous MFI, BEA, and CHA samples at temperatures between 298 and 423 K proceed through a transition state similar in composition to that in the homogenous phase reaction, with the micropores providing a physical basis for catalysis that effectively concentrate the transition state species and thereby accelerate a homogeneous-like reaction. The observed reaction orders here agree with the results of Artioli et al. [3], and thus support the premise that a transition state of similar composition is being formed on all of the microporous materials investigated. Note, however, that these kinetic results do not provide any information about the connectivity of the atoms in the transition state; rather, they merely indicate that the complex has a composition of $[N_2O_4]^{\ddagger}$.

3.3.3 Effect of Temperature

Reaction rates were measured on all materials as a function of temperature from 298-423 K (Figure 3.10)¹. Specific rates (per gram of catalyst) for the carbon samples are very similar (Figure 3.10.a), and are comparable in magnitude to the rate on Na-SSZ-13 (Figure 3.10.b). Among the zeolite samples, Na-SSZ-13 exhibited the highest rates, followed by H-SSZ-13 and then pure-silica CHA. This trend suggests that in addition to the transition state stabilization by the framework through confinement effects and van der Waals interactions, the exchanged cations can provide additional stabilization of the transition state through electrostatic interactions. The electrostatic effect of Na⁺ is examined further in Section 3.3.4.

¹ Evidence for NO oxidation reactivity at moderate temperatures over H- and Na-SSZ-13 was first observed by Artioli et al. [11].



Figure 3.10. Arrhenius plots of the forward NO oxidation rates (100 Pa NO, 5 kPa O₂, 100 sccm, 0.1 g catalyst) at 298-423 K on a) porous carbon materials and b) SSZ-13 and Basolite A100 materials [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

The Arrhenius plots show that the apparent activation energies for all samples are negative, but note that the slopes are not constant. The downward curvature of the data in Figure 3.10 indicates that reaction rates at lower temperatures (T < 348 K) are lower than what would be expected if a linear trend held throughout the entire temperature range. One possible cause for the non-linearity is that a change in reaction mechanism occurs at ~348 K. This scenario, however, seems unlikely given that the reaction orders obtained over all materials at 333 K and 373 K were identical. A more plausible explanation for the varying slope in Figure 3.10 is that increased amounts of surface species are forming at low temperatures as a result of the increased conversion of NO into NO₂. Several studies [12-15] have utilized diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and other in-situ FTIR techniques to identify N_xO_y adsorbates formed on H- and Na- forms of ZSM-5 and Y zeolites upon exposure to gas mixtures of NO and O_2 . The results from these reports established that at 298 K a variety of adsorbed species (NO₂, N₂O₄, N₂O₃, (NO)₂, NO⁺, ONNO⁺, NO₃⁻) are present in large amounts. At higher temperatures (373 K), typically only NO⁺ and NO_3^{-} species are thermally stable, and the other surface adsorbates desorb. We have observed the accumulation of NO₂ and N₂O₄ within the micropores of our samples: upon heating the reactor, desorption of these species from the catalysts were observed by the transient appearance of spikes in the IR spectra at frequencies characteristic of gas-phase NO₂ and N₂O₄. At the temperatures investigated in our experiments (298-423 K), it appears that the adsorbed species have no active or catalytic role to accelerate the reaction. Rather, they occupy space within the micropores where more reaction events could be occurring, especially below ~348 K. As a result, the reaction is inhibited by the physical presence of these species, yielding the curvature observed in Figure 3.10.

In view of this lack of linearity, activation energies (E_a) were estimated over a temperature range (348-423 K) where the data are linear (Table 3.3). The E_a values (-24.9 to -37.5 kJ mol⁻¹) are much more negative than the reported value of -4.41 kJ mol⁻¹ for the homogeneous phase reaction [9], indicating a considerable decrease in the reaction barrier. These values are similar to the activation energies reported by Artioli et al. [18] for siliceous zeolites. The H-SSZ-13 and Na-SSZ-13 materials

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exhibit the most negative activation energy values, a result attributed primarily to the electrostatic stabilization of the extra-framework cations on the transition state. But since it is known that multiple nitrogen oxides are formed inside the zeolite pores under these reaction conditions [12-14], other factors could be affecting the activation energy, such as the ability of an $[N_2O_4]^{\ddagger}$ complex to be 'solubilized' inside a 'pool' of NO_x species in the zeolite pores. The three Carboxen samples have very similar activation energies of approximately -31 kJ mol⁻¹, reflecting a similar stabilization effect of the transition state on the three porous carbons.

Rates per gram of catalyst for the three Carboxen samples are, in fact, very similar (Figure 3.10.a), a finding that is surprising given the different microporous volumes of the materials. Reaction rates on the porous carbons were compared further on surface area and micropore volume bases to identify broadly the key variable determining reactivity. In both cases, the reaction rates scale in the following order: Carboxen 569 > Carboxen 1003 > Carboxen 1000. The oxidation rates on Carboxen 569 at 343 K on microporous volume and surface area bases are 1.95 and 2.15 times greater, respectively, than the rates on Carboxen 1000. Similarly, oxidation rates on Carboxen 1003 at 343 K on microporous volume and surface area bases are 1.39 and 1.33 times greater, respectively, than the rates on Carboxen 1000. The data suggest that the pores of Carboxen 569 better fit the size of the transition state, raising reaction rates significantly despite there being less void space compared to the other materials. It appears then that neither micropore volume nor surface area are good descriptors in themselves of the reaction rate behavior and are unable to "collapse" the data into one line. This indicates that a molecular-level description of the reaction space is needed and that average properties such as micropore volume, surface area, and similar

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structural features do not explain the observed results. Additionally, the similar activation energies for the materials (Table 3.3) suggests that the entropy of the formation of the transition state (ΔS^{\ddagger}) could be the driving force in causing the different observed rate behavior over microporous volume and surface area bases (see discussion in section 3.3.6).

Table 3.3. Measured activation energies calculated from rate data for catalyzed NO oxidation reaction (348-423 K) [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

Material	E _a [kJ mol ⁻¹]
Pure-silica CHA	-24.9
H-SSZ-13 (SiO ₂ /Al ₂ O ₃ = 12)	-37.5
Na-SSZ-13 (SiO ₂ /Al ₂ O ₃ = 12)	-35.6
Carboxen 569	-31.8
Carboxen 1000	-31.4
Carboxen 1003	-31.2
Basolite A100	-32.6

Homogeneous reaction rates were measured under the same conditions as those used for the catalyzed reactions to assess the homogeneous contribution to the overall measurements. Normalizing the reaction rates by reactor volume allowed for direct comparison of the catalyzed and homogeneous phase rates (Figure 3.11). Reactivity over the catalyst samples was observed to be ~2-4 orders of magnitude larger than that for the gas phase reaction, indicating that homogeneous phase oxidation pathways accounted for a minimal fraction of the observed catalytic rates and thus did not need to be considered in the calculations.



Figure 3.11. Forward NO oxidation rates (100 Pa NO, 5 kPa O₂, 100 sccm, 0.1 g catalyst) normalized by reactor volume as a function of temperature (298-423 K) over SSZ-13 materials and in the homogeneous phase [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

To assess the importance of confinement effects on catalytic activity, a control experiment was conducted in which oxidation rates were compared as a function of temperature (298-423 K) over porous (Carboxen 1000) and non-porous (Carboxen 1016) carbon materials. The non-porous carbon sample provides some rate enhancement over the homogeneous phase reaction, implying that physisorption of the transition state can offer a small measure of stabilization. However, measured rates over Carboxen 1000 were found to be ~250 times larger than those measured over Carboxen 1016 at 333 K (100 Pa NO, 5 kPa O₂). This large difference in activity clearly indicates that the microporous structure is instrumental in providing a more effective stabilization of the transition state. Artioli et al. [3] compared reaction rates

over siliceous zeolites to those over amorphous silica and observed a similar result, with rates measured over the zeolite samples being ~20 times greater than those measured over silica.

3.3.4 Electrostatic Effects of Na⁺ Cations on Catalytic Rates

Reaction rates as a function of temperature (298-423 K) were compared for pure-silica CHA and Na-SSZ-13 samples (SiO₂/Al₂O₃ = 12 and 24) to understand the contribution of electrostatic effects from extra-framework cations toward the enthalpic stabilization of the transition state (Figure 3.12). All samples show similar temperature dependence, and a clear increase in oxidation rate is observed for samples with lower SiO₂/Al₂O₃ ratios, which contain greater amounts of Na⁺ cations. At 323 K, the rate on Na-SSZ-13 (SiO₂/Al₂O₃ = 12) is greater than the rate on Na-SSZ-13 (SiO₂/Al₂O₃ = 24) by a factor of 1.79, while at 373 K that factor is 1.95.



Figure 3.12. Forward NO oxidation rates (100 Pa NO, 5 kPa O₂, 100 sccm, 0.1 g catalyst) normalized by grams of catalyst as a function of temperature (298-423 K) on Na-SSZ-13 (SiO₂/Al₂O₃ = 12), Na-SSZ-13 (SiO₂/Al₂O₃ = 24), and pure-silica CHA [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

The turn-over-frequencies (TOF) per mol of Na⁺ for the two Na-SSZ-13 samples (SiO₂/Al₂O₃ = 12 and 24) were estimated to assess if the cation contribution to the rate was independent of SiO₂/Al₂O₃ ratio (Figure 3.13). In the determination of the TOFs, the rate contribution for the pure-silica CHA sample was subtracted from the total rate for the Na-SSZ-13 samples so that the 'framework' contribution to the stabilization of the transition state was factored out of the calculation. At the two SiO₂/Al₂O₃ ratios tested, TOF values were found to be very similar, indicating that there is little interaction between Na⁺ sites, even at SiO₂/Al₂O₃ ratios as low as 12.



Figure 3.13. Turn-over-frequencies (TOF) per mol Na⁺ for NO oxidation as a function of temperature (298-423 K) on Na-SSZ-13 (SiO₂/Al₂O₃ = 12) and Na-SSZ-13 (SiO₂/Al₂O₃ = 24) [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

In addition to providing electrostatic effects that stabilize the transition state and enhance the reaction rate, Na⁺ and H⁺ cations enable the formation of charged species in the presence of NO and O₂, such as NO⁺, which is coordinated to negatively charged lattice oxygen atoms within the zeolite framework [14, 16-18]. The extent of disproportionation of the adsorbed N₂O₄ is likely to be different for the Na⁺ and H⁺ samples. As Mignon et al. [17] discussed in a density functional theory (DFT) study of N₂O₄ disproportionation over alkali-cation-exchanged zeolite Y materials, the degree of electron transfer between basic oxygen atoms linked to aluminum atoms and the π^* orbital of NO⁺ varies depending on the basicity of the oxygen atoms. In examining N₂O₄ disproportionation over Na⁺, K⁺, and Rb⁺-exchanged zeolite Y, the authors showed that lattice oxygen atoms are more basic in the presence of the larger cations (i.e. Rb⁺) [17]. An ongoing study by our group [19] indicates that NO⁺ shows IR absorbances at 2160 cm⁻¹ on Na-SSZ-13 and 2195 cm⁻¹ on H-SSZ-13, which is in agreement with the predictions presented by Mignon et al. [17]. Similarly, Gil et al. [20] observed IR bands for NO⁺ at 2165 cm⁻¹ on Na-ZSM-5 and 2190 cm⁻¹ on NaH-ZSM-5 (77% Na/H exchange degree). The observation of decreased NO⁺ stretching frequency for the Na-SSZ-13 sample, along with the results of Mignon et al. [17], suggests that Na-SSZ-13 oxygen atoms are more basic compared to the same atoms in H-SSZ-13. The increased effective charge of Na⁺ leads to greater charge transfer ability for Na-SSZ-13. This results in a larger electrostatic charge for NO⁺ which can consequently provide additional stabilization of the transition state in the NO oxidation reaction and further increase reaction rates. The higher reaction rates observed for Na-SSZ-13 relative to H-SSZ-13 support this reasoning.

Along with the favorable effects of NO⁺ on reaction rates, though, the associated formation of HNO₃ or NaNO₃ [12, 21, 22] within the pores from N₂O₄ disproportionation has a negative impact on reaction rates by decreasing the available reaction space. As a result, extra-framework cations within SSZ-13 have both positive and negative effects on the reaction rates. Overall, the positive effects are predominant, as indicated by the increased reactivity of samples with lower SiO₂/Al₂O₃ ratios.

3.3.5 Inhibition Effects of NO₂ on Catalytic Rates

Another important aspect of the NO oxidation reaction to consider is the inhibition effect of NO₂. Since there is no specific catalytic site for this oxidation reaction, all space within the micropore voids can be considered catalytically 'active'.

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The presence of NO₂ in the micropores thus reduces the availability of valuable catalytic space, and interferes with the ability of the transition state to form. As discussed in section 3.3.3, previous reports using *in-situ* IR techniques have established that numerous N_xO_y species can form within the zeolite framework upon exposure to NO/O₂ gas mixtures. These IR studies have shown that within the zeolite pores, most of the NO₂ is present as dimers (N₂O₄), which are in fact stabilized by the zeolite pores because they are larger than NO₂ and will have enhanced van der Waals interactions. N₂O₄ and NO₂ exist in equilibrium (Eq. 3.7), with N₂O₄ being highly favored at lower temperatures (T < 300 K).

$$2NO_2 \rightleftharpoons N_2O_4 \tag{3.7}$$

It is also likely (in particular for the Na-SSZ-13 samples) that N_2O_4 disproportionation into NO⁺ and NO₃⁻ readily occurs inside the pores of the sodium and acid zeolites, but this effect is difficult to assess quantitatively. To examine the inhibition effect of NO₂, varying amounts of NO₂ (0.0, 0.015, and 0.030 kPa) were introduced in the feed stream to the reactor along with NO (0.10 kPa) and O₂ (5 kPa). NO₂ steady-state outlet concentrations were measured as well. In this case, however, differential reactor analysis could not be used due to the high levels of NO₂.

To account for the product inhibition and obtain the related model parameters, the rate expression must incorporate a term for the concentration of NO₂. Based on Langmuir-Hinshelwood kinetic principles, this term should be of the form $\theta^* = \frac{1}{1+K_1C_x}$, leading to an equation of the form shown in Eq. 3.8.

$$r_{NO_2} = \frac{k[NO]^2[O_2]}{1 + K_1[N_2O_4] + K_2[NO_2] + K_3[NO^+NO_3^-] + K_4[N_2O_3] + \dots}$$
(3.8)

It is likely that N₂O₄ is the dominant species within the micropores, and therefore the equilibrium constants K_1 and K_3 (due to the equilibrium between N₂O₄ and NO⁺NO₃⁻) will be much larger compared to the others in the denominator. This allows Eq. 3.8 to be simplified (Eq. 3.9).

$$r_{NO_2} \simeq \frac{k[NO]^2[O_2]}{1 + (K_1 + K_3)[N_2O_4]} = \frac{k[NO]^2[O_2]}{1 + K'[NO_2]^{\gamma}} = \frac{Aexp(\frac{-E_a}{RT})[NO]^2[O_2]}{1 + Bexp(\frac{-H_NO_X}{RT})[NO_2]^{\gamma}}$$
(3.9)

Note that the equilibrium relation in Eq. 3.7 was used to obtain an expression in terms of [NO₂] rather than [N₂O₄]. We simulated the reactor using the integral model approach [23] to solve for the expected outlet NO₂ molar flow rates from the reactor, and then employed an optimization routine to minimize the difference between the expected and experimental NO₂ outlet flow rates and obtain the four parameters (A, E_a , B, ΔH_{NOx}) related to the rate (k) and equilibrium (K_C) constants in Eq. 3.9. The exponent (γ) with respect to [NO₂] in the denominator of Eq. 3.9 was also included as a parameter and was allowed to vary between 1 and 2. The optimized parameter values are presented in Table 3.4. Measured activation energies and preexponential factors under differential conditions corresponded well with the values obtained from the optimization routine of the integral model. Additionally, there is an evident indication of a quantitatively significant inhibition effect of NO₂ on the reaction rates in many cases. For instance, at 343 K with 150 ppm of NO₂ in the feed, $1/(1 + K'[NO_2]^{\gamma})$ in Eq. 3.9 equals ~0.86 for the reaction on Carboxen 1003, which indicates that the term in the denominator is not negligible. The reaction order γ with respect to NO₂ in the denominator of Eq. 3.9 was found to be very close to 2 for all materials except for H-SSZ-13, which showed a γ value of 1.51. The different species that form on the surface and within the micropores of H-SSZ-13 as a result of N₂O₄ disproportionation may account for the clear difference in the value for γ . These species could give rise to different potential reactivity or reaction mechanisms, especially at higher temperatures where the confinement effects are not as strong. Examining the high-temperature reactivity of the acid samples is beyond the scope of the present work.

	П	ıtegral rea	ctor analys	is		unerenuar analysi	eactor s
Material	A [L ³ mol ⁻² s ⁻¹ g _{cat} ⁻¹]	E _a [kJ mol ⁻¹]	B [mol L ⁻¹] ⁻¹	AH [kJ mol ⁻¹]	γ	\mathbf{A} [L ³ mol ⁻² s ⁻¹ g _{cat} ⁻¹]	E _a [kJ mol ⁻¹]
pure-silica CHA	12.2	-25.1	9 x 10 ¹³	31.2	1.98	10.1	-24.9
H-SSZ-13	31.3	-38.9	$4 \ge 10^{13}$	32.5	1.51	30.1	-37.5
Na-SSZ-13	33.1	-37.6	$8 \ge 10^{13}$	36.6	1.94	40.8	-35.6
Carboxen 569	22.8	-26.9	$7 \ge 10^{13}$	32.2	1.97	25.5	-31.8
Carboxen 1000	19.5	-27.2	2×10^{13}	30.5	1.93	25.9	-31.4
Carboxen 1003	25.7	-30.5	$4 \ge 10^{13}$	31.4	1.95	29.7	-31.2
Basolite A100	9.6	-25.8	$9 \ge 10^{13}$	30.2	2.00	11.8	-32.6

Table 3.4. Optimized parameters for NO₂ inhibition model (Eq. 3.9) [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

3.3.6 Transition State Theory: Enthalpic and Entropic Parameters

Transition state theory formalisms are useful to understand the kinetic benefits associated with confinement of the reactants within the catalyst micropores. Specifically, the Gibbs free energy difference from the gaseous reactants to the confined transition state (ΔG^{\dagger}) can be related to measured parameters to validate the kinetic similarity of the homogenous and heterogeneous reaction pathways. The enthalpic and entropic contributions to the free energy change are related to the activation energies (E_a) and rate constants (k) obtained from the optimization of the integral reactor model (Table 3.4), respectively (Eqs. 3.10 and 3.11) [24, 25].

$$\Delta H^{\dagger} = E_a - mRT \tag{3.10}$$

$$k = 2\kappa \frac{k_B T}{h} exp\left(\frac{\Delta S^{\dagger}}{R}\right) exp\left(\frac{-\Delta H^{\dagger}}{RT}\right) \left[\frac{1 \ mol}{m_{ref}^3}\right] \left[\frac{1 \ mol}{m_{gas}^3}\right]^{-3}$$
(3.11)

In Eqs. 3.10 and 3.11, *m* is the number of molecules involved in forming the transition state (3 for $[N_2O_4]^{\ddagger}$) and κ is the transmission coefficient (unit value assumed).² The standard state of the reactants and transition state is 1 mol $(m_{ref}{}^3)^{-1}$, where the relevant reference volume, $m_{ref}{}^3$, is the microporous volume of the materials to account for the confined space within which the reaction occurs. The calculated transition state theory parameters for each sample are listed in Table 3.5.

² In Eq. 3.11, a factor of 2 is inserted because measured reaction rate constants for the NO oxidation reaction involve the formation of 2 moles of NO₂, but the rate constants associated with the formation of the transition state only involve the formation of one transition state ($k_{NO_2} = 2k^{\ddagger}$).

Material	∆ <i>H</i> [‡] [kJ mol ⁻¹]	ΔS [‡] [J mol ⁻¹ K ⁻¹]
Pure-silica CHA	-33.7	-272.2
H-SSZ-13 (SiO ₂ /Al ₂ O ₃ = 12)	-47.1	-304.8
Na-SSZ-13 $(SiO_2/Al_2O_3 = 12)$	-46.4	-301.9
Carboxen 569	-35.3	-277.2
Carboxen 1000	-36.2	-286.1
Carboxen 1003	-39.7	-280.2
Basolite A100	-34.8	-300.8

Table 3.5. Activation enthalpies (ΔH^{\dagger}) and entropies (ΔS^{\dagger}) calculated from transition state theory formalisms (Eqs. 3.10 and 3.11) for catalyzed NO oxidation (298-423 K) [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

 ΔH^{4} values range from -33.7 kJ mol⁻¹ (pure-silica CHA) to -47.1 kJ mol⁻¹ (H-SSZ-13). Entropic losses range from -272.2 J mol⁻¹ K⁻¹ (pure-silica CHA) to -304.8 J mol⁻¹ K⁻¹ (H-SSZ-13), and are a consequence of taking the reactants from the gas phase to the confined transition state within the micropores of the catalysts. The activation enthalpies reflect the stabilization of the transition state by confinement, and have a thermodynamically favorable effect on the Gibbs free energy change for the chemical reaction. The entropic losses are quite large and kinetically unfavorable, reflecting the kinetic effects of restricted translational, vibrational and rotational freedom that the transition state experiences within the micropores. Nevertheless, at lower temperatures these entropic barriers become less significant and enthalpic stabilization predominates, leading to the high catalytic activity observed.

The values of ΔH^{\dagger} and ΔS^{\dagger} calculated here are of the same magnitude as the values reported by Artioli et al. [3], although our ΔH^{\dagger} values for the siliceous CHA samples are slightly lower (-33.7 kJ mol⁻¹ here vs. -41.2 kJ mol⁻¹ reported by Artioli et al. [3]), perhaps because they did not consider NO₂ inhibition in their analysis. The activation enthalpies for the Carboxen samples range from -35.3 (Carboxen 569) to -

39.7 kJ mol⁻¹ (Carboxen 1003) (Table 3.5). Carboxen 1000 and 1003 exhibit more negative enthalpy values compared to Carboxen 569, a result consistent with the fact that Carboxen 569 has a significantly larger micropore size and decreased void space. Pore size distributions indicate that Carboxen 1000 has a large fraction of small pores with a width of ~5.5 Å, Carboxen 1003 has a smaller percentage of pores with widths of ~6-7 Å, and Carboxen 569 has a larger pore size of ~11 Å (see Figures 3.3-3.5). The greater negative enthalpy difference for the Carboxen 1000 and 1003 samples with smaller micropores indicates a greater degree of stabilization of the transition state. However, as observed in section 3.3.3, reaction rates normalized per surface area and micropore volume scale in the following order: Carboxen 569 > Carboxen 1003 >Carboxen 1000. This ordering is not consistent with the enthalpic stabilizing properties of the samples, and suggests that the catalytic differences observed are attributed primarily to entropic differences. Carboxen 1000 has, for instance, the most unfavorable entropy difference between the transition state and the gaseous reactants (-286.1 J mol⁻¹ K⁻¹) of the three carbon materials, but not the largest adsorption heat, suggesting that perhaps the pores are slightly too small to maximize the stabilization energy. Nonetheless, they constrain the mobility of the transition stare more than the other two carbon samples. The smaller pores of Carboxen 1000 approach the molecular size of the transition state and frustrate its translational, vibrational, and rotational modes of freedom. Conversely, the larger micropores of Carboxen 569 seem to better accommodate the transition state from an entropic standpoint, while still being small enough to provide enthalpic stabilization to a significant degree. Thus, in a trade-off between enthalpy and entropy gains and losses associated with confinement, the entropy term appears to dictate catalytic behavior for the Carboxen materials. Note

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also that the entropy losses in the carbons are comparable to the entropy loss in the pure-silica CHA sample. This is, in fact, as expected since in all of these cases there are no electrostatic interactions that would tend to localize the position of the transition state within the pores.

To further evaluate the hypothesis that the heterogeneously catalyzed reaction proceeds through an $[N_2O_4]^{\dagger}$ activated complex species similar to that in the homogeneous phase reaction, the ΔH^{\dagger} values listed in Table 3.5 were compared to isosteric heats of adsorption ($\Delta H_{ads.}$) of ethane and propane on H-MFI (SiO₂/Al₂O₃ = 600), silicalite-1, and MOF M₂(dobdc) (M = Mg, Mn, Fe, Co, Ni, Zn; dobdc = 2,5dioxido-1,4-benzenedicarboxylate) materials reported in the literature (Table 3.6) [26-28].

Table 3.6. Isosteric heats of adsorption ($\Delta H_{ads.}$) of ethane and propane as reported in literature and measured in this study [30]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

Material	ΔH _{ads.} (ethane) [kJ mol ⁻¹]	ΔH _{ads.} (propane) [kJ mol ⁻¹]	Reference
H-MFI $(Si/Al = 300)$	31-32	41-45	[25]
SIL-1	31-33	43-46	[24]
MOF M ₂ (dobdc)	25-26	34-35	[26]
Pure-silica CHA	26-27	32-36	This report

MOF M₂ is also commonly known as MOF-74, and its framework consists of onedimensional channels in a hexagonal array lined with five-coordinate M²⁺ ions [28]. We have measured ethane and propane adsorption isotherms over pure-silica CHA at several temperatures and used the Clausius-Clapeyron equation (Eq. 3.12) to compute $\Delta H_{ads.}$ for additional comparison with ΔH^{\dagger} values (Table 3.6).

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{ads.}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
(3.12)

If a N₂O₄ structure is in fact the transition state, then the ΔH^{\dagger} values should be comparable to the adsorption enthalpies for ethane and propane, which have similar molecular volumes to N₂O₄ based on liquid densities [29]. Comparison of the enthalpy values in Tables 3.5 and 3.6 shows similarity between our calculated values from transition state theory and the experimental values reported for propane adsorption on the materials in Table 3.6. This resemblance provides further evidence that the homogenous and catalyzed reactions proceed through a similar activated complex. The ethane $\Delta H_{ads.}$ values are lower than the ΔH^{\dagger} values for the NO oxidation reaction we obtained from transition state theory, suggesting that the $\Delta H_{ads.}$ for propane compares more directly with the adsorption enthalpy of the transition state being formed in the NO oxidation reaction.

3.4 Conclusions

In this chapter, I have shown that NO oxidation is effectively catalyzed by SSZ-13 (H⁺, Na⁺, and siliceous samples), porous carbon materials (members of the Carboxen series), and MOF Basolite A100 at temperatures between 298 K and 423 K. Within this regime stoichiometric reaction orders were similar to those observed in the homogeneous phase reaction. Apparent activation energies were negative in all cases (-24.9 kJ mol⁻¹ to -37.5 kJ mol⁻¹), and were much more negative than the value of -4.4 kJ mol⁻¹ for the homogeneous reaction. Evidence was presented indicating the

occurrence of a homogeneous-like reaction within the catalyst micropores, with reaction rates accelerated as a result of physical confinement effects that stabilize a $[N_2O_4]^{\ddagger}$ transition state. Electrostatic effects from extra-framework cations within SSZ-13 samples were shown to provide additional stabilization of the transition state and further enhance reaction rates. Using transition state theory formalisms, negative enthalpies (-33.7 kJ mol⁻¹ to -47.1 kJ mol⁻¹) and entropies (-272.2 J mol⁻¹ K⁻¹ to -304.8 J mol⁻¹ K⁻¹) of formation of the transition states were obtained. These values show that the catalytic enhancements observed are due to the enthalpic stabilization of the transition state, as was also observed by Artioli et al. [3]. The entropy differences associated with the formation of the transition state for the Carboxen materials dictate catalytic activity more so than in the zeolite and MOF materials, possibly a result of the irregular pore structure of these materials. Lastly, the inhibition effect of NO₂ was experimentally investigated and quantitatively assessed using the integral reactor approach and Langmuir-Hinshelwood kinetic models. The presence of NO₂ in the feed stream was shown to negatively affect reaction rates with a reaction order close to -2.

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Chapter 4

OXIDATION OF ZEOLITE ACID SITES IN NO/O₂ GAS MIXTURES AND THE CATALYTIC PROPERTIES OF THE NEW SITE IN NO OXIDATION

4.1 Introduction

There have been many investigations on the kinetics and reaction mechanism of NO oxidation over metal-containing zeolites, particularly those with copper and iron species [1-3]. Less attention has been given to the high-temperature NO oxidation mechanism on materials without transition metals. Early reports by Halasz et al. [4, 5] showed that H-ZSM-5 was capable of catalyzing NO oxidation, while Li-ZSM-5 showed minimal activity at temperatures above 473 K. The authors suggested that the Brønsted acid sites were the likely active sites for the reaction. Järås and co-workers [6-8] studied NO oxidation on mordenite (MOR) zeolites, and ranked zeolite catalysts based on observed reaction rates in the order of H-MOR > Fe-MOR > Cu-MOR for NO oxidation, but in the reverse order for the NO reduction by NH₃-SCR. The NO oxidation rate was dependent on the aluminum content for the H-MOR catalyst, and the authors suggested that surface NO⁺ is involved in the catalytic cycle [8]. Yogo and coworkers [9-11] observed that the NO oxidation rate on Na/H-ZSM-5 increased with increasing proton exchange level, and deduced that acid sites in ZSM-5 were responsible for the activity. They also noted a strong inhibition of the reaction by water. Stakheev et al. [12] found that H-ZSM-5 was in fact more active than Co/H-ZSM-5 catalysts with low levels of Co exchange ($< \sim 30\%$), and suggested that the Co ions only become catalytically active at increased loadings when cobalt oxide particles form. Lonyi et al. [13] recently observed activity on H-ZSM-5 at temperatures between 573 K and 823 K, though it was substantially lower compared to Co-H-ZSM-5; the activity of H-ZSM-5 was assigned to the Brønsted acid sites, though they did not propose a reaction mechanism. Miller et al. [14] observed acid forms of ZSM-5 and MOR to be effective for NO oxidation at 573 K, while USY and silica-alumina exhibited poor activity. Other recent reports [15, 16] have shown that siliceous zeolites and microporous materials can very effectively catalyze NO oxidation at temperatures below 423 K.

In-situ infrared (IR) spectroscopy techniques are often applied to characterize the structure and stability of N_xO_y surface species. Previous reports [13, 17-22] have examined NO/O₂/NO₂ adsorption on zeolites to identify N_xO_y adsorbates that may have a role in the NO oxidation reaction: many surface species are present, especially at low temperatures. The nitrosonium ion (NO⁺) is frequently observed and discussed because of its mechanistic importance in NH₃-SCR and NO oxidation. There is general agreement that NO⁺ exhibits an IR signature around 2100-2200 cm⁻¹, although uncertainty remains about the conditions under which it is stable and its precise role in the mechanisms of NH₃-SCR and NO oxidation on various catalysts. The importance of NO⁺ in NH₃-SCR may be linked to ammonium nitrite (NH₄NO₂), a key reaction intermediate that decomposes quickly into nitrogen and water. The nitrogen atoms from the ammonium group and nitrite group in NH₄NO₂ have formal oxidation states of 3- and 3+, respectively. NO⁺ and NO₂⁻ (nitrite) are the only N_xO_y species with nitrogen in a 3+ formal oxidation state.

In Chapter 3, it was reported that NO oxidation is catalyzed by several kinds of microporous materials, such as activated carbons, metal-organic frameworks (MOFs),

and zeolites in the proton, sodium, and siliceous forms at temperatures below 423 K [16]. Measured rates were observed to be ~100-10,000 times larger than the homogeneous phase reaction rates. The catalytic properties of the materials were attributed to their ability to stabilize a $[N_2O_4]^{\ddagger}$ transition state within the micropores through non-covalent van der Waals and electrostatic forces. This confinement effect accelerates the homogenous-like reaction and leads to large and negative activation energies (-24.9 kJ mol⁻¹ to -37.5 kJ mol⁻¹) compared to the homogeneous phase reaction (-4.4 kJ mol⁻¹).

In this chapter we examine the NO oxidation reaction at high temperatures (T > 423 K) catalyzed by three zeolite frameworks (CHA, MFI, BEA) and investigate the effects of the Si/Al ratio and extra-framework cations (H⁺, Na⁺ and siliceous) on reaction rates. The results show that NO oxidation is catalyzed effectively on H- and Na-exchanged zeolites (BEA, MFI, and CHA), and that the zeolite structure and composition considerably affect NO oxidation rates. We have used *in-situ* Fourier transform infrared (FTIR) spectroscopy to monitor N_xO_y surface species formed on zeolite materials, and show that NO⁺ coordinated to framework aluminum sites within the zeolite pores is directly involved in the catalysis. FTIR studies also reveal that NO⁺ is in equilibrium with gas phase NO, and that desorption of NO⁺ (as NO) results in an oxidized zeolite site. Based on these data we propose a reaction mechanism for the catalytic high temperature NO oxidation on high silica H-SSZ-13 (CHA).

4.2 Materials and Methods

4.2.1 Catalyst Synthesis

Pure-silica and alumino-silicate samples of SSZ-13 (CHA) were prepared using a previously reported synthesis procedure [16]. ZSM-5 (MFI) materials with Si/Al ratios of 12 and 18 were synthesized using a procedure described by Kim et al. [23]. Commercial forms of zeolite beta (BEA) (CP 814E^{*}, Si/Al = 12.5; CP 814C^{*}, Si/Al = 19) and ZSM-5 (CBV 8014, Si/Al =40; CBV 28014, Si/Al = 140) were obtained from Zeolyst International. Samples were calcined in air at 823 K for 8 h using a ramping rate of 180 K h⁻¹ to generate the Brønsted acid sites from the ammonium-form zeolite.

4.2.2 Analytical

Powder X-ray diffraction (XRD) patterns were collected using a Phillips X'pert diffractometer with a Cu K α source. Textural characterization of the samples was determined using N₂ physisorption at 77 K. Isotherms were collected on a Micrometrics ASAP 2020 and analyzed using the *t*-plot method to calculate microporous volumes. Scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDX) spectra were collected on a JEOL JSM7400F microscope to provide information regarding sample morphology and elemental composition, respectively. ²⁹Si and ²⁷Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectra of zeolite samples were recorded on a Bruker AVIII-500 solid-state NMR spectrometer. The spectrometer was operated at a Larmor frequency of 500.138 MHz for ¹H and 99.362 MHz for ²⁹Si. A 4-mm HX MAS probe was used for all measurements. All spectra were recorded at a MAS frequency of 10 kHz, controlled to within \pm 2 Hz using a Bruker MAS controller. ²⁹Si single pulse and cross-polarization

(CP) measurements have been performed as well. For ²⁹Si single pulse MAS experiments, a 90° pulse with a width of 4.3 μ s was used and the recycle delay was 30 s. For {¹H}-²⁹Si CP MAS experiments, the ¹H 90° pulse duration was 2.5 μ s. A linear amplitude ramp (80-100%) on ¹H was used with a contact time of 4.5 ms, and the recycle delay was 5 s. SPINAL64 ¹H decoupling with an RF field strength of 100 kHZ was applied during the acquisition period for both SP and CP MAS measurements. For ²⁷Al single-pulse MAS experiments, a 90° pulse with a width of 1.25 μ s was used with a recycle delay of 1 s. Silicon resonance intensities in the NMR spectra were used to estimate Si/Al ratios of the zeolite materials according to Eq. 4.1, where *I* is the intensity of a particular silicon resonance and *n* is the number of coordinated Al atoms for that resonance. Deconvolution techniques were used to accurately determine the intensities of overlapping resonances. Elemental analysis was also carried out using inductively coupled plasma (ICP) mass spectrometry.

$$\frac{Si}{Al} = \frac{\sum_{n=0}^{4} I_{Si(nAl)}}{\sum_{n=0}^{4} 0.25 n I_{Si(nAl)}}$$
(4.1)

4.2.3 NO Oxidation Rate Measurements

NO oxidation rates were measured using a differential reactor flow system (see Figure 2.4 in Chapter 2). Reactant gases (2% NO/He, 1% NO₂/He, 15% O₂/He) and He carrier gas (99.995%) were controlled using electronic mass flow controllers (Brooks 5850E series) to provide a range of inlet reactant partial pressures (0.02-0.10 kPa NO, 1-5 kPa O₂, 0.005-0.05 kPa NO₂) at a total flow rate of 100 sccm. Zeolite catalysts were treated in flowing 10% O₂/He at 793 K for 2 h prior to catalytic rate measurements. Outlet stream concentrations were monitored using a heated transmission infrared (IR) gas cell (Specac Cyclone C2 fixed 1 M pathlength) within a Fourier transform infrared (FTIR) spectrometer (Nicolet Nexus 470). NO oxidation rate measurements are reported on a specific basis (mol s⁻¹ g_{cat.}⁻¹) and as turnover frequencies (s⁻¹) per acid site for H-form zeolites. NO conversions were maintained below 10% for all measurements to ascertain differential reaction conditions. Control experiments were conducted in the absence of a catalyst to assess the contribution of the gas-phase reaction to observed reaction rates. Reaction orders α , β , and γ with respect to NO, O₂, and NO₂ were measured over the different catalysts by analyzing the rate dependency on reactant concentration using the following relation (Eq. 4.2):

$$r_{NO_2} = \frac{k_{app.}[NO]^{\alpha}[O_2]^{\beta}}{1 + K[NO_2]^{\gamma}}$$
(4.2)

Eqs. 4.3 and 4.4 were used to model the reaction and obtain the rate constants and associated kinetic parameters in the absence or presence of NO_2 in the feed gas, respectively.

$$r_{NO_2} = k_{app._1} [NO]^{\alpha} [O_2]^{\beta}$$
(4.3)

$$r_{NO_2} = k_{app._2} [NO]^{\alpha} [O_2]^{\beta} [NO_2]^{-\gamma}$$

$$4.4)$$

4.2.4 In-situ IR Spectroscopy Studies

A flow system was used to introduce $NO/O_2/NO_2$ gas mixtures to the zeolite samples during FTIR spectroscopy surface experiments. Typical inlet concentrations consisted of combinations of 500-2,000 ppm NO, 5% O₂, and 100 ppm NO₂ to approach gas compositions of combustion gases. Tests were carried out using the same spectrometer described above. The spectrometer was operated at a spectral resolution of 4 cm⁻¹, and the obtained spectra were averaged from 100 collected scans. The IR spectra presented in this report represent those that reached steady-state under the conditions listed. Zeolite samples were loaded into an *in-situ* transmission infrared cell, which was built in accordance with the original design by the Ribeiro group [24]. Briefly, the FTIR cell is comprised of a cell body, sample holder, and aluminum heating block. Approximately 50 mg of zeolite was required to make the sample pellet/waffer, which was loaded onto the sample holder disks. The sample holder was held in place within the cell body along the IR beam path. CaF₂ IR-grade windows (25.4 mm diameter, 10 mm thickness, Redoptronics) were chosen to provide a spectral range of 4000-1100 cm⁻¹. Gas lines connected to the cell body allowed the gases to contact the samples in a controlled flow pattern. A heating block housed the assembled IR cell, and utilized 4 heating rods (McMaster Carr, 125 W) connected to a temperature controller (Omega CSI32K benchtop controller) to regulate the sample temperature. A thermocouple (Omega, K-type, 1/16 in. diameter) was positioned through an insert in the cell body to measure the sample temperature. Zeolite samples were pre-treated in 15% O₂/He at 573 K (300 K/h ramp rate) for 3 h to remove adsorbed water and other surface contaminants. Afterwards, background spectra of the activated samples were collected at the temperatures for which the studies were conducted.

4.3 **Results and Discussion**

4.3.1 Material Characterization

Powder XRD patterns (Figure 4.1) revealed no impurities and confirmed that all zeolite samples were highly crystalline with the expected framework structures.



Figure 4.1. Powder XRD patterns of H-SSZ-13, H-ZSM-5, and H-BEA [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

Microporous volumes and external surface areas were determined from the analysis of the N_2 adsorption isotherms (Table 4.1). These data are all consistent with samples of high crystallinity.

Material	Microporous Volume [cm ³ g ⁻¹]	External Surface Area [m ² g ⁻¹]	Si/Al Ratio
H-SSZ-13	0.28	32	6.4
H-SSZ-13	0.27	32	11.8
H-ZSM-5	0.12	100	12.1
H-ZSM-5	0.12	102	18.3
H-BEA	0.17	162	12.7
H-BEA	0.18	165	18.7

Table 4.1. Microporous volumes, external surface areas, and estimated Si/Al ratios for H-SSZ-13, H-ZSM-5, and H-BEA materials [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

EDX chemical analyses of the zeolite samples were used to estimate the Si/Al ratios. Solid-state magic-angle-spinning NMR (²⁹Si and ²⁷Al) confirmed that the content of extra-framework aluminum species was low for all zeolite samples (Figure 4.2). Framework Si/Al ratios were also estimated from the solid-state MAS NMR spectra (Table 4.1).



Figure 4.2. (a) ²⁷Al MAS NMR spectra of H-ZSM-5. (b) ²⁷Al MAS NMR spectra of H-BEA. (c) ²⁹Si MAS NMR spectra of H-ZSM-5. (d) ²⁹Si MAS NMR spectra of H-BEA [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

4.3.2 Effects of Temperature, Framework, and Extra-framework Cations on NO Oxidation Rates

NO oxidation rates were measured as a function of temperature from 298-623 K on H-, Na-, and siliceous CHA materials to observe the effects that aluminum atoms and the extra-framework cation (H^+ , Na⁺) have on reactivity (Figure 4.3). NO₂ was the

only product observed, with no detectable quantities of N₂O or any other side products. The materials exhibit two reaction regimes as a function of temperature, as indicated by the V-shape curve in Figure 4.3. Below a temperature of approximately 423 K, all materials display substantial catalytic reactivity, and reaction rates *decrease* with increasing temperature, resulting in negative apparent activation energies (-24.9 to -37.5 kJ mol⁻¹). These low-temperature results were described in Chapter 3 [15, 16], with the catalytic activity attributed to a confinement effect in the materials' micropores that accelerate a homogeneous-like reaction by stabilizing a N₂O₄[‡] transition state inside the zeolite crystals.



Figure 4.3. Arrhenius plots of the forward NO oxidation rates $(1,000 \text{ ppm NO} + 5\% \text{ O}_2, 100 \text{ sccm}, 0.1 \text{ g catalyst})$ at 298-623 K on SSZ-13 (CHA) materials [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

The trend with temperature changes above 423 K, and reaction rates on H-SSZ-13 and Na-SSZ-13 increase with increasing temperature (left-hand side of V curve), a clear indication that a different reaction mechanism occurs above 423 K. The reaction rates on *siliceous* CHA are low and unaffected by temperature above 423 K, indicating that the material has minimal catalytic activity in this temperature regime. This is in contrast to the alumino-silicate samples, which showed significant catalytic rates, approximately 10-100 times than those on siliceous CHA. Note that thermodynamic equilibrium limitations become significant at temperatures greater than 623 K (beyond the maximum temperature investigated here), and our measurements did not indicate any substantial influence of the reverse reaction at the temperatures investigated.

Above 423 K reaction rates scale as follows: H-SSZ-13 > Na-SSZ-13 > puresilica CHA. This differs from the order below 423 K, where reaction rates were highest for Na-SSZ-13, followed by H-SSZ-13 and then pure-silica CHA. The higher activity for H-SSZ-13 compared to Na-SSZ-13 at high temperatures is consistent with an earlier report by Halasz et al. [5] that showed fast catalytic rates for H-ZSM-5 but substantially lower rates for Li-ZSM-5. In both instances, the proton form of the zeolite shows faster reaction rates than the alkali metal-exchanged zeolite. This difference in catalytic rates indicates that the acid site is directly involved in the catalytic reaction. The observation that pure-silica CHA is inactive above 423 K further supports the notion that framework aluminum atoms with exchanged cations are necessary to observe activity. In the high-temperature regime, reaction rates on H-SSZ-13 change more rapidly with temperature compared to those on Na-SSZ-13. We also found that reaction rates were independent of the starting temperature; that is, proceeding from high to low temperature and from low to high temperature resulted in

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the same reaction rates (Figure 4.4). The activation energies (E_a) obtained from the Arrhenius plots in Figure 4.3 (using the data above 423 K) were 18.2 kJ mol⁻¹ for Na-SSZ-13 and 39.6 kJ mol⁻¹ for H-SSZ-13. The difference is substantial and suggests differences in the reaction mechanism for the Na⁺ versus the acid sample in this high temperature regime (see below). This is the opposite of what is observed at low temperatures, where the sodium sample has higher (more negative) activation energy than the proton sample, a difference that was attributed to the larger electrostatic interaction between the sodium cation and the transition state than is the case with the acid sample.



Figure 4.4. Independence of initial starting temperature on NO oxidation reaction rates (1,000 ppm NO + 5% O_2) on H-SSZ-13 (298-673 K) [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

To assess the effect of the zeolite structure on the NO oxidation reaction, rates were measured as a function of temperature in the high temperature regime (423-623 K) over three zeolites (CHA, MFI, BEA) in the proton form and with Si/Al ratios ranging from 6-140. Note that the three frameworks have different pore systems: CHA is a small-pore zeolite with a three-dimensional 8-membered rings pore system (3.72 Å diameter), MFI is a medium-pore zeolite with 10-membered rings (~5.6 Å diameter), and BEA is a large-pore zeolite with 12-membered rings (~7.6 Å diameter). Reaction rates are plotted as turnover frequencies (TOFs) per mol of Brønsted acid sites in Figure 4.5.



Figure 4.5. NO oxidation turn-over-frequencies (TOFs) per Brønsted acid site on H-SSZ-13, H-ZSM-5, and H-BEA with varying Si/Al ratios (T = 423-623 K) [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

The order of NO oxidation rate is: H-SSZ-13 > H-ZSM-5 > H-BEA. This trend suggests that reaction rates increase with decreasing pore size. Turnover frequencies for each framework were found to be relatively consistent and independent of Si/Al ratio; however, TOF variation was observed to be as high as ~20% at certain temperatures over the H-ZSM-5 framework. Additionally, TOFs on H-ZSM-5 with Si/Al = 12 were consistently greater than those on H-ZSM-5 with Si/Al = 18 as a function of temperature; this may be due to site-site interactions in H-ZSM-5 that are more prevalent in this zeolite because it has a lower microporous volume than beta or chabazite (at a given Si/Al ratio). The reaction rates on the three zeolite frameworks are affected differently by temperature, with H-BEA having an E_a value of 54.2 kJ mol⁻¹, and H-ZSM-5 and H-SSZ-13 having E_a values of 45.1 kJ mol⁻¹ and 35.9 kJ mol⁻¹ ¹, respectively. Consequently, a larger difference between reaction rates is observed at lower temperatures of the reaction regime, while at higher temperatures, the differences in reactivity become smaller. The observed TOFs can be compared to reported values for NH₃-SCR to determine whether or not the NO oxidation reaction is kinetically relevant to the SCR reaction. Ellmers et al. [25] reported a TOF of $\sim 2.5 \times 10^{-3}$ s⁻¹ on Fe-ZSM-5 at 523 K under a feed of 1,000 ppm NO, 1,000 ppm NH₃, and 2% O₂, which is several orders of magnitude greater than the TOFs we measured $(8 \times 10^{-5} \text{ s}^{-1} \text{ on H-SSZ-13 and } 5 \times 10^{-5} \text{ s}^{-1} \text{ on H-ZSM-5})$ for NO oxidation at the same temperature. Thus, it appears that although the zeolites used in this study are quite active in catalyzing the NO oxidation reaction relative to the gas-phase reaction, the observed rates are still significantly lower than those reported for standard SCR.

4.3.3 Reaction Orders with Respect to NO, O₂, and NO₂

NO oxidation rates were measured on H-SSZ-13 (Si/Al = 12) while varying the NO, O₂, or NO₂ inlet concentrations to determine reaction orders (α , β , and γ) for NO, O₂, and NO₂, respectively, at 473 K (Figure 4.6). The following rate expression (Eq. 4.5) accurately fits the reaction rate data:

$$r_{NO_2} = k_{app.}[NO][O_2][NO_2]^{-1}$$
(4.5)



Figure 4.6. NO oxidation rates on H-SSZ-13 (Si/Al = 12) at 473 K vs. NO partial pressure (200-1,000 ppm) + 5% O₂ (\bullet), O₂ partial pressure (1-5%) + 500 ppm NO (\blacksquare), and NO₂ partial pressure (50-500 ppm) + 500 ppm NO + 5% O₂ (\blacktriangle) [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

NO oxidation rates are proportional to NO and O₂ concentrations, and inversely proportional to NO₂ over the range of investigated inlet concentrations. These reaction orders have been observed previously by Weiss and Iglesia [26, 27] on Pd/Al₂O₃ and Pt/Al₂O₃ under similar reaction conditions. Note that these reaction orders differ from those found in the low temperature reaction regime (2 for NO and 1 for O₂), providing further evidence that a change in the reaction mechanism occurs at ~423 K [15, 16]. Residual error plots of the data fit in Figure 4.6 were examined to verify that the variation of the residuals was random, and sample plots are shown in Figure 4.7. The plots show no discernible patterns or trends, indicating that the reaction rate model describes the observed behavior adequately.



Figure 4.7. Residual errors for NO oxidation rates on H-SSZ-13 (Si/Al = 12) at 473 K versus a) NO, b) O_2 , and c) NO₂ pressure [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

Reaction orders for the acid form of the other zeolites structures (ZSM-5, BEA) at high temperature were found to be similar (Table 4.2). The agreement of the

reaction orders for all of the materials at high temperatures suggests a similar NO oxidation reaction mechanism: differences in activation energy are most likely due to the difference in stabilization of the transition state by the various zeolites.

Material	T (K)	NO Reaction Order	O2 Reaction Order
H-ZSM-5 (Si/Al = 12)	498	1.05 ± 0.04	0.98 ± 0.05
H-BEA (Si/Al = 12.5)	498	1.03 ± 0.06	1.07 ± 0.04
H-SSZ-13 (Si/Al = 6)	548	0.93 ± 0.05	1.04 ± 0.06
Na-SSZ-13	498	1.06 ± 0.04	1.02 ± 0.05

Table 4.2. Reaction orders with respect to NO and O₂ on various zeolite catalysts [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

Table 4.3 summarizes reaction rates, turnover frequencies (TOF), and kinetic parameters (E_a , k_o) for the high temperature NO oxidation on H-SSZ-13, H-ZSM-5, and H-BEA with Si/Al ratios near 12. The rate constants were calculated assuming the experimentally observed reaction orders (first order with respect to NO and O₂). The reaction rate on H-SSZ-13 at 473 K is approximately two times larger than the rate on H-ZSM-5 and about 8 times larger than the rate on H-BEA.

Table 4.3. Measured NO oxidation rates and turn-over-frequencies (T = 473 K), and calculated activation energies (E_a) and pre-exponential factors (k_o) (T = 423-623 K) for H-SSZ-13 (Si/Al = 12), H-ZSM-5 (Si/Al = 12), and H-BEA (Si/Al = 12.5) [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

Material	Rate [mol s ⁻¹ g _{cat.} -1]	<i>E_a</i> [kJ mol ⁻¹]	k ₀ [L ² mol ⁻¹ s ⁻¹]	TOF [s ⁻¹]
H-SSZ-13	6.12×10 ⁻⁸	39.6	3.44×10^{3}	6.74×10 ⁻⁵
H-ZSM-5	2.09×10 ⁻⁸	45.1	9.58×10^{3}	2.32×10 ⁻⁵
H-BEA	8.21×10 ⁻⁹	54.2	2.78×10^{4}	9.35×10 ⁻⁶

Activation energies estimated over the temperature range of 423-623 K for H-SSZ-13 (Si/Al = 12), H-ZSM-5 (Si/Al = 12), and H-BEA (Si/Al = 12.5) are 39.6 kJ mol⁻¹, 45.1 kJ mol⁻¹, and 54.2 kJ mol⁻¹, respectively. Note that as pore size increases, activation energy increases. The lower activation energy for H-SSZ-13 indicates that there is a greater enthalpic stabilization to the transition state compared to the other zeolite frameworks ($E_a = \Delta H^{\dagger} + mRT$). Previous kinetic studies of high-temperature NO oxidation on zeolites and other catalytic materials have reported a wide range of apparent activation energies (Table 4.4) [6, 28-36]. The activation energies measured in this study fall within the broad range of these reported values (8.9-75.3 kJ mol⁻¹).

Material	<i>Ea</i> [kJ mol ⁻¹]
Cu-SSZ-13	57.6 [28]
Cu-SSZ-13	52.5 [29]
Commercial SCR Cu-zeolite	29-31 [30]
Commercial SCR Cu-zeolite	32 [31]
Cu-ZSM-5	8.9 [32]
Fe-ZSM-5	39-43.2 [33-35]
Fe-MFI	43.1 [34]
Cu-MFI	75.3 [34]
Fe-FER	59.7 [35]
H-MOR	46 [6]
H-MOR	21 [6]
Pt/Al ₂ O ₃	39 [36]

Table 4.4. Activation energies for NO oxidation on zeolite materials reported in the literature [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

Average TOFs and kinetic parameters (E_a , k_o) were calculated for each zeolite framework with different Si/Al ratios (Table 4.5) based on the data from Figure 4.3. Activation energies for each framework type with different Si/Al ratios were found to
be in good agreement and thus independent of the Si/Al ratios tested. Greater variation was seen for H-ZSM-5 compared to the other zeolite frameworks; the origin of this variability remains uncertain.

Table 4.5. Average NO oxidation turn-over-frequencies (T = 473 K) and calculated activation energies (E_a) and pre-exponential factors (k_o) (T = 423-623 K) for H-SSZ-13, H-ZSM-5, and H-BEA [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

Material	TOF [s ⁻¹]	<i>E_a</i> [kJ mol ⁻¹]	k ₀ [L ² mol ⁻¹ s ⁻¹]
H-SSZ-13	$4.72 \times 10^{-5} \pm 0.071 \times 10^{-5}$	40.8 ± 1.1	$3.53 \times 10^3 \pm 0.15 \times 10^3$
H-ZSM-5	$2.21{\times}10^{\text{-5}}\pm0.26{\times}10^{\text{-5}}$	45.7 ± 2.6	$7.05 \times 10^3 \pm 3.4 \times 10^3$
H-BEA	$1.02 \times 10^{-5} \pm 0.11 \times 10^{-5}$	55.5 ± 1.8	$2.86{\times}10^4 \pm 0.13{\times}10^4$

4.3.4 *In-situ* IR Spectroscopy Studies of N_xO_y Surface Species on SSZ-13 Zeolites at Temperatures Between 423 K and 623 K

In-situ IR spectroscopy experiments were conducted to examine N_xO_y surface species formed on the zeolite under reaction conditions from exposure to flowing gas mixtures of NO, O₂, and NO₂. The aim is to identify relationships between the species observed by IR spectroscopy and catalytic activity. H-SSZ-13 was chosen for this investigation since it showed the highest NO oxidation activity in the high-temperature reaction regime (423-623 K) and has a simpler structure than MFI or BEA. We monitored in particular the presence of the nitrosonium ion (NO⁺), which has been observed to form during NO oxidation on zeolites at low temperatures [17-22]; these reports, however, have not investigated the N_xO_y surface species that form at elevated temperatures. Additionally, it is known that NO⁺ plays a role in the NH₃-SCR reaction mechanism on certain metal-exchanged zeolites [37-40]. NO⁺ formation over acid zeolites occurs at low temperatures through the heterolytic dissociation of N_2O_4 at Brønsted acid sites (Eq. 4.6).

$$N_2 O_4 \rightleftharpoons N O^+ + N O_3^- \tag{4.6}$$

Because of the charge of NO^+ , it can ion-exchange with the proton in the Brønsted acid site. N₂O₄ is present from the dimerization of NO₂, a reaction that is favored inside the zeolite pore at low temperatures. At the high temperatures investigated here, however, it is uncertain if this mechanism is responsible for NO⁺ formation. Above 390 K, the equilibrium between NO₂ and N₂O₄ results in very low N₂O₄ concentrations, suggesting that an alternate mechanism may be responsible for NO⁺ formation at temperatures above this point.

Figure 4.8 shows the IR spectra resulting from the adsorption of NO and coadsorption of NO and O₂ at 573 K on H-SSZ-13. Initially, gas containing 1,000 ppm NO is fed to the IR cell/reactor and no detectable changes in the spectra are observed (spectrum 2 in Figure 4.8). After introducing 5% O₂/He—in addition to the 1,000 ppm of NO— to the gas flowing into the IR cell, two intense IR bands are observed: a positive band at 2185 cm⁻¹, and a negative band at 3610 cm⁻¹ (spectrum 3 in Figure 4.8). We did not detect any other absorbance associated with adsorbed N₂O₄ (typically observed at 1745 cm⁻¹) at these elevated temperatures. The IR absorption peak at 2185 cm⁻¹ is characteristic of NO⁺ in zeolites, which has been identified between 2133-2200 cm⁻¹ depending on the zeolite structure and the concentration of the NO/O₂ gas mixture [41-43]. This result demonstrates the ability of NO⁺ to form at high temperatures, in agreement with the result obtained by Lonyi et al. [13] over H-MOR. The negative absorbance at 3610 cm⁻¹ results from the disappearance of Brønsted acid sites due to the replacement of the proton with NO⁺. Other commonly found adsorbed N_xO_y species at low temperatures (NO₃⁻, NO₂⁻, N₂O₄, NO₂, N₂O₃) were not observed, possibly because they do not remain on the surface at such high temperatures [17-22]. NO⁺ is the only stable surface species observed at elevated temperatures, and thus is potentially a reaction intermediate in the observed NO oxidation activity.



Figure 4.8. IR spectra obtained on H-SSZ-13 at 573 K showing formation of NO^+ (2185 cm⁻¹) and disappearance of Brønsted acid sites (3610 cm⁻¹) [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

After turning off the O₂ flow it is observed that under 1,000 ppm NO, the NO⁺ IR signal remains stable but at a reduced intensity as compared to the case when O₂ was present (spectrum 4 in Figure 4.8). Concurrently, the acid site signal at 3610 cm⁻¹ becomes less negative, but does not diminish completely. The OH signal that remains could be due to water impurities within the cell, as the reaction between NO⁺ and water yields acid sites (Eq. 4.7). Additional evidence for the presence of water is indicated by the broad signal around 3400 cm⁻¹, which is characteristic of -OH vibrational modes for hydrogen bonded species at Brønsted or silanol sites, and the sharp peak at 3575 cm⁻¹, which represents the v_s(H₂O) vibrational mode for molecularly adsorbed water [43].

$$NO^+ + H_2O \rightleftharpoons H^+ + HNO_2 \tag{4.7}$$

In the absence of NO or O_2 , the NO⁺ signal decreases monotonically until it disappears entirely after several minutes under He flow (spectrum 5 in Figure 4.8). Gas containing 1,000 ppm NO was then reintroduced and an immediate restoration of the NO⁺ IR signal at 2185 cm⁻¹ (spectrum 6 in Figure 4.8) was observed. The reappearance of the NO⁺ *in the absence* of O_2 suggests that the zeolite acid site has been altered to allow for an alternative route of NO⁺ formation. Under initial conditions, NO⁺ did not form from exposure to 1,000 ppm NO; however, once the NO⁺ was generated by co-adsorption of NO and O_2 , then NO⁺ could reform in the presence of only NO. This result suggests an electron-transfer reaction involving lattice oxygen atoms of the zeolite framework and NO⁺ (Eq. 4.8).

$$\mathbf{Si} - \mathbf{0}^{-}(\mathbf{N0}^{+}) - \mathbf{Al} \quad \mathbf{Si} - \mathbf{0}^{\bullet} - \mathbf{Al} + \mathbf{N0}$$
(4.8)

In the presence of NO or NO/O₂ gas mixtures, the NO⁺ species at Brønsted acid sites is stable (Z·NO⁺). However, under an inert gas (flowing He), NO⁺ leaves the surface and in the process accepts an electron from the zeolite to become NO in the gas phase, leaving behind a single electron hole [Si–O[•]–Al]. The reaction thus forms a singleoccupied molecular orbital (SOMO) at one of the bridging lattice oxygen atoms connected to an aluminum atom. When NO is reintroduced to the zeolite, the oxidized zeolite then quickly accepts an electron from NO to reform the surface NO⁺ radical cation.

NO is a stable radical species, though it has a low ionization energy (I.E.) of 9.26 eV due to its unpaired electron located on an antibonding orbital, which significantly increases its susceptibility to ionization. NO⁺ is strongly electrophilic with a reversible redox potential of $E^{\circ} = 1.28$ V vs. SCE [44]. Note that upon thermal dehydroxylation (~1,023 K) of high-silica zeolites, the formation of single electron vacancies at framework oxygen atoms has been proposed to occur for zeolites exposed to air at high temperatures [45]. Yun and Lobo [46] have found that such oxidized zeolite samples can easily extract an electron from naphthalene, (I.E. of 8.14 eV), through an electron-transfer reaction forming a naphthalene radical cation. Although the I.E. value of NO is higher than that for naphthalene, it is still low compared to most stable compounds. The zeolite oxidation process observed here is different in that it occurs at significantly lower temperatures compared to the commonly observed dehydroxylation of Brønsted acid sites, indicating that the presence of NO and O₂ in our system facilitates this oxidation chemistry. Chemistry involving NO is unique and

complex because of the ability of nitric oxide to change redox states through oneelectron processes [47].

To date there have been few direct structural investigations to characterize the geometry of the NO⁺ site in the zeolite framework. Using FTIR spectroscopy in conjunction with isotopic labeling techniques, Hadjiivanov et al. [43] showed that NO⁺ is coordinated to lattice oxygen atoms at cationic positions ($O_{lattice}$ –NO⁺). The authors detected an IR band at 977 cm⁻¹, nearby to the theoretical vibration of 1,000 cm⁻¹ for this interaction, and also confirmed that gas-phase O₂ is not involved in the bond. A computational investigation by Pidko et al. [48] on NaX zeolite indicates that NO⁺ coordinates to the zeolite via a single oxygen atom and not via multiple lattice oxygen atoms. The weak O-O bond has a bond-dissociation-energy of 142.3 kJ mol⁻¹ and can be easily broken at low temperatures, suggesting that NO⁺ may bond through an O-O interaction with the zeolite oxygen atom [49]. On the other hand, the unpaired electron of NO is likely to reside at the nitrogen atom, since oxygen has a high electron affinity, thus making the O-O bond structure less plausible.

Similar NO/O₂ co-adsorption experiments were conducted on the Na-SSZ-13 and siliceous CHA materials to identify any differences that arose in the IR spectra from the absence of Brønsted acid sites or framework aluminum atoms. NO⁺ formation was observed to occur on Na-SSZ-13 under the same conditions tested for H-SSZ-13, as indicated by an IR band at 2164 cm⁻¹ (Figure 4.9). The IR signal intensity of NO⁺ formed on Na-SSZ-13 was much weaker compared to that on H-SSZ-13, suggesting that this species forms much more readily in the presence of Brønsted acid sites. In addition to the positive IR band for NO⁺, a negative band at 3695 cm⁻¹ was observed. This band is attributed to hydroxyl groups located on Na⁺ cations,

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based on the assignment by Sedlmair et al. [50] in their study of NO/O_2 co-adsorption on NaY.



Figure 4.9. IR spectra showing effect of NO partial pressure (5000-2,000 ppm NO + 5% O₂) on NO⁺ signal over Na-SSZ-13 at 523 K [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

Over siliceous CHA, NO⁺ formation was not observed in the IR spectra. No acidic OH IR bands were observed because, as expected, the sample was nearly free of aluminum impurities that would have led to acid sites. In fact, no N_xO_y surface species were observed on siliceous CHA at the temperatures investigated (T > 423 K) from exposure to NO/O₂/NO₂ gas mixtures. This result shows that framework aluminum atoms with charge-compensating cations are necessary for the development of NO⁺

and that siliceous CHA has no suitable sites for the NO⁺ species to coordinate. The absence of any adsorbed species on the catalyst at elevated temperatures (T > 423 K) explains the inability of this material to effectively catalyze the reaction in this high-temperature regime. Based on these results, 423 K is the approximate transition point at which the confinement effect responsible for the low-temperature catalytic activity of the zeolite materials is no longer able to increase oxidation reaction rates with respect to the gas phase reaction. Although the H-SSZ-13 and Na-SSZ-13 materials can catalyze, via a second mechanism (involving NO⁺), NO oxidation above ~423 K, siliceous CHA cannot facilitate the formation of these species. The high-temperature activity is thus unique to zeolite materials containing framework aluminum atoms, although it may be possible to form similar species on Fe^{III}- or Ga^{III}-containing zeolites and perhaps on other solid acids such as heteropolyacids or sulphated zirconia.

 NO^+ was found in H-SSZ-13 up to 623 K in the presence of 1,000 ppm NO and 5% O₂ (Figure 4.10). As the temperature increased, the intensity of the NO⁺ IR band diminished. Temperatures above 623 K were not investigated because this is the thermal stability limit of the IR cell.



Figure 4.10. IR spectra showing the effect of temperature (523-623 K) on NO⁺ signal over H-SSZ-13 under flow of 1,000 ppm NO + 5% O₂ [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

Similar studies carried out on Na-SSZ-13 showed that NO⁺ was also stable on this material throughout the same temperature range, although it was present in significantly lower concentrations (Figure 4.11).



Figure 4.11. IR spectra showing the effect of temperature (523-623 K) on NO⁺ signal over Na-SSZ-13 under flow of 1,000 ppm NO + 5% O₂ [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

The effect of NO partial pressure (0-2,000 ppm NO + 5% O_2) on the intensity of the NO⁺ signal (2185 cm⁻¹), as well as the concomitant decrease in the Brønsted acid site peak intensity (3610 cm⁻¹), was monitored at 523 K on H-SSZ-13 (Figure 4.12). A clear correlation exists between the growth of the NO⁺ IR band and the disappearance of the Brønsted acid site IR band as the NO partial pressure increases. This observation is consistent with the premise that NO⁺ is forming at the expense of zeolite Brønsted acid sites.



Figure 4.12. Correlation between NO⁺ IR band and Brønsted acid site IR band on H-SSZ-13 at 523 K [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

To determine whether NO⁺ formation has a direct effect on NO oxidation reaction rates over H-SSZ-13, rates were measured at 523 K as a function of NO partial pressure (0-2,000 ppm NO + 5% O₂) and separately the intensity of the NO⁺ absorption band was recorded under the same conditions using the *in-situ* IR cell. The oxidation rates and NO⁺ areas are plotted as a function of the inlet NO partial pressure in Figure 4.13, where we observe a linear correlation between the intensity of the NO⁺ IR signal and the NO oxidation rate as a function of inlet NO pressure. This correlation strongly suggests that NO⁺ is involved in the reaction mechanism.



Figure 4.13. Correlation between measured NO oxidation rates and formation of NO⁺ IR signal peak area on H-SSZ-13 at 523 K (500-2,000 ppm NO + 5% O₂) [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

Identical experiments carried out on Na-SSZ-13 indicated a similar correlation between the NO⁺ IR signal and NO oxidation rate (Figure 4.14).



Figure 4.14. Correlation between measured NO oxidation rates and formation of NO⁺ peak area on Na-SSZ-13 at 523 K (500-2,000 ppm NO + 5% O₂) [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

To understand the formation of NO⁺ and the conditions under which it is stable on H-SSZ-13, the NO⁺ signal was monitored as a function of time under different gas compositions at a temperature of 573 K using IR spectroscopy (Figure 4.15). Initially, flow of 1,000 ppm NO did not produce an IR signal for NO⁺ at 2185 cm⁻¹, but switching on O_2 led to the observation of a NO⁺ signal that remained stable while the NO/O_2 gas mixture passed over the zeolite. Then, the O_2 was shut off while NO flow was maintained; the IR signal for NO^+ diminished to about half of its initial intensity but it did not disappear. This is different from when NO was first introduced to the catalyst, in which NO⁺ was not observed, and indicates that the zeolite acid sites have been altered to now form NO⁺ in the presence of NO. Feeds of NO and NO/ O_2 mixtures were cycled to ensure that the results were consistent (the IR signal levels verify this expectation). Pure He gas was subsequently introduced, and the NO⁺ signal disappeared entirely within several minutes. 1,000 ppm NO was reintroduced at this point, and the NO⁺ IR signal reemerged to its previous level. This is again different from the initial properties, because at the beginning the addition of NO to the sample did not produce the NO⁺ signal. Increasing the concentration of NO to 2,000 ppm resulted in a further increase in the NO⁺ IR signal strength, indicating that NO⁺ concentration is directly affected by the NO concentration in the gas phase and that the sites are not saturated at 1,000 ppm. Additionally, in a separate experiment, NO⁺ was observed under exposure to a gas stream of NO₂ (100-200 ppm), and its IR signal intensity was also proportional to the concentration of NO₂ (spectra not shown).

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Figure 4.15. Area of the NO⁺ IR signal (2185 cm⁻¹) monitored as a function of time for various inlet gas compositions (He, 1,000 ppm NO, 2,000 ppm NO, 1,000 ppm NO + 5% O₂) on H-SSZ-13 at 573 K [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

At a higher concentration of NO₂ in the feed, additional surface species were observed to form at 473 K (Figure 4.16). NO⁺ was observed to replace the acid site, as indicated by a positive IR band at 2170 cm⁻¹ and a negative band at 3613 cm⁻¹. A complex set of IR bands at lower wavenumbers was also observed; these absorption bands are attributable to other charged N_xO_y species but cannot be assigned with certainty. The band at 2004 cm⁻¹ could be from NO₂⁺, which has been observed between 2000-2100 cm⁻¹ on NaY upon exposure to NO₂ [51], although NO₂⁺ also has a vibrational frequency of 2350 cm⁻¹ [51], which was not observed here. The band at 1629 cm⁻¹ likely derives from the *cis* isomer of nitrites, whose N=O stretching mode results in an absorption in the 1630-1600 cm⁻¹ region [52], but it could also be due to chemisorbed water [52]. The band at 1227 cm⁻¹ could be attributed to surface nitrites [53]. The band at 952 cm⁻¹ can be assigned with certainty to the $O_{lattice}$ -NO⁺ bond [43]. Lastly, note that a negative band at 3740 cm⁻¹ is also observed, indicating that NO⁺ species may form on internal or external silanol groups. This was not observed in the experiments with NO and O₂.



Figure 4.16. Time evolution of IR spectra on H-SSZ-13 after exposure to a feed containing 2,500 ppm NO₂ at 473 K [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

The finding that oxidation of the zeolite acid site is possible at relatively low temperatures (T < 623 K) may be significant. This protocol (co-addition of NO/O₂ followed by flushing with He) is experimentally simple and can be used for the investigation of the oxidized acid sites in future studies. Further study of the properties of these sites is outside the scope of this thesis.

4.3.5 High-temperature NO Oxidation Reaction Mechanism on H-SSZ-13

Based on our investigation of the reaction kinetics and surface species present on H-SSZ-13, we propose that NO^+ is acting as a reactive intermediate in the hightemperature regime according to the series of reactions involving NO and O₂ illustrated in Scheme 4.1.

Scheme 4.1. Proposed NO oxidation reaction mechanism on H-SSZ-13 in the high-temperature regime (T > 423 K). In this sequence Z_{\cdot} represents the oxidized zeolite acid site.

(A)	Z + NO		Z-NO+
(B)	Z ⁻ NO ⁺ + O ₂		Z ⁻ NO ₃ ⁺
(C)	$Z^{-}NO_{3}^{+} + NO$		$Z^{-}NO_{2}^{+} + NO_{2}^{-}$
(D)	Z ⁻ NO ₂ ⁺	~	Z + NO ₂

The NO_x⁺ species described in Scheme 4.1 are important ions in atmospheric chemistry [54, 55]. NO₃⁺ is known to form from the reaction between NO⁺ and O₂, with Collisionally Activated Dissociation (CAD) spectra showing that the species has O₂-NO connectivity as opposed to a trigonal NO₃⁺ structure [56]. Additionally, computational studies have shown that the NO⁺·O₂ complex is the lowest energy form of NO₃⁺; the enthalpy of formation for the NO⁺·O₂ complex has been estimated to be 231.2 kcal mol⁻¹ [57]. This large enthalpy value indicates that step (B) in Scheme 4.1 is a strongly endothermic reaction, and is likely to be the elementary step with the largest energy barrier in Scheme 4.1. The ionization energies (I.E.) of NO, NO₂, and NO₃ are 9.26, 9.59, and 12.57 eV, respectively. These values show that NO⁺ has the lowest energy of formation amongst the NO_x⁺ species, and is therefore the most stable. NO_3 is a radical species with a high electron affinity that commonly exists as the nitrate anion (NO_3^-); the NO_3^+ species is infrequently encountered due to the large I.E. of NO_3 . The I.E. values suggest that a zeolite-adsorbed NO_2^+ will be lower in energy compared to NO_3^+ , but will be slightly higher in energy compared to NO^+ . Our IR spectroscopy results agree that NO^+ is more stable compared to NO_2^+ and NO_3^+ , since NO^+ was the only NO_x^+ species detected.

At this point, using the pseudo-equilibrium approximation in combination with our experimental results, we can suggest the step most likely to be the ratedetermining step (RDS) in the proposed mechanism. Recall that the fractional coverage of NO⁺ is much greater compared to that of the other NO_x⁺ cations (NO₂⁺ or NO₃⁺ were not detected), indicating that NO⁺ is more stable and can be identified as the most abundant reaction intermediate (MARI). Thus, the NO₂⁺ and NO₃⁺ that form in the mechanism illustrated in Scheme 4.1 will react quickly, making it less likely that steps (C) and (D) are rate-determining. Allowing step (B) of Scheme 4.1 to be the RDS, and assuming that all other steps are equilibrated, the following rate expression can be derived:

$$r_{NO_2} = \frac{k_{app.}(P_{NO})(P_{O_2})}{1 + K_{1.eq.}(P_{NO})}$$
(4.9)

Eq. 4.9 shows that at low coverage of Z^-NO^+ , for which $K_{1_{eq.}}$ is << 1, the expression simplifies to $r \sim (P_{NO})(P_{O_2})$. At higher Z^-NO^+ coverages the rate expression is better approximated by $r \sim (P_{NO})^{\alpha}(P_{O_2})$, where $0 < \alpha < 1$. In section 4.3.3, we established that the measured reaction orders for NO and O₂ were both ~1 on H-SSZ-13 at 473 K. This analysis shows that under conditions of low Z^-NO^+ coverage, and where step

(B) in Scheme 4.1 is the RDS, the measured reaction orders agree with the proposed reaction mechanism (Scheme 4.1).

Assuming steps (C) and (D) of Scheme 4.1 to be rate determining leads to the following rate expressions (Eqs. 4.10 and 4.11, respectively):

$$r_{NO_2} = \frac{k_{app}(P_{NO})^2(P_{O_2})}{1 + K_{1.eq}(P_{NO})}$$
(4.10)

$$r_{NO_2} = \frac{k_{app.}(P_{NO})^2(P_{O_2})}{(P_{NO_2})[1+K_{1\cdot eq.}(P_{NO})]}$$
(4.11)

From Eq. 4.10, we can see that low coverages of Z^-NO^+ lead to a simplified rate expression $r \sim (P_{NO})^2 (P_{O_2})$, which does not agree with the experimentally observed reaction order of ~1 for NO. At higher Z^-NO^+ coverages, the rate expression becomes $r \sim (P_{NO})^{\alpha} (P_{O_2})$ with $1 < \alpha < 2$, which, in the limit, agrees with the experimentally observed value of 1.02. Nonetheless, under our reaction conditions NO⁺ coverage is, with all likelihood, low, especially at the high end of the temperature range investigated (623 K), and thus step C is unlikely to be rate limiting. If step (D) is the RDS, the rate expression (Eq. 4.11) simplifies to $r \sim (P_{NO})^2 (P_{O_2}) (P_{NO_2})^{-1}$ for low coverages of Z^-NO^+ , which again is inconsistent with the experimentally observed reaction order for NO. At higher Z^-NO^+ coverages, the rate expression becomes $r \sim (P_{NO})^{\alpha} (P_{O_2}) (P_{NO_2})^{-1}$ with $1 < \alpha < 2$. As described above, under the reaction conditions investigated NO⁺ coverage is likely to be low and thus step (D) is also not likely the RDS. Mechanistic studies using ${}^{18}\text{O}_2/{}^{16}\text{O}_2$ isotopic switching will be necessary to provide additional evidence validating the reaction mechanism proposed in Scheme 4.1, but these experiments are beyond the scope of this report.

Scheme 4.2 shows a qualitative energy diagram for the proposed reaction mechanism in Scheme 4.1, with step (B) as the RDS. As discussed earlier, NO_3^+ is higher in energy compared to the other adsorbed NO_x^+ species, and therefore step (B) will be strongly endothermic, as illustrated in Scheme 4.2. According to the Hammond postulate then, we can surmise that the activated complex for this step will closely resemble in structure and be nearer in energy to the NO₃⁺ product rather than the reactants. The apparent activation energies that were determined experimentally reflect the energy barrier for step (B) and consist of three terms: (1) the heat of adsorption for the molecular physisorption of O_2 within the zeolite pores, (2) the heat of adsorption of NO on the oxidized zeolite site to yield NO⁺, and (3) the intrinsic activation energy of the reaction. The heat of adsorption of O₂ on zeolites should be ~15-20 kJ mol⁻¹ [58-60]; we have assumed a value of 17 kJ mol⁻¹ for our calculations on H-SSZ-13. Using the Van't Hoff equation and the data in Figure 4.10, we estimated the heat of adsorption term of NO on the oxidized zeolite site for H-SSZ-13 to be -42.4 kJ mol⁻¹. Accordingly, the intrinsic activation energy for step (B) over H-SSZ-13 was determined to be 99 kJ mol⁻¹, which is considerably greater than the measured activation energy of 40.8 kJ mol⁻¹ and shows that the heat of adsorption terms lead to a sizeable decrease in the reaction barrier for the catalytic reaction.

Scheme 4.2. Qualitative energy diagram for the proposed NO oxidation reaction mechanism on H-SSZ-13, assuming step (B) as the RDS. Reproduced with permission from *Journal of Catalysis* (Elsevier).



Since our analysis of the rate expressions shows that step (B) is likely the RDS, it is constructive to examine the components of the apparent rate constant in Eq. 4.9 to understand the physical significance of the term. The mathematical derivation of Eq. 4.9 shows that the apparent rate constant, $k_{app.} = k_2 K_{0eq.} K_{1eq.}$, is the product of a reaction rate constant and two adsorption equilibrium constants of elementary steps. $K_{0eq.}$ represents the equilibrium constant for the molecular physisorption of O₂ within the zeolite pores, and is expected to be small since the heat of adsorption of O₂ in H-chabazites is low (~15-20 kJ mol⁻¹) and the concentration of O₂ inside the zeolite pores should be similar to the gas phase concentration. $K_{0eq.}$ was estimated to be 35.5 using the same standard state (1 mol m⁻³) in the gas phase and in the zeolite

micropores, thus confirming that it is small and will not contribute significantly to the apparent rate constant. By defining the standard state as ideal gas 1 mol m⁻³_{pore}, ΔS for O₂ physisorption is equal to zero, since O₂ will behave as an ideal gas both in the gas phase and when it is physisorbed within the zeolite pores, and thus will not experience a loss in entropy.

$$K_{0_{eq.}} = exp\left(\frac{-\Delta H}{RT}\right)exp\left(\frac{\Delta S}{R}\right)$$
(4.12)

 $K_{1_{eq.}}$ represents the equilibrium constant for the adsorption of NO at vacant zeolite sites (Z•) to form NO⁺; this process is exothermic, and our IR spectroscopy studies have confirmed that the amount of NO⁺ attached to the zeolite decreases with increasing temperature (see Figure 4.10). Since the apparent rate constant $k_{app.}$ in Eq. 4.9 was observed to increase with increasing temperature, it seems that $K_{1_{eq.}}$ also contributes minimally to the temperature dependence of $k_{app.}$. Eq. 4.12 can be used again to estimate $K_{1_{eq.}}$, but in this case ΔS will not equal zero, since a significant loss in entropy is expected when transitioning from mobile NO molecules in the gas phase to immobile NO⁺ attached the zeolite acid site. Using the assumption that the translational entropy will dominate the entropic losses compared to the rotational and vibrational partition functions, the Sackur-Tetrode equation (Eq. 4.13) can be used to estimate ΔS .

$$S_{trans.} = R \cdot ln \left[\frac{e^{5/2} \cdot V}{N_A} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right]$$
 (4.13)

 $S_{trans.}$ for NO (g) was found to equal 132.7 kJ mol⁻¹, while $S_{trans.}$ for Z^-NO^+ was assumed to equal 0, since the NO⁺ attached to the zeolite acid site is expected to have minimal translational movement; therefore, ΔS_{ads} for NO adsorption was estimated to be -132.7 kJ mol⁻¹. With an experimentally determined ΔH_{ads} value of -42.4 kJ mol⁻¹ for the adsorption of NO at the oxidized zeolite site (discussed earlier and calculated using the Van't Hoff equation), $K_{1eq.}$ was estimated to equal 8.56×10^{-4} . Therefore, the intrinsic rate constant k_2 for elementary step (B) must be the dominant term in $k_{app.}$. According to the principles of transition state theory, the reaction rate is proportional to the concentration of the activated complex, allowing the rate expression to be rewritten as follows (Eq. 4.14).

$$r_{NO_2} = \frac{2k_B T}{h} [NO_3^+]^{\ddagger} \tag{4.14}$$

Assuming that step (B) is the RDS, the activated complex has an expected composition of $[NO_3^+]^{\ddagger}$. Since step (B) is an endothermic reaction, and recalling that the rate constants were observed to scale in the order of H-SSZ-13 > H-ZSM-5 > H-BEA, we can infer that the ability of the zeolite to stabilize the NO₃⁺ intermediate decreases as the zeolite pore size increases. Noting that $[NO_3^+]^{\ddagger}$ is in equilibrium with Z^-NO^+ and O₂ (ad.), Eq. 4.14 can be expanded into a rate expression in terms of measurable quantities (Eq. 4.15). To ensure consistent units, the rate in Eq. 4.15 should be expressed as a turnover frequency (per Brønsted acid site).

$$r_{NO_2} = \frac{\frac{2k_B T}{h} K_B^{\dagger} K_{0eq.} K_{1eq.} [NO][O_2] \left(\frac{1 \ mol \ NO^{\dagger}}{1 \ mol \ Al}\right)}{\left(\frac{1 \ mol}{1 \ mol}\right)^2}$$
(4.15)

As mentioned, k_2 is expected to be the dominant term of the apparent rate constant $k_{app.} = k_2 K_{0eq.} K_{1eq.}$ since the product of $K_{0eq.}$ and $K_{1eq.}$ is small and exothermic. Eq. 4.15 shows that $k_2 = \frac{2k_BT}{h} K_B^{\ddagger}$, where K_B^{\ddagger} is given by Eq. 4.16 and represents the equilibrium for step (B) in Eyring formalism for Schemes 4.1 and 4.2.

$$K_B^{\ddagger} = \frac{\left(\frac{\left[NO_B^{\ddagger}\right]^{\ddagger}}{\left(\frac{1 \ mol}{mol \ Al}\right)}\right)}{\left(\frac{\left[NO^{+}\right]}{\left(\frac{1 \ mol}{mol \ Al}\right)}\right)\left(\frac{\left[O_2\right]}{\left(\frac{1 \ mol}{m_{pore}}\right)}\right)}$$
(4.16)

At this point, K_B^{\ddagger} can be calculated because the apparent rate constant ($k_{app.} = \frac{2k_BT}{h}K_B^{\ddagger}K_{0eq.}K_{1eq.}$) was measured experimentally, and $K_{0eq.}$ and $K_{1eq.}$ were estimated earlier in this section. At 573 K, $k_{app.} = 9.22 \times 10^3$ L mol Al⁻¹ s⁻¹ for H-SSZ-13; therefore K_B^{\ddagger} was found to equal 1.27×10⁻⁸, resulting in a value of 3.04×10⁵ L mol (mol Al)⁻¹ s⁻¹ for k_2 . The small value for K_B^{\ddagger} confirms that the equilibrium for step (B) lies far towards Z^-NO^+ rather than $Z^-NO_3^+$, and is consistent with our observation that NO⁺ is the only reaction intermediate present within the zeolite pores in appreciable quantities. This value also suggests that a large energy barrier exists in order to form NO₃⁺. Comparing the values for the three components of the apparent rate constant ($k_2 = 3.04 \times 10^5$ L mol Al⁻¹ s⁻¹, $K_{0eq.} = 35.5$, $K_{1eq.} = 8.56 \times 10^{-4}$), k_2 is seen to be several orders of magnitude larger than $K_{0eq.}$ and $K_{1eq.}$ and hence it dictates the behavior of the apparent rate constant.

The pre-exponential factors (k_0) for H-SSZ-13, H-ZSM-5, and H-BEA were presented in section 4.3.3 (Table 4.3), and can be related to the entropy of formation of the transition state (ΔS^{\dagger}) from the gas-phase reactants. ΔS^{\dagger} becomes more negative and kinetically unfavorable as the pre-exponential factor decreases; that is, the transition state has a more rigid structure compared to the gas-phase reactants. This is expected because the reactants (NO and O_2) are gas molecules and the activated complex is bound to the acid site inside the zeolite pores. The values in Table 4.3 indicate that the calculated pre-exponential factors decrease as follows: H-BEA > H-ZSM-5 > H-SSZ-13. This order follows the decreasing zeolite pore size. The modest entropic gains that result from increased pore size do not result in higher reactivity, confirming that the stabilization of the transition states is an enthalpy-controlled process that benefits from smaller zeolite pore size. For instance, H-BEA, the sample exhibiting the largest activation energy and pre-exponential factor, showed the lowest reaction rates. ΔS^{\dagger} values were calculated for each zeolite framework according to Eq. 4.17, which relates the entropy to the measured rate constant. ΔS^{\dagger} values for H-BEA, H-ZSM-5, and H-SSZ-13 were found to equal -307.3, -317.8, and -320.9 J mol⁻¹ K^{-1} , respectively. The entropic losses are quite substantial and are greatest for H-SSZ-13. However, the higher activity observed on H-SSZ-13 confirms that the ΔH^{\dagger} term prevails over the entropic term^[3].

$$k_{app.} = 2\kappa \frac{k_B T}{h} exp\left(\frac{\Delta S^{\dagger}}{R}\right) exp\left(\frac{-(E_a - 2RT)}{RT}\right) \left[\frac{mol}{m_{gas}^3}\right]^{-2}$$
(4.17)

Further understanding of the enthalpic stabilization of transition states can be gained from examining heats of adsorption of gas species such as N_2 and CO_2 in these

^[3] Note that ΔH^{\dagger} and ΔS^{\dagger} were also estimated using the Eyring equation, and the values were found to be in close agreement with those calculated using Eq. 4.17 and the relation $E_a = \Delta H^{\dagger} + mRT$.

zeolite frameworks. It would be better to examine such data for NO; however, we were not able to find any reliable values in the open literature, and instead have used the widely reported data for N₂ and CO₂ (Table 4.6). Heats of adsorption increase as the pore size decreases but the magnitude of the change is much lower (~35%) than the observed differences in activation energy for the NO oxidation reaction. The data thus suggest that differences in the heat of adsorption of the NO₃⁺ surface intermediate (or more precisely, the transition state $[NO_3^+]^{\ddagger}$ leading to NO₃⁺ formation) between the three zeolites do not completely explain the difference in magnitude in activation energy (Differences in activation energy are ~15 kJ mol⁻¹, and for adsorption they are just 5 kJ mol⁻¹) It could also be that the observed differences reflect the fact that N₂ and CO₂ are not charged and are thus not good models for $[NO_3^+]^{\ddagger}$.

Motorial	$Q_{ m st.}$	$Q_{ m st.}$
Material	[kJ mol ⁻¹] CO ₂	[kJ mol ⁻¹] N ₂
BEA (siliceous)	18.6 [61]	11.2 [61]
MFI (siliceous)	24.2 [61]	16.2 [61]
CHA (siliceous)	23.0 [61]	13.6 [61]
H-BEA (Si/Al =20)	33.0 [62]	19.0 [62]
H-ZSM-5 (Si/Al =30)	38.0 [63]	20.7 [63]
H-SSZ-13 (Si/Al =6, 80)	35.2 [64]	19.3 [65]

Table 4.6. Isosteric heats of adsorption ($Q_{st.}$) of N₂ and CO₂ on selected zeolite structures [66]. Reproduced with permission from *Journal of Catalysis* (Elsevier).

4.4 Conclusions

The results presented in this chapter together with the data reported in Chapter 3 show the occurrence of two reaction regimes for the oxidation of NO on H- and Na-

zeolites: activity increases with decreasing temperature below 423 K, and activity increases with increasing temperature above 423 K. In the high temperature regime, our experiments show that the zeolite framework (CHA, BEA, MFI) has a substantial effect on NO oxidation rates, with activity being inversely proportional to the zeolite pore size. Activation energies scale in the order of CHA < MFI < BEA, and application of transition state theory shows that the smaller pores provide significantly greater enthalpic stabilization for the activated complex that more than compensate for the larger entropic costs. Siliceous samples show little activity at elevated temperatures (> 423 K), indicating that the confinement effect responsible for activity in the low-temperature regime is no longer substantial and that framework aluminum atoms are required for NO oxidation activity above 423 K [15, 16]. A change in the reaction mechanism at ~423 K is deduced by a change in activation energy and the reaction orders: rates are second order in NO at low temperature [15, 16], but first order in NO at high temperature. *In-situ* FTIR studies reveal that NO⁺ is the only observable $N_x O_y$ species present in significant concentrations on the alumino-silicate zeolites at high temperatures, and we have proposed plausible mechanisms for the formation of NO⁺ at framework aluminum positions within the zeolite pores. We also show that NO⁺ is in equilibrium with gas phase NO, and desorbs (as NO) leaving behind an oxidized acid site (Si–O•–Al). We have identified oxidizing conditions that yield this new site, allowing future studies to examine its potential role in other reactions. We have shown that NO oxidation activity is directly proportional to the amount of NO⁺ present, and have confirmed that siliceous samples are unable to form NO⁺ or any other surface species above 423 K (within the limits of detection of the IR method). Finally, we have proposed a mechanism for the high-temperature NO

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oxidation reaction on H-SSZ-13, and have identified the most probable RDS that is consistent with the observed reaction orders and observed reaction intermediates. Finally, note that the activities displayed by all of the materials in this report were observed under dry conditions; it is very likely that the presence of water would significantly diminish their catalytic properties for NO oxidation, since NO⁺ can react with water and produce nitrous acid. The results from this investigation suggest that other solid acid catalysts, such as metal oxides over alumina or acidic polyoxometallates, may be capable of catalyzing the NO oxidation reaction by similar mechanisms. The results from this work may also have significance in the NH₃-SCR NO_x mechanism over zeolites, although the measured TOFs for NO oxidation appear to be considerably lower than those seen for NH₃-SCR.

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Chapter 5

NO OXIDATION REACTION ON COPPER ZEOLITES

5.1 Introduction

The discovery of the small pore zeolite Cu-SSZ-13 as an excellent catalyst for commercial applications of NH₃-SCR initiated an intense period of research around 2010 aimed at understanding the reaction mechanism and characterizing the active site. Although great progress has been made, the work continues today due to several unresolved issues. NO oxidation is considered to be an important step in the NH₃-SCR reaction mechanism, and in recent years it has been at the center of the discussion and debate among researchers as opposing ideas have emerged about its precise role. Several earlier reports suggested that NO oxidation was the overall rate-determining step (RDS) in the NH₃-SCR mechanism on H-ZSM-5 [1], [2] and Fe-ZSM-5 [3], and Kiovsky et al. [4] proposed that NO oxidation was the RDS on all zeolite catalysts. This thought was based on the fact that many proposed NH₃-SCR reaction mechanisms begin with the oxidation of NO to NO₂. Additionally, the much higher rates observed under fast SCR conditions (NO/NO $_2 = 1$) suggested that NO oxidation to NO₂ would be rate-determining. On the contrary, more recent evidence [5]-[7] denies that NO oxidation is the RDS for the reaction on Cu- and Fe-promoted zeolites. The authors of these reports point out that NO oxidation rates are much slower than SCR rates at temperatures between 473 K and 823 K, and that water strongly inhibits NO oxidation rates but has a negligible effect on SCR rates [5-7]. However, it remains unclear as to why Cu-SSZ-13 is such an effective NH₃-SCR catalyst but a relatively

poor NO oxidation catalyst. Regardless of whether NO oxidation is the RDS, it is likely that the reaction has mechanistic importance in NH_3 -SCR [8]. Additionally, a sound understanding of NO oxidation will assist efforts in understanding the more complex chemistry associated with the NO_x reduction.

Key aspects in identifying the NH₃-SCR reaction mechanism are obtaining a clear understanding of the nature of the Cu species present in the zeolite under different reaction conditions and discerning which species are active in the NO oxidation and NH₃-SCR reaction pathways. Currently, many uncertainties remain regarding these topics. Various Cu species have been postulated to be active or present within the zeolite, such as dimeric Cu species, isolated cationic species, and CuO_x clusters [9]. Complicating matters further is the fact that the Cu species that form are influenced by a number of factors, including the framework type, gas composition, and the Cu/Al and Si/Al ratios. Regarding the CHA framework, it has been determined that Cu species can occupy several different locations within the framework (see Figure 5.1): (1) in the center of the double six-membered rings (position I in Figure (5.1), (2) in the CHA cavity near the face of the six-membered ring (position II), (3) in the CHA cavity along the three-fold axis (position III), and (4) in or near the eightmembered ring window (position IV) [10]. Early reports using synchrotron X-ray diffraction (XRD) [11]] and X-ray absorption spectroscopy (XAS) [12] indicated that Cu ions are located in the six-membered rings of the double six-member prisms via formation of Cu-O bonds with lattice oxygen atoms. A more recent study [13] indicated that Cu ions can also occupy sites in the larger zeolite cavities, associated with the eight-membered rings. These species typically form at higher Cu loadings, and have easier access to incoming gases because of their closer proximity to the pore

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openings [14]. Further, it has been shown that Cu species are quite mobile within the CHA framework, especially in the presence of water. Under wet-reducing conditions, the interactions between Cu^{2+} ions and lattice oxygen atoms weaken because of interactions between water and Cu^{2+} ions, which allows Cu^{2+} ions to move toward the large cages, where they are more reducible [14]. Several groups have observed evidence that Cu^{2+} ions can "self-reduce" to Cu^+ at high temperatures *in vacuo* or under inert (He) flow, although the mechanism by which this occurs remains to be well understood [15-17]. Finally, Giordanino et al. [9] showed that $[Cu^{II}(OH)]^+$ species can exist in Cu-SSZ-13 samples, and Verma et al. [18] have suggested the occurrence of Cu_xO_y ($x \ge 2$, $y \ge 1$) species for samples with Cu/Al ratios greater than 0.20.



Figure 5.1. Possible Cu cation positions in the CHA structure. Image taken from reference [10] and reproduced with permission from *Topics in Catalysis* (Springer Science and Business Media).

In this chapter, the NO oxidation reaction mechanism is investigated on Cuzeolites. The effects of framework (SSZ-13, ZSM-5, BEA), Cu/Al ratio, and pretreatment conditions (5% O₂/He, 1% CO/He, 1% NH₃/He, 500 ppm NH₃ + 500 ppm NO) on reactivity were examined. It is shown that samples pretreated in 1% CO/He exhibit significantly greater activity compared to pre-oxidized samples. Additionally, the reaction orders with respect to NO and O₂ were investigated after different pretreatment conditions. Over Cu-SSZ-13, the effect of Cu loading on reaction rates was investigated, and rates were normalized either per gram of catalyst or per mol of Cu (turnover frequencies) to examine any differences in trends. UV-vis spectroscopy studies were used to examine the Cu speciation in Cu-zeolite samples following O₂ or CO pretreatments. DRIFTS spectra were collected under *in-situ* conditions to examine the N_xO_y surface species that formed depending on the Cu loading of the zeolite. Finally, a mechanism is presented for the reaction on Cuzeolites pretreated in 1% CO/He.

5.2 Materials and Methods

5.2.1 Catalyst Synthesis

H-SSZ-13 (CHA) samples with Si/Al ratios of 6 and 12 were prepared using a previously reported synthesis procedure [19], which was also described in detail in Chapter 3. Subsequently, H-SSZ-13 samples were converted into NH₄-SSZ-13 through a liquid ion exchange procedure. 1 g of zeolite was added to a 500 mL aqueous solution of ammonium nitrate (NH₄NO₃) at 353 K, and the solution was stirred using a magnetic stir bar for 12 h. Then, Cu-SSZ-13 samples were prepared through aqueous ion exchange of the NH₄-SSZ-13 samples with copper(II) acetate

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(Cu(CH₃CO₂)₂) solutions at 353 K. Approximately 150 mL of solution was used per gram of catalyst during the ion exchange procedure. The solutions were stirred using a magnetic stir bar for 3 h. The amount Cu(CH₃CO₂)₂ added to the solution was varied to prepare samples with Cu/Al ratios in the range of 0.025-0.40, corresponding to exchange rates of 5-80%. After the Cu exchange, the product was recovered by vacuum filtration, rinsed several times with deionized (DI) water, and dried at 373 K overnight in air. The sample was then calcined in air at 823 K for 8 h using a ramping rate of 180 K h⁻¹ to remove the occluder or remaining impurities. ZSM-5 (MFI) samples were synthesized with Si/Al ratios of 12 using a procedure described by Kim et al. [20]. A commercial form of zeolite beta (BEA) (CP 814E*, Si/Al = 12.5) was obtained from Zeolyst International. Cu forms of ZSM-5 and BEA with Cu/Al ratios of 0.40 were prepared by adding Cu(CH₃CO₂)₂ to aqueous solutions of the NH₄-form zeolites. Finally, samples were calcined with the same procedure used for the SSZ-13 samples.

5.2.2 Characterization

Powder XRD patterns were collected to verify the crystallinity of the zeolite samples. BET surface areas and *t*-plot micropore volumes were determined by N_2 physisorption measurements. ICP measurements were performed by Galbraith Laboratories (Knoxville, TN) to determine the elemental compositions of the zeolite samples.
5.2.3 Laboratory Flow Reactor Experiments

Reaction rates were measured on Cu-SSZ-13, Cu-ZSM-5, and Cu-BEA samples using the flow reactor system described in Chapter 2. Catalyst samples were pretreated at 773 K in either 5% O₂/He for 3 h or 1% CO/He for 4 h prior to all rate measurements. Alternatively, samples were pretreated at 523 K in 1% NH₃/He or 500 ppm NO + 500 ppm NH₃ for 4 h, and then the flow was switched to He and the reactor was heated to 773 K to remove any adsorbed NH₃. NO oxidation rates were measured as a function of temperature from 523-823 K. NO and O₂ reaction orders were measured at 423 K and 623 K by varying the inlet partial pressures of the reactants. The NO reaction order was determined by varying the inlet NO concentration from 250-750 ppm NO while maintaining the O₂ concentration at 5%. The O₂ reaction order was determined by varying the O₂ concentration from 2-6% while maintaining the NO concentration at 750 ppm. Reaction rates were also measured on SSZ-13 samples with different Cu loadings (0-3.12 wt%) at 573 K under a flow of 750 ppm NO + 5% O₂. Forward reaction rates (r_+) were calculated from the observed rate ($r_{obs.}$) and the approach to equilibrium factor (η), as shown in Eqs. 5.1 and 5.2.

$$r_{obs.} = r_{+} - r_{-} = r_{+}(1 - \eta)$$
(5.1)

$$\eta = \frac{[NO_2]^2}{K_C[NO]^2[O_2]} \tag{5.2}$$

Note that r_{-} in Eq. 5.1 represents the rate of the reverse reaction (NO₂ decomposition) and K_c in Eq. 5.2 is the equilibrium constant for the NO oxidation reaction. Conversion levels were maintained below 10% for all rate measurements, and calculated η values verified that equilibrium was not reached.

5.2.4 DRIFTS

Infrared (IR) spectra were collected with a Nicolet Nexus 470 Fourier transform infrared (FTIR) spectrometer equipped with a mercury cadmium telluride (MCT) detector. A Praying Mantis accessory (Harrick Scientific) was used with a HVC-VUV environmental chamber (Harrick Scientific) to collect diffuse reflectance spectra. Zeolite powder samples were loaded onto a wire mesh screen within the reactor cell. A temperature controller (Watlow Series 989) controlled the temperature of the reactor cell, and a type K thermocouple (Omega) measured the temperature of the catalyst sample. The IR spectra are the average of 125 scans collected with a spectral resolution of 4 cm⁻¹ over the range of 4000-500 cm⁻¹. Mass flow controllers (Brooks 5850E series) were used to control the flow of NO, O₂, and He gases into the reactor cell. Gas transfer lines were maintained at 423 K to minimize the presence of water. Catalysts were pretreated by heating from room temperature to 773 K at a rate of 5 K min⁻¹ and holding at that temperature for either 3 h in a flow of 5% O₂, 3 h in a flow of He, or 4 h in a flow of 1% CO/He. After the pretreatment and prior to introducing the reactant gases, background spectra were collected at the experiment temperatures.

5.2.5 UV-Vis spectroscopy

Diffuse reflectance UV-vis spectra were collected using a UV-vis spectrometer (JASCO, V-5500) equipped with an integrating sphere (JASCO ISV-469). Barium sulfate (BaSO₄, Sigma Aldrich) in a U-shaped quartz tube was used to collect a background spectrum prior to all measurements. Then, approximately 125 mg of material was placed in a U-shaped quartz tube, which was connected to gas lines for each experiment. The U-tube was wrapped in heating tape and insulation, and heated

at a rate of 5 K min⁻¹ to 723 K in either 1% CO/He or O₂ flowing at 20 sccm. The temperature was controlled using a temperature controller (Watlow, Series 965) and a K-type thermocouple, which was placed around the outside of the tube at the sample location. The reactor was held at 723 K for 2 h. Then, the temperature was lowered to room temperature while continuing to flow gas. Once room temperature was reached, the heating tape was removed and UV-vis spectra were collected by securing the U-shaped tube at the opening of the integrating sphere of the spectrometer. Spectra were collected from 220 nm to 850 nm. This setup allowed for UV-vis spectra to be collected under gas flow at room temperature following treatment at elevated temperatures.

5.3 Results and Discussion

5.3.1 Material Characterization

XRD patterns (Figure 5.2) indicate that no phase impurities were present in the Cu-zeolite samples.



Figure 5.2. XRD patterns of Cu-ZSM-5 (Cu/Al = 0.40, Si/Al = 12) and Cu-SSZ-13 (Cu/Al = 0.40, Si/Al = 12) samples.

BET surface areas and micropore volumes as determined by N_2 physisorption are listed in Table 5.1. The values are in good agreement with those reported in the literature [21]-[23].

Table 5.1. BET surface areas and *t*-plot micropore volumes for Cu-SSZ-13, Cu-ZSM-5, and Cu-BEA materials (Cu/Al = 0.40 and Si/Al = 12 for all samples).

Material	BET Surface Area (m ² g ⁻¹)	Micropore Volume (cm ³ g ⁻¹)
Cu-SSZ-13	653	0.28
Cu-ZSM-5	406	0.13
Cu-BEA	671	0.15

ICP analysis indicated that the Si/Al ratios of all Cu-SSZ-13 samples were ~11.4. Table 5.2 provides the nominal and actual Cu/Al ratios of Cu-SSZ-13 samples.

Cu/Al Ratio	Nominal Cu wt%	Actual Cu wt% (ICP)
0.025	0.195%	0.27%
0.05	0.39%	0.37%
0.10	0.78%	0.74%
0.20	1.56%	2.05%

Table 5.2. Nominal and actual Cu loadings (determined by ICP analysis) for Cu-SSZ-13 (Si/Al = 12) samples.

5.3.2 Effect of Catalyst Pretreatment on NO Oxidation Activity and Kinetic Parameters

Figure 5.3 presents NO oxidation rates (per gram of material) on Cu-form (Cu/Al = 0.40) and H-form SSZ-13 and ZSM-5 zeolite samples as a function of temperature after various pretreatments. Rates on the H-form zeolites were ~1-2 orders of magnitude lower than those on the Cu-form zeolites, and thus the contribution to the rate from the acid sites in the Cu-samples was neglected. The reactivity of the Cu-zeolites can therefore be attributed entirely to the Cu-sites present within the samples. Overall, Cu-ZSM-5 samples showed higher levels of activity compared to Cu-SSZ-13 samples. Depending on the reaction temperature and pretreatment conditions, rates on Cu-ZSM-5 samples were ~2-5 times greater than rates on Cu-SSZ-13 samples.

Pretreatment conditions had a significant effect on reaction rates. Pretreatment in 1% CO/He led to greater catalytic activity for both zeolites. Rates on Cu-SSZ-13 pretreated in 1% CO/He were ~3-5 times greater than those on the pre-oxidized Cu-SSZ-13 sample. Similarly, rates on Cu-ZSM-5 pretreated in 1% CO/He were approximately one order of magnitude greater compared to those on the pre-oxidized Cu-ZSM-5 sample. Pretreatment in 1% NH₃ or 500 ppm NO + 500 ppm NH₃ led to lower activity compared to the pre-oxidized samples for both zeolite frameworks. The approach to equilibrium factor (η) became greater than 0 at reaction temperatures above 673 K, signifying that the reverse reaction (NO₂ decomposition to NO and O₂) began to occur. Nonetheless, η values always remained less than 0.34, which indicated that the reaction remained far away from equilibrium and ensured that reliable kinetic data could be measured.



Figure 5.3. NO oxidation rates measured as a function of temperature on Cu-SSZ-13 (Si/Al = 12, Cu/Al = 0.40) and H-SSZ-13 (top panel), and on Cu-ZSM-5 (Si/Al = 12, Cu/Al = 0.40) and H-ZSM-5 (bottom panel). Reaction conditions: 750 ppm NO + 5% O_2 , T = 400-823 K, total flow rate = 125 sccm.

The higher activity of the Cu-zeolite samples pretreated in 1% CO/He suggests that Cu⁺ cations are more active in catalyzing NO oxidation compared to Cu²⁺ species. Based on this assumption, then, it is expected that the samples pretreated in 1% NH₃/He or 500 ppm NO + 500 ppm NH₃ should have been more active than those pretreated in 1% CO/He, since NH₃ is a stronger reducing agent. However, this was not observed, as the samples pretreated in 1% NH₃/He or 500 ppm NO + 500 ppm NH₃ actually had lower activity than those pretreated in 5% O₂/He. One possible explanation for this observation is that NH₃, which is a strong Lewis base, easily binds to Cu sites and blocks the access of NO and O₂ to the Cu⁺ site, therefore lowering the observed activity. NH₃ can bind to either isolated Cu²⁺ cations or [Cu²⁺OH]⁺ complexes, and is thermally stable up to 773 K [24]. Additionally, the presence of linear [Cu⁺(NH₃)₂]⁺ complexes, which form inside the zeolite cavities in the presence of NH₃ [24], could block the active sites.

Regarding the samples pretreated in 1% CO/He, it is possible that Cu⁺–CO complexes could form and either be active in the catalytic cycle or hinder activity. To test for the presence of these complexes, the samples were reduced in 1% CO/He at 673 K. Then, the gas flow was switched to He until no CO was detected by the mass spectrometer. Increasing the temperature from 673 K to 873 K under the flow of He did not result in the release of any adsorbed species, which indicates that Cu⁺–CO complexes did not form during the reduction at 673 K and thus were not responsible for the high catalytic rates subsequently observed. Additionally, TPD profiles (not shown) indicated that adsorbed CO species did form, but desorbed at 612 K on Cu-ZSM-5 and 549 K on Cu-SSZ-13. The fact that CO desorbed at these temperatures, despite the fact that high reaction rates were observed at temperatures up to 823 K,

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suggests that adsorbed CO complexes on Cu^+ sites do not have a significant role in the catalytic cycle; rather, Cu^+ itself is the likely active site.

Activation energies (E_{meas.}) for the reactions on Cu-SSZ-13 and Cu-ZSM-5 samples were estimated from Arrhenius plots over the temperature range of 523-823 K. Table 5.3 presents the E_{meas} values, as well as measured reaction rates at 623 K. Among the Cu-ZSM-5 samples, E_{meas.} was greatest for the reaction after pretreatment in 1% CO/He, with a value of 31.2 kJ mol⁻¹. In contrast, E_{meas}, was the lowest for the reaction on Cu-ZSM-5 after pretreatment in 5% O₂/He, with a value of 18.2 kJ mol⁻¹. It should be noted that among Cu-ZSM-5 samples, the greatest NO oxidation rate and E_{meas.} value occurred for the sample pretreated in 1% CO/He. The same trend was observed for the Cu-SSZ-13 samples as well. These observations are surprising, as typically reaction rates increase with a decrease in the activation energy. The higher activity of the samples pre-reduced in 1% CO/He, despite the associated increase in activation energy, suggests that the pre-exponential factor (k_0) is much larger in these cases. A large pre-exponential factor indicates a slightly negative or even positive entropy of formation of the transition state (ΔS^{\ddagger}), and is characteristic of a monomolecular reaction involving the dissociation of a 'loose' activated complex during the RDS [25].

Previous investigations have reported a wide range of activation energies for NO oxidation on Cu-SSZ-13 and Cu-ZSM-5 samples. Measured activation energies of 57.6 kJ mol⁻¹ [7], 56 kJ mol⁻¹ [26], and 52 kJ mol⁻¹ [18] have been reported for pre-oxidized Cu-SSZ-13 samples. On Cu-ZSM-5, Olsson et al. [8] used kinetic modelling and flow reactor experiments to determine an activation energy of 8.9 ± 1.11 kJ mol⁻¹

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(T = 298-773 K). Meanwhile, Capek et al. [27] reported an activation energy of 75.3 kJ mol⁻¹ for Cu-MFI (T = 473-623 K).

Table 5.3. Measured NO oxidation rates normalized per gram of catalyst (T = 623 K) and measured activation energies ($E_{meas.}$) for Cu-SSZ-13 (Si/Al = 12, Cu/Al = 0.40) and Cu-ZSM-5 (Si/Al = 12, Cu/Al = 0.40). $E_{meas.}$ values were estimated over the temperature range of 523-823 K for Cu-samples and 423-623 K for H-samples.

Material	Pretreatment	Rate at 623 K (mol s ⁻¹ g _{cat} . ⁻¹)	E _{meas.} (kJ mol ⁻¹)
	1% CO	$1.15 imes 10^{-5}$	25.7
Cu 887 13	5% O ₂	3.47×10^{-6}	24.1
Cu-552-15	500 ppm NO + 500 ppm NH_3	$1.05 imes 10^{-6}$	16.9
	1% NH ₃	$2.35 imes 10^{-6}$	15.8
	1% CO	$3.29 imes 10^{-5}$	31.2
Cu-ZSM-5	5% O ₂	$6.51 imes 10^{-6}$	18.2
Cu Zowi 5	500 ppm NO + 500 ppm NH ₃	4.13×10^{-6}	19.4
	1% NH ₃	$2.62 imes 10^{-6}$	23.1
H-SSZ-13	5% O ₂	2.80×10^{-7}	40.8
H-ZSM-5	5% O ₂	$1.24 imes 10^{-7}$	45.7

As was discussed in Chapter 3, H-SSZ-13 exhibits higher reactivity compared to H-ZSM-5 because of its smaller pore size, which results in a more favorable enthalpic stabilization of an [NO•O₂][‡] activated complex. For the Cu-zeolite samples, though, it appears that enthalpy is no longer the driving force that leads to higher reactivity, since Cu-ZSM-5 (with its larger pore size) shows higher catalytic activity than Cu-SSZ-13. Additionally, the differences in activation energy between samples are not very large (15.8-25.7 kJ mol⁻¹ for Cu-SSZ-13 samples, 18.2-31.2 kJ mol⁻¹ for Cu-ZSM-5 samples), and samples with higher activity tend to have higher activation energies. For example, among samples pretreated in 1% CO/He, Cu-ZSM-5 exhibited higher activity than Cu-SSZ-13, but their respective activation energies were 31.2 kJ mol⁻¹ and 25.7 kJ mol⁻¹. This indicates that ΔS^{\dagger} is more consequential in determining the reactivity of the samples compared to ΔH^{\dagger} . Alternatively, the differences in activity could be a result of the different Cu species present or the reducibility of these species in each framework.

To check for changes to the catalysts over time, rates were measured by increasing the temperature from 523 K to 823 K, and then decreasing the temperature back down within the same range. Figure 5.4 shows the results for Cu-SSZ-13 and Cu-ZSM-5. Reaction rates were very similar in both cases, indicating that no changes occurred over time to the catalysts which cause an increase or decrease in catalytic activity.



Figure 5.4. NO oxidation rates measured on Cu-SSZ-13 and Cu-ZSM-5 materials (Cu/Al = 0.40 and Si/Al = 12 for both samples) as a function of temperature. Experiments were carried out by progressing either from low temperature to high temperature or from high temperature to low temperature.

NO oxidation rates were also measured on Cu-SSZ-13 samples with different Cu/Al ratios at 423 K and 623 K by independently varying the NO and O₂ inlet concentrations to determine the reaction orders α and β for NO and O₂, respectively. The following rate expression (Eq. 5.3) accurately fit the reaction rate data for samples pretreated in 5% O₂/He at 773 K for 3 h:

$$r_{NO_2} = k_{app.}[NO][O_2]$$
(5.3)

Rates were found to be approximately proportional to NO and O₂ concentrations over the range of investigated inlet concentrations for all Cu-SSZ-13 samples (Table 5.4). At higher temperatures (T = 623 K), it was observed that Cu-SSZ-13 samples with higher Cu/Al ratios (Cu/Al = 0.20 and 0.40) showed a slightly stronger dependence on NO concentration compared to the other samples. Reaction orders with respect to NO at 623 K on these samples were 1.28 (Cu/Al = 0.20) and 1.27 (Cu/Al = 0.40), whereas the reaction orders were much closer to 1 in all other cases. Reported reaction orders for NO and O₂ in the literature are generally inconsistent with one another, which could be attributed to differences in the sample compositions (Si/Al ratio, Cu loading) or the reaction conditions (temperature, the presence or absence of NO₂). For comparison, Verma et al. [18] observed reaction orders of 1.6 ± 0.2 and 0.9 ± 0.1 for NO and O_2 , respectively, on Cu-SSZ-13 samples (Si/Al = 4.5) with Cu/Al ratios ranging from 0.31-1.60 under a feed of 300 ppm NO + 10% O₂ +150 ppm NO₂ at 573 K. On the other hand, Metkar et al. [26] measured reaction orders of 0.9-1 and 0.55-0.59 for NO and O₂, respectively, on a Cu-CHA catalyst under gas feeds of 100-800 ppm NO + 0-5% O₂ at 473-563 K.

Cu/Al Ratio	T (K)	α (NO reaction order)	β (O ₂ reaction order)
0.025	423	0.94	0.96
0.025	623	0.99	0.95
0.05	423	0.95	0.97
0.05	623	1.01	0.98
0.10	423	1.07	0.99
0.10	623	1.02	1.09
0.20	423	1.04	0.96
0.20	623	1.28	1.03
0.40	423	1.12	1.05
0.40	623	1.27	0.93

Table 5.4. Reaction orders with respect to NO (250-750 ppm NO + 5% O₂) and O₂ (750 ppm NO + 2-6% O₂) at 423 K and 623 K on Cu-SSZ-13 samples (Si/Al = 12, Cu/Al = 0.025-0.40). Samples were pretreated in 5% O₂/He at 773 K for 3 h.

Reaction orders for NO and O_2 were also measured on Cu-zeolite samples following the other pretreatment methods (Table 5.5). Pretreatment conditions, rather than zeolite framework, tended to have a more significant effect on reaction orders. For example, pretreatment in reducing conditions (1% CO/He, 500 ppm NO + 500 ppm NH₃, or 1% NH₃/He) resulted in reaction orders that were ~1 with respect to NO concentration and ~0.5 with respect to O_2 concentration for both Cu-SSZ-13 and Cu-ZSM-5. In contrast, pretreatment in 5% O_2 /He resulted in reaction orders that were ~1 with respect to both NO and O_2 concentrations.

Pretreatment	Material	α (NO reaction order)	β (O2 reaction order)
500 ppm NO +	Cu-ZSM-5	1.22	0.52
500 ppm NH ₃	Cu-SSZ-13	1.10	0.49
10/ NU.	Cu-ZSM-5	1.09	0.57
1 % INH3	Cu-SSZ-13	1.03	0.53
10/ CO	Cu-ZSM-5	0.94	0.54
1% CO	Cu-SSZ-13	0.88	0.63
50/ 0.	Cu-ZSM-5	1.08	0.98
5% U 2	Cu-SSZ-13	1.27	0.93

Table 5.5. Reaction orders with respect to NO (250-750 ppm NO + 5% O₂) and O₂ (750 ppm NO + 2-6% O₂) at 623 K on Cu-SSZ-13 and Cu-ZSM-5 samples (Cu/Al = 0.40, Si/Al = 12).

5.3.3 Effect of Cu Loading on NO Oxidation Rates

Figure 5.5 shows the effect of Cu loading (0-3.12 wt%) on NO oxidation rates measured on Cu-SSZ-13 samples at 573 K after pretreatment in 1% CO/He. Rates are normalized either per gram of catalyst (lower panel) or per mol of Cu present in the sample (upper panel), and two different trends are observed as a function of Cu loading. Reaction rates normalized per gram of catalyst increase linearly at Cu loadings below ~0.5%. For example, the rate of NO₂ formation on H-SSZ-13 (Cu wt% = 0) is 1.05 mmol NO₂ h⁻¹ g_{cat.}⁻¹ at 573 K, while the rate on Cu-SSZ-13 (Cu wt% = 0.195%) is 43.2 mmol NO₂ h⁻¹ g_{cat.}⁻¹. At Cu loadings above 0.5%, the reaction rate increases nonlinearly with increased Cu loading until a value of 2.04%. Further increase of the Cu loading to 3.12% did not result in higher catalytic activity. Kwak et al. [7] observed that the NO oxidation activity did not depend significantly on the Cu ion exchange level in the range of 20-80% over the temperature range of 423-573 K. At temperatures greater than 573 K, the authors showed that NO oxidation rates increased with higher Cu loading, and rates were significantly greater when a Cu ion exchange level of 80% was reached [7]. It should be noted that the experiments described in Kwak et al. [7] were conducted in the presence of 10% H_2O on preoxidized samples; in contrast, the studies presented here were carried out under dry conditions with pre-reduced samples.



Figure 5.5. NO oxidation rates measured on Cu-SSZ-13 samples (Si/Al = 12, Cu wt% = 0-3.12%) and normalized per gram of zeolite (lower panel) or per mol of Cu (upper panel). Rates were measured after pretreatment in 1% CO/He at 773 K for 4 h. Reaction conditions: 750 ppm NO + 5% O₂, T = 573 K, total flow rate = 125 sccm, catalyst mass = 10 mg.

NO oxidation rates normalized per mol of Cu showed a different trend as a function of Cu loading at 573 K (see upper panel in Figure 5.5). The reaction rate was

highest at low Cu loading and decreased dramatically as the Cu loading increased. For example, the reaction rate was measured to be 1,286.4 mol NO₂ mol Cu⁻¹ h⁻¹ at a Cu loading of 0.318 wt%, while the rate was measured to be only 208.7 mol NO₂ mol Cu⁻¹ h⁻¹ at a Cu loading of 3.12 wt%. Increasing the Cu loading beyond ~0.5 wt% did not yield significant changes in the normalized rates. This trend occurs because the catalytic activity per gram only increased from 43.2 mmol NO₂ h⁻¹ g_{cat.}⁻¹ to 105.7 mmol NO₂ h⁻¹ g_{cat.}⁻¹ (a factor of ~2.5) with an increase in Cu wt% from 0.195% to 3.12% (a factor of 16). Thus, when rates are normalized by mol of Cu, the activity for the sample with 0.195 wt% Cu is much greater than that for the sample with 3.12 wt% Cu.

The reaction order with respect to Cu wt% for rates normalized per gram of catalyst was obtained by plotting the data from the curved region in Figure 5.5 (Cu loading of 0.19% to 2.04%) on a log vs. log scale. The reaction order was observed to be 0.36 with respect to Cu wt%, and thus the rate expression in Eq. 5.3 was modified to include a term for the dependence of the rate on Cu wt% (Eq. 5.4). In contrast, the rates normalized per mol of Cu show a negative dependence of -0.69 on Cu loading.

$$r_{NO_2} = k_{app.}[NO][O_2][Cu wt\%]^{0.36}$$
(5.4)

The results from Figure 5.5 suggest that, for samples pretreated in 1% CO/He, isolated Cu^+ sites are the primary active site responsible for catalyzing the reaction. The figure also indicates that Cu loading beyond 0.5 wt% does not lead to substantial increases in reactivity. As previously discussed, it is known that certain Cu^{2+} sites (those near the 6MR) are difficult to reduce, and will remain in the 2+ oxidation state even after treatment in a reducing gas. At higher Cu loadings, then, it is likely that a greater fraction of Cu remains in the 2+ oxidation state, and thus rates normalized per mol of Cu decrease since increased amounts of Cu²⁺ species, which appear to be considerably less active than Cu⁺, are present. Cu²⁺ sites or Cu-dimers are likely present in the samples with higher loadings, but their activity is much lower than that of the Cu⁺ sites, and thus rates normalized per mol of Cu do not increase with higher loadings. The trends observed in Figure 5.5 for pre-reduced samples differ from what has been reported for pre-oxidized samples [6], [18]. Reports by Verma et al. [18] and Ruggeri et al. [6] have shown that NO oxidation activity over pre-oxidized Cu-SSZ-13 is minimal for samples with low Cu loadings, increases monotonically per mol of Cu above Cu/Al ratios of 0.2, and saturates at Cu/Al ratios of 1.6. The authors identified that only O-bridged Cu-dimers (Cu_xO_y), which readily form at intermediate to higher Cu loadings according to Eq. 5.5, are capable of catalyzing NO oxidation over preoxidized Cu-SSZ-13, and that isolated Cu²⁺ species located near the faces of the 6membered rings (6MR) are not very active in catalyzing the reaction. Verma et al. [18] suggested that isolated Cu⁺ ions could also have a role in NO oxidation, but that Cu dimers are the most likely active site in pre-oxidized samples. The Cu-dimers can form rather easily since isolated Cu^{2+} ions are highly mobile within the SSZ-13 framework [18].

$$[Cu(OH)]^{+} + [Cu(OH)]^{+} \rightleftharpoons [Cu - O - Cu]^{2+} + H_2O$$
(5.5)

5.3.4 UV-vis Spectroscopy

UV-vis spectroscopy was used to investigate the Cu species present in the Cu-SSZ-13 and Cu-ZSM-5 samples after exposure to various gases at elevated

temperatures. Figure 5.6 shows the spectra collected at room temperature of Cu-ZSM-5 samples following pretreatments in O₂ at 723 K or 1% CO/He at 673 K. Additionally, a spectrum of a "fresh" (hydrated) sample is included for comparison. In the 12,000 cm⁻¹ to 20,000 cm⁻¹ region, a broad absorption band centered around 14,000 cm⁻¹ was observed on Cu-ZSM-5 after pretreatment in O₂, and is characteristic of the d \leftarrow d transitions of Cu²⁺ [28]. The broadness of the absorption band indicates a wide distribution of Cu²⁺ cations within the ZSM-5 framework. This feature is also observed on the hydrated sample, though it is less pronounced. In contrast, this broad feature was not observed for the Cu-ZSM-5 sample following treatment in 1% CO/He, presumably because the sample only contained Cu⁺ species after the reduction. Cu⁺ has fully occupied d orbitals $(3d^{10})$ and thus does not have d \leftarrow d transitions. The absence of this band indicates that the copper ions in this sample were fully reduced to Cu⁺. At higher wavenumbers, the "fresh" sample shows a band at 38,600 cm⁻¹, and then the signal increases. Likely, an intense band is centered at 48,000 cm⁻¹ (beyond the range of detection), which is characteristic of ligand to metal charge transfer (LMCT) transitions $(O^2-Cu^{2+} \rightarrow O^-Cu^+)$ [9]. After O₂ treatment, the LMCT maximum underwent a redshift to 38,800 cm⁻¹ as a result of the decomposition of the aqua complexes present in the "fresh" sample. The removal of water ligands allows Cu²⁺ cations to more strongly interact with framework oxygen atoms and to be stabilized in a stronger distorted local environment. A redshift of a LMCT band is a clear indication of an increase in the degree of covalency in the ligand to metal bond. Following pretreatment in 1% CO/He, the intensity of the LMCT band significantly decreased because of the increased presence of Cu⁺.

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Figure 5.6. Diffuse reflectance UV-vis spectra of Cu-ZSM-5 (Cu/Al = 0.40, Si/Al = 12) samples collected at room temperature following different treatments. The "fresh" sample is Cu-ZSM-5 in the hydrated form, the "after O₂ treatment" sample was treated in flowing O₂ at 723 K for 2 h, and the "after 1% CO treatment" sample was treated in flowing 1% CO/He at 673 K for 2 h (spectra have been stacked for clarity).

Figure 5.7 shows the UV-vis spectra collected of Cu-SSZ-13 samples following the same pretreatment processes used for the Cu-ZSM-5 samples. The O₂ treated sample shows three discernable d \leftarrow d transitions, in contrast to the single broad transition observed for the analogous Cu-ZSM-5 sample. These features are observed at 12,600 cm⁻¹, 16,300 cm⁻¹, and 19,400 cm⁻¹, and are in close agreement

with the d \leftarrow d quadruplet (bands at 11,000 cm⁻¹, 13,600 cm⁻¹, 16,500 cm⁻¹, and 19,700 cm⁻¹) previously reported for such samples (note that the 11,000 cm⁻¹ band is beyond the wavelength range reported in Figure 5.7) [9]. These multiple absorptions are caused by the Jahn-Teller splitting of highly distorted Cu^{2+} species [28]. The majority of Cu²⁺ species in Cu-SSZ-13 are located in the plane of the 6-membered rings and are coordinated to three framework oxygen atoms. O₂ treatment also resulted in the formation of a broad shoulder feature in the 22,000 cm⁻¹ to 31,000 cm⁻¹ range, which was not present in the hydrated sample. Bands in this region are indicative of copper complexes containing bonds with extraframework oxygen. O₂ treatment resulted in the decomposition of aqua complexes, allowing Cu^{2+} cations to interact stronger with framework oxygen atoms and to be stabilized in a stronger distorted local environment. It is possible that this transition (along with the feature observed at 19,400 cm⁻¹) can be assigned to planar bis(μ - η^2 : η^2 peroxo)dicopper complexes, which show characteristic electronic transitions in the ranges of 29,600-27,300 cm⁻¹ and 19,700-17,000 cm⁻¹ [29]. After treatment in 1% CO/He, the d \leftarrow d transitions and the broad shoulder around 29,000 cm⁻¹ both disappeared, indicating that the Cu species present in the sample were reduced to Cu⁺. However, the broad feature at 38,500 cm⁻¹ increased considerably in intensity after CO treatment. In contrast, this feature underwent a significant reduction in intensity for Cu-ZSM-5 after CO treatment. It is known that Cu atoms are more difficult to reduce in Cu-SSZ-13 than in Cu-ZSM-5, but it is unclear if this is the reason for the large LMCT band observed in the Cu-SSZ-13 sample after CO treatment.

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Figure 5.7. Diffuse reflectance UV-vis spectra of Cu-SSZ-13 (Cu/Al = 0.40, Si/Al = 12) samples collected at room temperature following different treatments. The "fresh" sample is Cu-SSZ-13 in the hydrated form, the "after O₂ treatment" sample was treated in flowing O₂ at 723 K for 2 h, and the "after 1% CO treatment" sample was treated in flowing 1% CO/He at 673 K for 2 h (spectra have been stacked for clarity).

UV-vis spectra were also collected for a Cu-SSZ-13 with lower Cu loading (Figure 5.8). The d \leftarrow d transitions and the broad shoulder at 29,000 cm⁻¹, which had been evident for the sample with higher loading (Cu/Al = 0.40), are not apparent on

this sample. O_2 and CO treatments resulted in a redshift of the LMCT band to 39,000 cm⁻¹, with the band being slightly intensified after CO treatment.



Figure 5.8. Diffuse reflectance UV-vis spectra of Cu-SSZ-13 (Cu/Al = 0.025, Si/Al = 12) samples collected at room temperature following different treatments. The "fresh" sample is Cu-SSZ-13 in the hydrated form, the "after O₂ treatment" sample was treated in flowing O₂ at 723 K for 2 h, and the "after 1% CO treatment" sample was treated in flowing 1% CO/He at 673 K for 2 h (spectra have been stacked for clarity).

5.3.5 Temporal Evolution of NO Oxidation

The temporal evolution of the NO oxidation reaction on Cu-zeolite samples was monitored at 523 K after pretreatment in either 5% O₂/He or 1% CO/He at 773 K. Figure 5.9 shows the time on stream NO oxidation rates for the three zeolite frameworks (SSZ-13, ZSM-5, BEA). Pretreatment in 1% CO/He compared to 5% O₂/He resulted in enhanced NO oxidation activity for all zeolite frameworks. Among the samples pretreated in 1% CO/He, the reactivity on Cu-ZSM-5 is 3.3 times larger than the reactivity on Cu-SSZ-13 and 5.4 times greater than the reactivity on Cu-BEA. In addition to showing greater catalytic activity, Cu-ZSM-5 reached steady-state activity faster compared to Cu-SSZ-13 and Cu-BEA. The reaction on Cu-ZSM-5 reached steady-state in only 20 minutes, while the reaction on Cu-BEA took ~30 minutes to reach steady-state and the reaction on Cu-SSZ-13 took ~40 minutes. Zeolite framework had less of an effect on catalytic rates following pretreatment in 5% O₂/He (Figure 5.9.a). Rates scaled in the order of Cu-SSZ-13 was only 1.2 times larger than the rate on Cu-BEA and 1.3 times larger than the rate on Cu-ZSM-5.



Figure 5.9. NO oxidation rates measured on Cu-SSZ-13 (Si/Al = 12, Cu/Al = 0.40), Cu-ZSM-5 (Si/Al = 12, Cu/Al = 0.40), and Cu-BEA (Si/Al = 12, Cu/Al = 0.40) following pretreatment in a) 5% O₂/He at 773 K for 3 h or b) 1% CO/He at 773 K for 4 h. Reaction conditions: 750 ppm NO + 5% O₂, T = 523 K, total flow rate = 125 sccm, catalyst mass = 10 mg.

Table 5.6 shows the steady-state rates from the data in Figure 5.9. Pretreatment conditions had the largest effect on reaction rates on Cu-ZSM-5. 1% CO/He pretreatment led to an order of magnitude increase in the rate on Cu-ZSM-5 compared to the rate after 5% O_2 /He pretreatment. In contrast, only a 2.4 time increase in the rate on Cu-SSZ-13 and a 1.8 time increase in the rate on Cu-BEA were observed between the two pretreatments. This observation suggests that the Cu⁺ cations are much more reducible in the ZSM-5 framework compared to the SSZ-13 and BEA frameworks.

Table 5.6. Steady state NO oxidation reaction rates measured on Cu-SSZ-13 (Si/Al = 12, Cu/Al = 0.40), Cu-ZSM-5 (Si/Al = 12, Cu/Al = 0.40), and Cu-BEA (Si/Al = 12, Cu/Al = 0.40) following pretreatment in 5% O₂/He at 773 K for 3 h or 1% CO/He at 773 K for 4 h. Reaction conditions: 750 ppm NO + 5% O₂, T = 523 K, total flow rate = 125 sccm, catalyst mass = 10 mg.

Material	Pretreatment	Rate (mol s ⁻¹ g _{cat.} ⁻¹)
Cu 887 12	5% O ₂	3.32×10^{-6}
Cu-55Z-15	1% CO	$1.01 imes10^{-5}$
Cu 78M 5	5% O ₂	$4.29 imes 10^{-6}$
Cu-ZSIVI-J	1% CO	$3.37 imes 10^{-5}$
	5% O ₂	$3.45 imes10^{-6}$
Cu-DEA	1% CO	$6.21 imes10^{-6}$

5.3.6 Temporal Evolution of N_xO_y Surface Intermediates on Cu-SSZ-13 During NO and NO/O₂ Gas Flows as Measured Using DRIFTS

Figure 5.10 shows the IR spectra collected during flow of 1,000 ppm NO + 5% O_2 on Cu-SSZ-13 (Si/Al = 12, Cu/Al = 0.40) at 523 K following pretreatment in 1% CO/He at 773 K. A complex series of IR bands form. The band at 1624 cm⁻¹ is attributed to adsorbed nitrite (NO₂⁻) or nitrate (NO₃⁻) species on Cu sites [6]. Ruggeri et al. [6] also observed the formation of nitrate IR bands on a commercial Cu-CHA

catalyst (in the presence of only gas-phase NO, [NO] = 500 ppm, T = 423 K), though the catalyst was pretreated in O₂ instead of CO. The IR bands at 1570 cm⁻¹ and 1361 cm⁻¹ are also likely attributable to nitrates or nitrites, which show typical bands in the 1650-1500 cm⁻¹ and 1400-1100 cm⁻¹ regions of the IR spectra [30]. No evidence was observed for the formation of Cu⁺—NO species, which show IR bands in the 1820-1740 cm⁻¹ region [31]. The nitrites/nitrates do not form at Brønsted acid sites at these temperatures, and recall from the DRIFTS spectra presented in Chapter 4 that no such bands were observed on H-SSZ-13 under similar conditions.

The IR band at 1879 cm⁻¹ can tentatively be assigned to NO adsorbed on Cu²⁺ cations. It is possible that some Cu species may exist as Cu²⁺ cations, even though the Cu-SSZ-13 sample was reduced in 1% CO/He prior to the admission of NO. Kwak et al. [32] observed the presence of both Cu⁺ and Cu²⁺ following a reduction in 1% CO/He at 673 K, citing that Cu²⁺ ions near the 6MR are difficult to reduce under these conditions. As described by Giordanino et al. [9], Cu²⁺(NO) adducts typically show absorptions in the 1970-1850 cm⁻¹ region. In transmission IR experiments conducted at 300 K on Cu-ZSM-5, Szanyi and Paffett [33] observed the formation of IR bands at 1875 cm⁻¹, which they attributed to the vibrations of NO molecules adsorbed onto Cu-oxide (CuO) species.

The band at 2018 cm⁻¹ could be due to adducts that form from an interaction between NO⁺ and NO, which would shift the IR band of NO⁺ to a lower wavenumber. It is unclear what the bands at 1055 cm⁻¹ and 1102 cm⁻¹ represent, as they are located at wavenumbers lower than typical IR bands for N_xO_y species. It is possible that they are due to framework vibrations of the zeolite, which can be perturbed by changes to the oxidation state of Cu.

An IR band at ~2150 cm⁻¹ also started to quickly form after exposure of the sample to 1,000 ppm NO + 5% O_2 . After several minutes, the peak split into two IR bands (2184 cm⁻¹ and 2140 cm⁻¹) which continued to increase in intensity. These bands indicate the formation of the nitrosonium species (NO⁺), which occupy cationic positions (either at Cu²⁺ sites or Brønsted acid sites) to compensate negative framework charges. It is likely that the band at 2184 cm⁻¹ is assignable to NO⁺ forming at Brønsted acid sites. This is in close agreement with the previous findings from Chapter 4 in which we observed an IR band for NO⁺ at 2190 cm⁻¹ on H-SSZ-13 [34]. The band at 2140 cm⁻¹ likely involves NO⁺ participating in an NO⁺—Cu⁺ ion pair, since this band was not observed on H-SSZ-13 samples. Alternatively, these two bands could reflect NO⁺ formation at different Cu sites within the CHA framework, such as the 6MR or the larger cages. Ruggeri et al. [6] observed similar bands at 2190 cm⁻¹ and 2140 cm⁻¹ on a pre-oxidized Cu-SSZ-13 sample, and attributed them to NO⁺ in the larger cages and 6MRs, respectively. NO⁺ formation occurs because gas-phase NO can reduce Cu^{2+} sites by donating the unpaired electron from its antibonding π orbital (Eq. 5.8). The NO^+ — Cu^+ ion pair that originates has the same overall charge compensation as Cu^{2+} within the zeolite framework, and thus the charge balance is maintained. As already mentioned, it is possible that some Cu species may exist as Cu^{2+} cations even following treatment in 1% CO/He [32]. Additionally, it is likely that some Cu^+ may become oxidized in the presence of O_2 and NO_2 .

$$Cu^{2+} + NO \to Cu^+ + NO^+ \tag{5.8}$$



Figure 5.10. Series of IR spectra during exposure of Cu-SSZ-13 (Si/Al = 12, Cu/Al = 0.40) to gas stream of 1,000 ppm NO + 5% O₂ at 523 K. The sample was pretreated in 1% CO/He at 773 K for 4 h prior to IR measurements.

The 2500-2200 cm⁻¹ region of the IR spectrum in Figure 5.10 showed very interesting behavior as a function of time. A broad feature initially developed in the 2500-2000 cm⁻¹ region. Within this broad feature, there were distinct shoulders centered at 2405 cm⁻¹ and 2280 cm⁻¹. After ~20 minutes of exposure to 1,000 ppm NO, the broad feature began to disappear as the sharp bands at 2184 cm⁻¹ and 2140 cm⁻¹ became more defined. The broad features at 2405 cm⁻¹ and 2280 cm⁻¹ can be

attributed to NO₂⁺ or NO⁺ species. Hadjiivanov [30] previously observed NO⁺ species to form in the 2290-2102 cm⁻¹ on Cu-zeolites, and NO₂⁺ to form in the 2392-2360 cm⁻¹ ¹ region. Adsorbed N₂O may be another assignment for the band at 2280 cm⁻¹. Zhang et al. [35] used density functional theory (DFT) calculations to show that the N—O vibrations of N₂O occur at 2367 cm⁻¹, 2339 cm⁻¹, and 2362 cm⁻¹. The authors detected an IR band at 2249 cm⁻¹ in transmission FTIR experiments during exposure of NO to Cu-SSZ-13 samples at 300 K, and assigned this to N₂O. N₂O can form from the dissociation of two NO molecules (Eq. 5.6), and $K_{eq.} = 4.38 \times 10^4$ at 523 K for this reaction.

The band at 919 cm⁻¹ could be attributed to several different species. One possibility is the $O_{lattice}$ -NO⁺ vibration, which has a theoretical vibration at 1000 cm⁻¹ [36]. We have previously observed a similar band at 952 cm⁻¹ on H-SSZ-13 [34], while Hadjiivanov and coworkers [36] have observed this IR band at 977 cm⁻¹. Alternatively, the band at 919 cm⁻¹ could be due to Cu²⁺ cations located within the large cavities or near the plane of the six-membered rings (6MR) of the CHA structure, as observed by Kwak et al. [32]. The authors attributed IR bands at 940 cm⁻¹ and 895 cm⁻¹ in their studies to Cu²⁺ ions located within the eight- and six-membered rings, respectively [32]. As previously mentioned, Cu²⁺ ions are likely to still be present in reduced Cu-SSZ-13 samples due to the difficulty associated with reducing certain Cu²⁺ ions to Cu⁺. Cu²⁺ cations may form as well in the presence of oxidizing agents (i.e., O₂ and NO₂) present in the IR cell under reaction conditions. Finally, the 919 cm⁻¹ IR band could be the δ (O-H) mode of the coper hydroxide complex [Cu²⁺(OH)]⁺, as Borfecchia et al. [37] observed a similar band at 905 cm⁻¹ on Cu-SSZ- 13. It is possible for Cu^+ sites to be oxidized by NO₂ (Eq. 5.9), which is a very strong oxidizing agent.

$$2Cu^{+} + NO_{2} + 2H^{+} \rightarrow 2Cu^{2+} + NO + H_{2}O$$
(5.9)

When H_2O is generated, copper-hydroxide $[Cu^{2+}(OH)]^+$ species can form according to Eq. 5.10.

$$2Cu^{+} + \frac{1}{2}O_{2} + H_{2}O \to 2[Cu^{2+}(OH)]^{+}$$
(5.10)

 $[Cu^{2+}(OH^{-})]^+$ can also form by the dehydration of $Cu^{2+}(H_2O)_n$ when two Z⁻ sites within the zeolite are close to each other, as is typical at lower Si/Al ratios (Eq. 5.11).

$$Cu^{2+}(H_2O)_n + 2Z^- \to [Cu^{2+}(OH^-)]^+ - Z^- + H^+ - Z^-$$
 (5.11)

During dehydration, H₂O dissociates to yield $[Cu^{2+}(OH^{-})]^+$ and a Brønsted acid site, each balancing the negative charges from the neighboring Z⁻ sites. At higher Si/Al ratios or when Z⁻ sites are not in close proximity, $[Cu^{2+}(OH^{-})]^+$ can form by the dehydration of $[Cu^{2+}(H_2O)_n(OH^{-})]^+$, as illustrated in Eq. 5.12.

$$[Cu^{2+}(H_20)_n(OH^-)]^+ + Z^- \to [Cu^{2+}(OH^-)]^+ - Z^- + H_20^{\uparrow}$$
(5.12)

In addition to the IR band at 919 cm⁻¹, a small IR band at 3646 cm⁻¹ and the band at 1879 cm⁻¹ in Figure 5.10 may also signify the formation of $[Cu^{2+}(OH)]^+$, based on

assignments by others [9]. Dedecek et al. [38] assigned an IR band at 1895 cm⁻¹ to such a species in an investigation on Cu-ZSM-5.

In the 4000-3000 cm⁻¹ region, negative bands at 3632 cm⁻¹ and 3661 cm⁻¹ signify the consumption of Brønsted acid sites and extraframework Brønsted acid sites. The positive bands at 3600 cm⁻¹ and 3577 cm⁻¹ may be assignable to v(O–H) modes of Brønsted acid sites which formed during dehydration of Cu²⁺(H₂O)_n (Eq. 5.11). A band at 3646 cm⁻¹ initially formed, but then went away with longer time on stream. This band is characteristic of $[Cu^{2+}(OH)]^+$ [37]. Additionally, external silanol groups appeared to be consumed, as indicated by a negative band at 3733 cm⁻¹.

An analogous DRIFTS experiment to the one just described on Cu-SSZ-13 (Cu/Al = 0.40) was carried out on a Cu-SSZ-13 sample with lower Cu loading (Cu/Al = 0.05) to identify any differences in N_xO_y surface species that formed as a result of the lower Cu content. Several notable differences were observed for the sample with lower Cu loading, including the absences of IR bands at 2018 cm⁻¹, 1879 cm⁻¹, 1570 cm⁻¹, and 1055 cm⁻¹ which were previously observed to form on the sample with higher Cu loading (Cu/Al = 0.40). The absence of the band at 1570 cm⁻¹ indicates less nitrate/nitrite formation (note that nitrate/nitrite bands were still observed at 1366 cm⁻¹ and 1622 cm⁻¹, similar to those seen at 1361 cm⁻¹ and 1624 cm⁻¹ on the sample with a Cu/Al ratio of 0.40), while the absence of the band at 1879 cm⁻¹ indicates no NO–Cu²⁺ formation, likely because more of the Cu is reduced to Cu⁺ in the sample with lower Cu loading. An IR band formed at 2187 cm⁻¹, similar to the band at 2182 cm⁻¹ at Brønsted acid sites. The intensity of the band on the sample with lower Cu content is much greater, presumably because of the increased number of Brønsted acid sites

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present. Additionally, the intensity of the IR band at 2148 cm⁻¹ (assignable to NO⁺– Cu⁺) is much lower on the sample with less Cu content because of the lower number of Cu sites. A strong negative band was observed at 3612 cm⁻¹ and is attributable to the consumption of Brønsted acid sites during the formation of NO⁺.



Figure 5.11. Series of IR spectra obtained during exposure of Cu-SSZ-13 (Si/Al = 12, Cu/Al = 0.05) to gas stream of 1,000 ppm NO + 5% O₂ at 523 K. The sample was pretreated in 1% CO/He at 773 K for 4 h prior to IR measurements.

5.3.7 Proposed Reaction Mechanism for NO Oxidation on Reduced Cu-Zeolites

The results from the previous sections have shown that the NO/O_2 chemistry on the Cu-zeolite samples is very complex and is affected by a number of factors,

including the zeolite framework, Cu/Al ratio, sample pretreatment, and temperature. The kinetic measurements suggest that Cu^+ is the active site, and thus a reaction mechanism is proposed below (Scheme 5.1) that begins with NO binding to Cu^+ (step 1). After NO binds to Cu^+ , O_2 then adsorbs onto the site to form an adsorbed nitrate (NO_3) species, and in the process oxidizes Cu^+ to Cu^{2+} (step 2). NO from the gas phase then reacts with the adsorbed nitrate to produce NO₂, leaving behind a nitrite (NO_2) species on the Cu²⁺ atom (step 3). Evidence for nitrates and nitrites coordinated to Cu^{2+} was provided during the DRIFTS experiments. In the final step (step 4), the nitrite desorbs as NO₂, and the Cu²⁺ atom reduces back to Cu⁺. Note that the reaction mechanism is consistent with the stoichiometry of the NO oxidation reaction, and that all species that adsorb or desorb in the cycle are stable molecules (i.e. NO, O_2 , NO_2) rather than fragments such as $(\frac{1}{2})$ O₂ or isolated ions such as OH⁻ or O₂⁻. As was shown in a previous report [39], nitrate formation is exothermic, but formation of nitrite after the release of the first molecule of NO₂ formed (step 3) is endothermic. The likely rate-determining step (RDS) for this catalytic cycle is the oxidation of Cu⁺ and the activation of O_2 to form nitrates (step 2).

Scheme 5.1. Proposed NO oxidation reaction mechanism on reduced Cu-zeolites.



Under the assumption that step 2 is the RDS, and using the pseudo-equilibrium approximation, the following rate expression can be derived:

$$r = \frac{k_2 K_1 K_4 (P_{NO}) (P_{O_2})}{\left(P_{NO_2}\right) + \frac{\left(P_{NO_2}\right)^2}{K_3 (P_{NO})} + K_1 K_4 (P_{NO}) + K_4}$$
(5.13)

At low conversion, the concentration of NO₂ is expected to be low, and the denominator terms that include (P_{NO2}) can be neglected. After additional mathematical simplifications, the rate expression in Eq. 5.13 becomes:

$$r = \frac{k_2 K_1(P_{NO})(P_{O_2})}{1 + K_1(P_{NO})}$$
(5.14)

At low coverage of surface intermediates, the denominator term $K_1(P_{NO})$ will be << 1, and the rate expression will simplify to $r \sim k_{app.}(P_{NO})(P_{O2})$, where $k_{app.}$ is a product of k_2 and K_1 . The experimental results in section 5.3.2 (Table 5.5) established that the reaction orders for NO and O₂ were ~1 and ~0.5, respectively, over the pre-reduced Cu-zeolite samples, which are inconsistent with the reaction orders in the above rate expression.

If step 3 is assumed to be rate-determining, the following expression is derived (Eq. 5.15). Under conditions of low conversion and low coverage of surface intermediates, the denominator terms are negligible, and the rate expression simplifies to $r \sim k_{app.}(P_{NO})^2(P_{O2})$, where $k_{app.} = k_3K_1K_2$. This expression is also inconsistent with the experimentally determined reaction orders for NO and O₂. Additionally, step 3 is less likely to be the RDS, since nitrates and nitrites typically exist in equilibrium within the zeolite. Step 4 as rate-determining was not considered, since it is merely desorption of NO₂.

$$r = \frac{k_3 K_1 K_2 (P_{NO})^2 (P_{O_2})}{1 + \frac{(P_{NO_2})}{K_4} + K_1 (P_{NO}) + K_1 K_2 (P_{NO}) (P_{O_2})}$$
(5.15)
In addition to the inconsistencies of this reaction mechanism with the experimentally determined reaction orders, several issues remain unresolved. First, it remains unclear why the activity (per mol of Cu) of pre-reduced Cu-SSZ-13 samples decreased with increasing Cu/Al ratio (upper panel in Figure 5.5). Although the IR spectra did indicate some subtle differences in the $N_x O_y$ species that formed, it is unknown if these differences are responsible for the observed differences in catalytic activity. Differences regarding NO⁺ formation were observed between the samples with different Cu loadings, but NO⁺ is a spectator species according to the proposed reaction mechanism (Scheme 5.1) and therefore plays no role in the catalysis. It is known that Cu ions will coordinate to the zeolite framework differently as the loading increases, which is likely a cause of the different activities per mol of Cu observed. At low loadings, Cu ions occupy sites near the windows of the 6MR with 2 Al T-sites, and form Cu-O bonds with lattice oxygen atoms. Additionally, some Cu cations can be pulled into the center of the double 6MRs, where they no longer form a Cu-O bond with the framework. At higher loadings, it is possible for Cu to exist as isolated cations that interact with 2 Al sites which are further apart, such as those in the 8MR. Alternatively, Cu species can charge-balance only one Al site as $[Cu^{2+}(OH)]^+$ or Cu^+ , or Cu dimers can form at higher Cu loadings (Cu/Al > 0.20). Based on the data from the upper panel in Figure 5.5, the Cu species that form at low Cu loadings and form Cu-O bonds with lattice oxygen atoms appear to be the most active sites, while Cu cations located in the 8 MR and Cu dimers, which form at higher Cu loadings, are notably less active in catalyzing the reaction. More detailed studies need to be conducted to verify this hypothesis, including an examination of the differences in reducibility of these samples. Secondly, it is unclear why differences exist regarding

the temporal evolutions of the reactions on pre-reduced and pre-oxidized samples. Rates on the pre-reduced samples reach steady-state relatively quickly (less than 20 minutes), but rate on the pre-oxidized samples take ~40 minutes to reach steady-state.

5.4 Conclusions

Incorporation of copper into the zeolite frameworks (SSZ-13, ZSM-5, BEA) resulted in substantially higher NO oxidation activity (by ~1-2 orders of magnitude) compared to the acid zeolites. Rates scaled in the order of Cu-ZSM-5 > Cu-SSZ-13 > Cu-BEA, which was different from the order on acid samples (H-SSZ-13 > H-ZSM-5 > H-BEA). In addition to the framework, pretreatment conditions had a substantial effect on the reactivity of the Cu-zeolite samples. For all frameworks (SSZ-13, ZSM-5, BEA), pretreatment in a flow of 1% CO/He led to higher activity compared to pretreatment in 5% O₂/He, 1% NH₃/He, or 500 ppm NO + 500 ppm NH₃. Reaction orders also were also affected by the different pretreatment conditions. Rates on Cuzeolite samples pretreated in 5% O_2 /He were observed to be first order with respect to NO and O₂ concentrations. For pre-reduced samples, the rate dependency on O₂ concentration changed to half order. Over Cu-SSZ-13, an investigation of Cu loading on reaction rates showed that rates normalized per gram of catalyst increased dramatically with increasing Cu loading up to ~1 wt%. Cu loadings beyond 1 wt% resulted in only slight increases to the rate. Meanwhile, rates normalized per mol of Cu (turnover frequencies) decreased substantially with increased Cu loading up to ~1 wt%, and were relatively independent of Cu loading at higher levels. DRIFTS spectra collected under *in-situ* conditions showed that different N_xO_y surface species, including NO₃⁻, NO₂⁻, and NO⁺, formed depending on the Cu loading of the zeolite. UV-vis spectroscopy studies showed that Cu-zeolite samples contained Cu²⁺ following

 O_2 pretreatment and mostly Cu^+ following CO pretreatment. A mechanism for the reaction on Cu-zeolites pretreated in 1% CO/He was presented and discussed.

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Chapter 6

INTRODUCTION TO CO₂ HYDROGENATION AND THE REVERSE WATER-GAS SHIFT (RWGS) REACTION⁴

6.1 CO₂ Hydrogenation: Using CO₂ Emissions as a Feedstock for Chemicals and Fuels

The capture and utilization of carbon dioxide (CO₂) is an important technology that must be quickly developed and implemented on a worldwide scale in order to address the problem of rising atmospheric CO₂ concentrations. CO₂ is the primary greenhouse gas (GHG) emitted from human activities such as the combustion of fossil fuels for energy and transportation purposes. The atmospheric concentration of CO₂ has increased dramatically over the past several hundred years, from ~280 ppm before the industrial revolution to ~390 ppm in 2010, and is projected to rise to ~570 ppm by 2100 [1]. Although this era has been a time of unprecedented technological achievements and advancements for human development, it has come at an extreme cost to the planet and has led to significant and possibly irreversible climate change [2]. Today, CO₂ continues to be released in very large amounts, with emission levels in the U.S. rising 7% from 1990-2013 [3]. These increases continue despite the growing awareness regarding the problems these emissions pose.

⁴ I would like to acknowledge Dr. Nagesh Rao Peela for assisting with the catalyst screening tests presented in this chapter.

The scientific community recognizes three possible strategies (which can be used in combination) for the control of CO₂ emissions: reduce, capture/store, and reuse. As the demand for energy and fuel continues to increase on a global scale, a reduction in CO_2 emissions can only come about through improvements in energy efficiency and a more diverse energy portfolio that arises from a switch from utilization of fossil fuels to increased usage of less carbon intensive energy sources such as renewable energy and hydrogen. These alternative energy sources remain largely undeveloped for large scale applications, however, and only account for a very small portion of the total worldwide energy usage [4], as shown in Figure 6.1. Even by 2035, renewable energy sources are projected to provide less than 10% of the world's total energy [4]. Oil, coal, and gas, meanwhile, will continue to be dominant, with projections indicating that they will provide 81% of the world's energy in 2035, down only a few percentages from the 86% they provided in 2013 [4]. Thus, humanity's continued dependence on fossil fuels means that CO₂ emissions will continue to be released in large amounts for the foreseeable future. Much more intensive efforts must be directed towards increasing the energy efficiency of carbon-based technologies and improving or developing renewable energy processes in order to reduce CO₂ emissions and mitigate the Greenhouse effect. Until these technologies mature, the combined approach of capturing, storing, and recycling CO2 as a chemical feedstock for the production of valuable chemicals (such as methanol) and fuels is of critical importance for reducing dependence on fossil fuels [5].



Figure 6.1. Past and future sources of primary energy (worldwide), as published in the *BP Energy Outlook 2035* [4].

 CO_2 is a desirable carbon source because of its abundance and low cost. In addition, it is non-toxic, non-corrosive, non-flammable, and can be easily stored without posing significant safety issues [6]. The chemical recycling of CO_2 is a very difficult problem, however, since it requires effective materials or processes for capturing CO_2 , economic means of storing the emissions, and catalysts that can then selectively convert CO_2 into useful products. CO_2 can be captured from power plant discharge or natural gas streams, and various technologies have been developed for these purposes. The most common approach involves the chemical absorption of CO_2 using amines such as monoethanolamine (MEA) [7]. The captured CO_2 produces hydrocarbonate or carbamate salts, which are subsequently decomposed at high temperatures to release the CO_2 [8], [9]. The CO_2 gas is then compressed and transported to a storage site. This process is not very economically viable, however, since it generates an excessive amount of amine waste and requires a high energy input to heat the salt solutions [10].

After CO₂ has been captured and stored, it can be converted into a variety of useful organic molecules such as CO, methanol, ethanol, formic acid, dimethyl ether (DME), and light alkanes or alkenes by hydrogenation reactions [11]. CO₂ is not currently used as a feedstock for many applications, so this reaction route represents an important new challenge and area of development for the field of heterogeneous catalysis. The production of urea, salicylic acid, and carbonates are the only industrial processes that presently use CO₂ as a source of carbon [1]. The limited use of CO₂ stems from the fact that it is highly thermodynamically stable, and that it requires a cheap and sustainable route of hydrogen production, which is currently unavailable and is itself a major challenge for the research community to solve. CO₂ hydrogenation only leads to a reduction in GHG emissions when the hydrogen is produced primarily from renewable or non-fossil fuel resources; otherwise, the emissions released during the production of hydrogen may be greater than the emissions saved by recycling CO₂ [11].

One critical reaction in the conversion of CO₂ by hydrogenation is the reverse water-gas shift (RWGS) reaction (Eq. 6.1), which is the reaction of CO₂ with H₂ to form CO and H₂O. The RWGS reaction, which occurs in many processes whenever CO₂ and H₂ are present, is an endothermic reaction (Δ H°_{298 K} = 41.2 kJ mol⁻¹) and thus is thermodynamically favorable at higher temperatures. The reaction is of great

fundamental and practical importance, and has rightly received significant attention from the research community.

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \tag{6.1}$$

The RWGS reaction can be part of a two-step hydrogenation process for the conversion of CO₂ to valuable products. First, CO₂ is reduced to CO via the RWGS reaction. Subsequently, CO is converted to either hydrocarbons or methanol. Conversion of CO to hydrocarbons occurs via the Fischer-Tropsch (FT) process. Ironbased catalysts have shown to be effective for this reaction [12]. Alternatively, the $CO_2/CO/H_2$ feed exiting the RWGS reactor can be fed to another reactor for the production of methanol via the CAMERE (CArbon dioxide hydrogenation to form **ME**thanol via a **RE**verse WGS reaction) process [13]. Cu-based materials, particularly Cu/Zn/Al₂O₃, have been investigated extensively for this reaction [14]. The CAMERE process may be advantageous over direct CO₂ hydrogenation to methanol because the thermodynamics for methanol production from CO are much more favorable than from CO_2 . Additionally, water is produced during the hydrogenation of CO_2 to methanol (Eq. 6.2) but not during the hydrogenation of CO (Eq 6.3). Water tends to inhibit the reaction, and therefore it is desirable and often necessary to remove water in situ, adding to the difficulty of the process. The Carbon Dioxide Reduction and Sequestration (CDRS) R&D Center in South Korea demonstrated on a pilot scale that this two-step approach using the RWGS for methanol synthesis is preferable to a single step approach in terms of higher catalyst productivity, lower gas recycle, and smaller reactor size [15]. For example, they showed that a single step process using a

CuO/ZnO/ZrO₂/Ga₂O₃/Al₂O₃ catalyst required a 6 L reactor to produce 600 g_{CH3OH} k_{gcat}^{-1} h⁻¹ (T = 523 K, P = 50 bar). Meanwhile, a two-step CAMERE process using ZnAl₂O₄ to catalyze the RWGS reaction and CuO/ZnO/ZrO₂/Ga₂O₃ to catalyze the conversion to methanol required only a 2 L reactor to produce 760 g_{CH3OH} k_{gcat}^{-1} h⁻¹ (T = 513 K, P = 27 bar) [15].

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \tag{6.2}$$

$$CO + 2H_2 \rightleftharpoons CH_3OH$$
 (6.3)

The methanol produced via the CAMERE process can be used as an alternative fuel, blended with gasoline, or used as the fuel source for direct-methanol fuel cells (DMFCs) [5], [16]. Additionally, it can undergo further reaction to produce gasoline by the methanol-to-gasoline (MTG) process [17] or olefins by the methanol-to-olefins (MTO) process [18]. Methanation of CO_2 is an undesired side reaction that decreases the selectivity toward CO or CH_3OH [19], and therefore Ni-based materials should generally be avoided for this reason. Figure 6.2 shows how the RWGS reaction fits into the overall picture of using CO_2 hydrogenation to produce valuable chemicals or fuels, and identifies the possible sources of CO_2 and H_2 .



Figure 6.2. Involvement of the RWGS reaction in CO_2 hydrogenation processes to produce valuable chemicals and fuels. Possible sources of CO_2 and H_2 are included in the diagram.

Some debate does exist, however, regarding the most favorable reaction route for methanol production and whether the RWGS reaction is beneficial for improving the yield. Several reports [20-22] have used isotopic labeling techniques to suggest that direct CO₂ hydrogenation to CH₃OH is preferred over a sequential process in which CO is first formed by the RWGS reaction and is subsequently hydrogenated to form CH₃OH. In one instance, the authors show that CO formation via RWGS and CH₃OH formation via CO₂ hydrogenation on industrial-like Cu/ZnO/Al₂O₃ catalysts display inverse kinetic isotope effects (KIE), but the magnitude of the KIE for CH₃OH formation is much greater [20]. The difference in the KIE values indicates that the two reactions do not share a common intermediate in the rate-determining step, and thus proceed via independent pathways. The authors suggest, therefore, that the RWGS activity should be minimized in order to increase the selectivity of CH₃OH [20]. Additionally, other reports have used ¹³C- [21] and ¹⁴C- [22] tracer studies to show that CO₂, not CO, is the direct source of CH₃OH on Cu-based materials. Thus, it seems that conflicting results are being reported about the role of the RWGS reaction in methanol production. Those proposing the CAMERE process show that a consecutive reaction procedure (RWGS reaction to form CO followed by CO hydrogenation to form CH₃OH) is favorable in order to increase CH₃OH yields [13-15]. On the contrary, others [20-22] indicate that CO_2 hydrogenation to CH_3OH and the RWGS reaction are competing reactions, and thus higher RWGS activity decreases the selectivity to CH₃OH. Clearly, a consensus on the best procedure for CH₃OH synthesis has yet to emerge, and it may be that the use of certain catalysts or reaction conditions favor direct conversion of CO₂ to CH₃OH, while others favor a sequential process in which CO is produced prior to CH₃OH. Further understanding of the RWGS reaction mechanism should help researchers understand how to better develop catalysts that promote or repress the reaction, depending on what particular process is desired.

6.2 Catalysts and Promoters for CO₂ Hydrogenation and the RWGS Reaction

Many catalysts have been investigated for their abilities to catalyze CO_2 hydrogenation and the RWGS reaction. This section discusses various catalyst metals, supports, and promoters that have been previously reported for having notable CO_2 hydrogenation, WGS, or RWGS activity. Cu-based materials have been widely studied for the WGS reaction, and thus have also been investigated in many instances for the RWGS reaction. Cu-Ni/Al₂O₃ [23], Cu/ZnO [24], Cu-Zn/Al₂O₃ [24], and Cu/SiO₂ promoted with potassium [25] have all shown good RWGS activity. However, Cu materials tend to deactivate by sintering at high temperatures (T > 773 K), which are required for high RWGS activity. Iron can be added as a thermal stabilizer for hightemperature applications. Chen et al. [26] showed that adding small amounts of iron to 10% Cu/SiO₂ resulted in stable RWGS activity for 120 h at 873 K and atmospheric pressure, while non-promoted 10% Cu/SiO₂ deactivated rapidly. Noble metals such as Pt, Au, and Pd on reducible metal oxide supports are also efficient for WGS and RWGS, as they can easily dissociate H₂. Burch and coworkers [27, 28] and Efstathious and coworkers [29] have performed many investigations of the WGS and RWGS reactions on Pt/CeO₂ with a focus on identifying the reaction mechanisms. Their investigations to discern between redox and associative reaction mechanisms are discussed in greater detail in Chapter 7. Wang et al. [30] studied the Au/CeO₂ catalyst for low-temperature WGS and RWGS applications, and conducted mechanistic studies with the catalyst using temporal analysis of products (TAP) measurements. Iron oxides (Fe_xO_y) have also been investigated extensively for CO_2 hydrogenation, and these materials are often used industrially for FT synthesis, WGS, and RWGS [31-33]. These materials are especially attractive for hydrocarbon synthesis because of the highly olefinic nature of the obtained products [12]. Iron carbide (Fe_5C_2) is the active phase for FT synthesis, while oxidic amorphous iron phases appear to be active for the RWGS reaction [34, 35].

Promoters are used to stabilize catalysts, increase reactivity, and optimize the product distribution for a reaction [36]. Electronic promoters donate or withdraw electron density near the valence band of the catalyst, modifying the local electron

density around the surface. This effect typically increases selectivity and conversion. Structural promoters, on the other hand, stabilize a catalyst's active phase, which results in better dispersion of the metal over the support and yields higher conversion. Overuse of promoters, though, can block active sites and cause the formation of unwanted products [37, 38]. Manganese (Mn) is a common promoter for CO₂ hydrogenation, and acts both structurally and electronically by suppressing CH₄ formation, promoting catalyst reduction, and increasing the catalyst's surface basicity [36, 39]. Cu and K are often used as promoters for Fe catalysts [40]. Cu facilitates the reduction of Fe oxides to promote the formation of the active phase [41] and enable H₂ dissociation [42]. Potassium enhances the strength of adsorption of CO or CO₂ [1, 43], and is also very cost-effective. Ceria promoters are highly active for the WGS reaction, but are not particularly active for CO₂ hydrogenation reactions and can even decrease the conversion in some instances [44].

Supports are used to stabilize the catalyst and prevent sintering or Oswald ripening of the active particles. Alumina (Al₂O₃) tends to be the best support, followed by silicas (SiO₂) and titanias (TiO₂) [17, 45-47]. Al₂O₃ is likely superior to other supports because it creates strong metal-support interactions which help prevent sintering and improve dispersion [48]. However, Kim et al. [49] showed that Pt/TiO₂ was more effective than Pt/Al₂O₃ for catalyzing the RWGS, citing a new active site located at the metal-support interface on the TiO₂-supported catalyst that led to high electron donating abilities. Yablonsky et al. [50] indicated that ceria-supported noble catalysts are promising next-generation WGS/RWGS catalysts, though currently these supports tend to quickly deactivate under realistic conditions [51]. Finally, zirconia

 (ZrO_2) has been considered to be a favorable support, and Fe/ZrO₂ displayed equal WGS activity to bulk iron but had improved stability at 623-773 K [52].

6.3 Catalyst Screening: Material Synthesis and Characterization

After conducting a literature review of catalysts that have been investigated for the RWGS or related reactions (i.e. WGS, Fischer-Tropsch), as described in Section 6.2, a variety of metal catalysts on metal-oxide supports (1% Pt/CeO₂, 15% Cu– 5% Ni/Al₂O₃, 4.5% Fe/Al₂O₃, 4.2% Fe-3.4% K/Al₂O₃, 1% Pt-Ce/ZrO₂, 5% Cr/ZrO₂, 1% Ni/CeO₂) were prepared and screened for their abilities to selectively catalyze the RWGS reaction. All catalysts were synthesized using the wetness impregnation method. 1% Pt/CeO₂ was prepared by combining ceria (CeO₂, Sigma Aldrich) and tetraamineplatinum (II) hydroxide solution ((NH₃)₄Pt(OH)₂, Alfa Aesar) in an aqueous solution and stirring with a magnetic stir bar at room temperature for 1 h. 15% Cu-5% Ni/Al₂O₃ was prepared by adding gamma alumina (γ -Al₂O₃, Alfa Aesar, 99.97%) to a 0.1 M aqueous solution of nickel (II) nitrate (Ni(NO₃)₂·6H₂O, Sigma Aldrich) and copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$, Sigma Aldrich) and stirring with a magnetic stir bar at room temperature for 1 h. 4.5% Fe/Al₂O₃ was prepared by adding gamma alumina $(\gamma-Al_2O_3, Alfa Aesar, 99.97\%)$ to an aqueous solution of 0.1 M iron nitrate (Fe(NO₃)₃·9H₂O, Aldrich, 99.99%) and stirring with a magnetic stir bar at room temperature for 1 h. 4.2% Fe–3.4% K/Al₂O₃ was prepared by adding gamma alumina $(\gamma-Al_2O_3, Alfa Aesar, 99.97\%)$ to an aqueous solution of 0.1 M iron nitrate (Fe(NO₃)₃·9H₂O, Aldrich, 99.99%) with potassium carbonate (K₂CO₃, Sigma Aldrich, \geq 99.0%) and stirring with a magnetic stir bar at room temperature for 1 h. 1% Pt-Ce/ZrO₂ was prepared by preparing a 0.1 M aqueous solution of cerium (IV) ammonium nitrate ((NH₄)₂Ce(NO₃)₆, Sigma Aldrich) and zirconium (IV) oxynitrate

(ZrO(NO₃)₂·xH₂O, Sigma Aldrich) (75 mol% CeO₂ and 25 mol% ZrO₂). Ceria and zirconium hydroxides were co-precipitated by the addition of an excess of ammonium hydroxide. The precipitate was washed with DI water and calcined at 1073 K for 1 h. The Ce/ZrO₂ support was then added to an aqueous solution of tetraamineplatinum (II) hydroxide solution $((NH_3)_4Pt(OH)_2, Alfa Aesar)$, and the mixture was stirred with a magnetic stir bar at room temperature for 1 h. 5% Cr/ZrO₂ was prepared by combining zirconium (IV) oxide (ZrO_2 , Sigma Aldrich) and chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O_3$, Sigma Aldrich) in an aqueous solution and stirring with a magnetic stir bar at room temperature for 1 h. 1% Ni/CeO₂ was prepared by combining ceria (CeO₂, Sigma Aldrich) and nickel (II) nitrate (Ni(NO₃) $_2$ ·6H₂O, Sigma Aldrich) in an aqueous solution and stirring with a magnetic stir bar at room temperature for 1 h. For all catalysts, the impregnation was performed by increasing the temperature to 353 K to slowly evaporate the water. Following the impregnation step, all samples were dried in a static oven at 383 K for 12 h in air. Dried samples were then crushed and calcined in a Thermolyne furnace in air by heating at a rate of 300 K h⁻¹ to 973 K and holding at that temperature for 4 h. Table 6.1 summarizes the compositions and BET surface areas of all catalysts screened for the RWGS reaction.

Material	BET Surface Area (m ² g ⁻¹)
1% Pt/CeO ₂	33.8
15% Cu– 5% Ni/Al ₂ O ₃	77.4
4.5% Fe/Al ₂ O ₃	79.0
4.2% Fe-3.4% K/Al ₂ O ₃	60.5
1% Pt–Ce/ZrO ₂	11.7
5% Cr/ZrO ₂	90.1
1% Ni/CeO ₂	35.1

Table 6.1. Catalyst compositions and BET surface areas.

Powder XRD patterns (Figures 6.3 and 6.4) only showed reflections associated with the catalyst supports. No reflections were present indicating the presence of bulk metal or metal oxides associated with the loaded metals.



Figure 6.3. Powder XRD patterns of 4.2% Fe – 3.4% K/Al₂O₃, 4.5% Fe/Al₂O₃, and γ –Al₂O₃.



Figure 6.4. Powder XRD patterns of 1% Pt-Ce/ZrO₂, 1% Pt/CeO₂, 1% Ni/CeO₂, 5% Cr/ZrO₂, and 15% Cu - 5% Ni/Al₂O₃.

6.4 Catalyst Screening: High-throughput Microreactor (HTM)

Catalyst samples were screened using a continuous high-throughput microreactor (HTM) developed by colleagues at the University of Delaware and the U.S. Army Research Laboratory [53]. The HTM system (illustrated in Figure 6.5) houses nine parallel packed bed channels and consists of six major parts: flow inlet tube, flow distributor, diffuser capillaries, reactors, catalyst beds, and reactor endcapillaries [53]. A conical distributor and end-capillary lengths of 30 mm were used to minimize entrance effects and minimize the average deviation in flow among channels. The developers of this system showed in a previous report [53] that the maximum deviation in the flow rates between channels was kept to less than 8% using this setup. Sample volumes in each packed bed were also kept the same in order to achieve a uniform flow distribution across all channels. 3D pressure profile simulations indicated that the majority of the pressure drop occurs in the capillary tube at the end of each reactor [53], and thus pressure differences between the channels at any axial position are negligible.



Figure 6.5. Illustration of high-throughput microreactor (HTM) with conical flow distributor and nine parallel packed bed reactor channels [53]. Reproduced with permission from *Industrial & Engineering Chemistry Research* (ACS Publications).

Mass flow controllers (model RS-485, MKS Instruments) were used to control reactant gases (CO₂, H₂) and inert (He) gas flows into the HTM. Flow rates through each channel were verified using a mass flow meter (model ADM2000, Agilent

Technologies). Gases were mixed in gas transfer lines before entering the conical distributor. Diffusor capillaries were placed between the distributor and the reactors to prevent back-mixing. Reactors were 75 mm in length, and catalyst bed lengths were ~ 10 mm. 1/16 in. capillary tubes (30 mm length, 0.4 mm inside diameter) were connected to the end of each reactor channel to ensure a smaller pressure drop in the reactor compared to the tube. Reactor effluents from the nine channels were selected one at a time for analysis using a 10-port selector (VICI Instruments). The selected effluent was sent to a four-channel micro-GC (model G3581A, Agilent Technologies), while the remaining eight effluents were vented. Gas transfer lines after the reactors and selector valve were heated to 433 K to minimize any condensation effects from water produced during the reaction. The GC contained three different capillary columns: molecular sieve 5A, porapak-U, and AlO_x. Each column was connected to an individual TCD detector. Reactors were heated with three heating cartridges, each with a heating capacity of 170 W. A PID controller was used to control the heating rate and setpoint of the setup. Exit temperatures of each reactor were monitored using 1/16" K-type thermocouples (Omega).

Catalyst samples were reduced under a flow of 10% H₂/He for 4 h at 873 K. Subsequently, catalysts were screened for CO₂ conversion and CO selectivity at temperatures between 723 K and 850 K. 0.30 g of catalyst were used, and samples were diluted with silicon carbide (SiC) particles in a 1:1 ratio. Catalyst and diluent particle sizes were kept the same. Inlet partial pressures for CO₂ and H₂ were 53 kPa and 48 kPa, respectively. The total inlet flow rate was 180 sccm CO₂ + 157 sccm H₂. SiC was loaded into one of the nine reactor chambers to ensure it did not contribute to the observed conversion levels. Quartz was also tested in one reactor to quantify any

contributions from the gas-phase reaction. Although the reproducibility of the HTM has been previously established [53], 1% Pt/CeO₂ was loaded into two of the reactor chambers for verification.

6.5 Catalyst Screening Results

Figure 6.6 shows the CO₂ conversion and CO selectivity as a function of temperature for each catalyst screened using the HTM. CO₂ conversion levels were greatest on Pt-Ce/ZrO₂ and Pt/CeO₂. At 783 K, CO₂ conversion levels were 25.9% on Pt/CeO₂, 25.1% on Pt-Ce/ZrO₂, 21.4% on both Fe-K/Al₂O₃ and Ni/CeO₂, 15.4% on Fe/Al₂O₃, and 14.2% on Cr/ZrO₂. The conversions of the Pt/CeO₂ catalysts in two different reaction channels were very similar to one another, indicating that the inlet flow was distributed evenly between the channels. For example, at 753 K the CO_2 conversions in each channel with Pt/CeO₂ were 21.6% and 22.3%. CO₂ conversions on SiC and quartz remained less than 1.5% at all temperatures, and thus their contributions to the conversion levels observed for the catalysts were small. Although the Pt materials did exhibit the highest activity among the materials tested, the cost of Pt is very high, and thus it was preferred to find a less expensive alternative which still displayed acceptable levels of activity. The activity on Fe-K/Al₂O₃ was ~15% lower than that on the Pt catalysts; however, as of August 2015, the prices of Pt and Fe were \$994.4/oz. and \$0.00145/oz., respectively. This price difference represents a huge cost savings with only a modest drop off in catalytic performance that can be obtained by using the Fe-based catalyst. The activity of the non-promoted Fe catalyst (Fe/Al₂O₃) was ~2-3 times lower than that of Fe-K/Al₂O₃, which signifies that the potassium promoter leads to a substantial increase in activity.

The selectivity plot (Figure 6.6.b) indicates that only two of the tested materials (Pt-Ce/ZrO₂, Ni/CeO₂) did not exhibit CO selectivity of ~100%. On Pt-Ce/ZrO₂, the CO selectivity decreased with increasing temperature, and ranged from 94% at 723 K to 85% at 847 K. On Ni/CeO₂, the selectivity was far worse and increased with increasing temperature, ranging from 53% at 723 K to 82% at 847 K. Methane was the only side product detected on both materials. Ni is known to be a very effective methanation catalyst, and thus the lower CO selectivity is expected on Ni/CeO₂. The Fe/Al₂O₃ and Fe-K/Al₂O₃ materials were chosen for further investigations because of their high CO selectivity and relatively high activities compared to the other materials tested. The results of the kinetic and mechanistic studies on these catalysts are discussed in Chapter 7.



Figure 6.6. a) CO₂ conversions and b) CO selectivities as a function of temperature (723-848 K) for the catalysts screened using the HTM.

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Chapter 7

Fe-K/Al₂O₃ AND Fe/Al₂O₃ AS REVERSE WATER-GAS SHIFT (RWGS) CATALYSTS⁵

7.1 Introduction

The reverse-water gas shift (RWGS) reaction is the reaction of carbon dioxide (CO₂) and hydrogen (H₂) to form carbon monoxide (CO) and water (H₂O). The reaction is endothermic ($\Delta H^{\circ}_{298 \text{ K}} = 41.2 \text{ kJ mol}^{-1}$) and the chemical equilibrium favors CO and H₂O as the temperature increases. The water-gas shift (WGS) should be mechanistically related to the RWGS reaction through the principle of microscopic reversibility, and has been investigated in great detail on many catalysts. With the growing importance of limiting anthropogenic CO₂ emissions, the RWGS reaction presents a straightforward alternative for the reduction of CO₂ to CO if an economically viable and carbon-neutral source of H₂ can be developed.

The WGS reaction is carried out on an industrial scale in two reactors connected in series; the first reactor is operated at "high temperature" (623-723 K) and uses Fe_xO_y -based catalysts with various promoters (Pt, Cu, Ag, Ba, K, Cr, etc.) and supports (Cr₂O₃, CeO₂-ZrO₂, MnO) [1]. Magnetite is believed to be the active phase of

⁵ I would like to acknowledge Dr. Matthew J. Wulfers and Dr. Nebojsa Marinkovic for their collaborations on the research described in this chapter. Specifically, Dr. Wulfers assisted with planning and performing experiments and analyzing the data, and Dr. Marinkovic assisted with the XANES experiments and analysis.

iron under high temperature WGS conditions and, when promoted with chromium, is the customary industrial catalyst for the high-temperature WGS reaction [2]. Chromium is a structural promoter that helps prevent the iron from sintering [3], [4]. The second WGS reactor is operated at "low temperature" (453-523 K) and uses Cu-Zn/Al₂O₃ as the catalyst [5].

In addition to WGS, supported iron is also known to catalyze the RWGS reaction [6], as well as a number of other industrially important reactions including: *i*) Fischer-Tropsch synthesis [7], *ii*) ammonia synthesis [8], *iii*) ethylbenzene dehydrogenation to styrene [9], and *iv*) selective catalytic reduction of nitrogen oxides (NO_x) with ethanol (EtOH-SCR) [10]. The RWGS and WGS reactions are often carried out in conjunction with Fischer-Tropsch synthesis on iron catalysts [11], in which case iron carbide is believed to be the active phase for hydrocarbon production [12], and iron oxide is the active phase for WGS and RWGS [1].

Promoters are often used with iron catalysts to enhance Fischer-Tropsch or RWGS rates and tune the selectivity to the desired products [13]-[17]. One known effect of potassium on iron is an increased CO₂ adsorption capacity [12]. Alkali metals are considered *electronic* promoters, as they can facilitate electron transfer and enhance electrostatic interactions with reacting molecules [18], [19]. Chen et al. [20] showed that for the RWGS reaction on Cu/SiO₂, promotion with potassium can lead to the creation of new active sites at the copper-potassium interface. *Structural* promoters such as Cr or Al are often used to prevent iron from sintering [12], [21].

Two key issues remain unresolved in regard to the WGS and RWGS reaction mechanism(s): *i*) distinction between the 'redox' and 'associative' mechanisms, and *ii*) determination of the structure of the carbon-containing intermediate in the associative

mechanism. The redox and associative models were proposed in 1920 by Armstrong and Hilditch [22], and provided the basis for many of the subsequent investigations with different catalysts [9], [23]-[26]. Temkin and coworkers [27]-[29] proposed that the redox mechanism was active for the WGS reaction on iron catalysts promoted with chromium. In this mechanism, the catalyst is first reduced by adsorbed H_2 (or CO in WGS), and is subsequently oxidized by CO₂ (or H₂O in WGS) to complete the redox cycle. A distinguishing feature of the redox mechanism is that the products can be generated in the absence of either reactant (as in a reactant switching-type experiment). The associative mechanism is a Langmuir-Hinshelwood (LMHW) type mechanism, and was suggested by Oki and coworkers to be the dominant mechanism for the WGS reaction on iron oxide catalysts [30], [31]. In this mechanism, both reactants must be adsorbed on the catalyst surface at the same time to create products. A number of carbon-containing intermediates have been proposed for the associative mechanisms, the most frequently suggested being a formate species [32]. Other suggested intermediates include carbonate [33], carbonyl [34], and carboxyl [35] species.

In this report it is shown that iron supported on alumina is a highly selective catalyst for the RWGS reaction at temperatures between 723 K and 753 K. It is also shown that the specific rate (per gram of material) is enhanced by addition of potassium. While it is not possible to describe the precise role(s) of potassium on a molecular level, it is shown that addition of potassium *i*) enhances reaction rates, *ii*) leads to formation of stable carbon-containing surface species, and *iii*) changes the catalyst behavior during H_2/CO_2 gas switching experiments. It is suggested that the

simple redox and associative mechanisms are insufficient to explain the observations from the gas-switching experiments, and a more complex reaction model is proposed.

7.2 Materials and Methods

7.2.1 Materials

Fe/Al₂O₃ and Fe-K/Al₂O₃ were prepared using the wetness impregnation method described in section 6.3. To recap, gamma alumina (γ -Al₂O₃, Alfa Aesar, 99.97%) was added to an aqueous solution of 0.1 M iron nitrate ($Fe(NO_3)_3$ ·9H₂O, Aldrich, 99.99%), with or without potassium carbonate (K_2CO_3 , Sigma Aldrich, \geq 99.0%), and the mixture was stirred with a magnetic stir bar at room temperature for 1 h. The quantities of metal precursor and γ -Al₂O₃ added to each solution are given in Table 7.1; the final elemental composition of the samples was determined by ICP-OES (Galbraith Laboratories, TN). The suspension was then heated to 353 K to evaporate water, and the resulting slurry was dried in a static oven at a temperature of 383 K for 24 h in air. The dried samples were subsequently calcined in a Thermolyne furnace in air by heating at a rate of 300 K h⁻¹ to 823 K and holding at that temperature for 4 h. Hematite (Fe₂O₃, Aldrich, 99.99%) and iron foil were used as standards for X-ray absorption near edge structure (XANES) experiments. Magnetite (Fe₃O₄, Aldrich, 99.99%) was used as a catalyst. Gases used were: CO₂ (Keen, Grade 5.0), H₂ (Matheson, UHP), helium (Keen, Grade 5.0), Argon (Ar, Keen, Grade 4.8) and D₂ (Cambridge Isotopes, 99.6% gas purity, 99.8% isotope purity). Potassium bromide (KBr, Alfa Aesar, spectroscopy grade) was used as the background in DRIFTS experiments.

Catalyst	Mass Fe Precursor (g)	Mass K Precursor (g)	Mass Al ₂ O ₃ (g)	Nominal Fe Loading (wt%)	Nominal K Loading (wt%)	Actual Fe Loading (wt %)	Actual K Loading (wt%)
1Fe 3K	0.22	0.19	2.75	1.05	3.7	0.9	3.5
4Fe	0.994		2.75	4.8		4.5	-
10Fe	1.99		2.75	9.1		9.1	-
8Fe 3K	1.99	0.243	2.75	8.7	4.3	7.7	3.4
5Fe 1K	1.50	0.10	2.75	6.9	1.9	6.7	2.3
4Fe 4K	0.994	0.243	2.75	4.5	4.6	4.2	3.4

Table 7.1. Catalyst precursor amounts, nominal weight loadings, and actual weight loadings.

7.2.2 Analytical

X-Ray Diffraction (XRD) patterns of catalyst powders were collected at room temperature on a Philips X'pert diffractometer using Cu K α radiation ($\lambda = 1.5418$ Å). Measurements were taken over the range 5° < 2 θ < 80° with a step size of 0.02° and a count time of 2 s at each step. Physisorption of N₂ was performed using a Micromeritics 3Flex instrument at a temperature of 77 K. The Brunauer–Emmett– Teller (BET) surface area was calculated from data points at relative pressures (p/p₀) between 0.05 and 0.25. Before adsorption, samples were degassed under vacuum (P < 150 mTorr) for 8 h at a temperature of 573 K. An Auriga 60 high resolution focused ion beam and scanning electron microscope (SEM) was used to collect SEM micrographs and energy-dispersive X-ray (EDX) spectra to provide information regarding sample morphology and elemental composition, respectively. The microscope was operated at an accelerating voltage of 3-10 kV and a current of 10 μ A.

7.2.3 Temperature Programmed Reduction (TPR)

Temperature programmed reduction (TPR) is a characterization technique used to identify the reduction conditions for catalyst samples. A gas stream containing H_2 is fed to an oxidized catalyst sample, and the temperature is slowly increased at a steady ramp rate, typically between 1K min⁻¹ and 10 K min⁻¹. The metal sites of the catalyst are reduced at certain temperatures, and H_2 is consumed. A thermal conductivity detector (TCD) measures changes in the thermal conductivity of the gas stream. The TCD signal in the TPR spectrum indicates the temperature at which a reduction occurs and the quantity of H_2 that is consumed during the reduction.

In this investigation, TPR was performed on the Fe/Al₂O₃ and Fe-K/Al₂O₃ catalysts using an Altamira 200ip catalyst characterization instrument. First, catalysts were calcined in 10% O₂/He for 2 h at 773 K. The TPR reactor was then cooled to room temperature. Catalysts were heated under a gas flow of 10% H₂/He from room temperature to 1073 K at a heating rate of 5 K min⁻¹.

7.2.4 Temperature Programmed Decarburization (TPDC)

TPDC is a characterization technique to monitor the formation of carbide species on the catalyst surface during a reaction. The RWGS reaction was first performed at 773 K for 2 h under a flow of 50% $CO_2 + 50\%$ H₂. After this time, the reactor was cooled in the presence of the reaction gas mixture. When the reactor reached approximately room temperature, the gas flow was switched to 10% H₂/He, and the reactor was heated at 5 K min⁻¹ to 1273 K. During the heating, m/z signals of 15, 18, and 44 were monitored to track the release of CH₄, H₂O, and CO₂ from the catalyst.

7.2.5 Flow Apparatus Used for Kinetics and Gas-switching Experiments

Reaction rates and selectivities were evaluated using a packed-bed microreactor operated in down-flow mode. Gas flows through the reactor were controlled by mass flow controllers (Brooks Instrument). Catalyst powders were pressed and sieved to obtain particle sizes within the range of 250-425 µm; the catalyst particles were supported on a quartz wool plug within a quartz tube reactor (7 mm I.D.). The quartz tube was placed inside a ceramic radiant full cylinder heater (Omega, CRFC-26/120-A), and the reaction temperature was controlled by an Omega CN/74000 temperature controller using the input from a thermocouple (Omega, Ktype, 1/16 in. diameter) placed around the outside of the quartz tube at the middle of the catalyst bed. Gas transfer lines for the effluent stream were heated to a temperature above 373 K and vented to atmospheric pressure. The composition of the effluent stream was analyzed online either by a gas chromatograph (GC, Agilent, 7890A) during continuous flow experiments or a mass spectrometer (MS, Pfeiffer, GSD320) during gas switching experiments. The GC was equipped with both a thermal conductivity detector (TCD) and a flame-ionization detector (FID). The TCD was used to quantify CO_2 , CO_2 , and H_2 concentrations, and the FID was used to quantify hydrocarbon concentrations. A Hayesep Q column (Agilent, 2 mm ID \times 12 ft) was used in the GC to separate products quantified with the TCD, and a HP-Plot Q column (Agilent, 0.32 mm ID \times 30 m) was used to separate products quantified with the FID.

7.2.6 Measurement of Product Formation Rates

Catalyst samples were pretreated before all experiments in the microreactor by increasing the reactor temperature at a rate of 5 K min⁻¹ to 773 K in a gas flow containing 10 kPa H₂. After being held at 773 K for 2 h, the temperature was lowered to the initial reaction temperature. The total flow rate under all conditions, including pretreatment, was 75 sccm. Helium was used as the balance gas.

Rates of CO formation were calculated assuming differential reactor operation according to Eq. 7.1:
$$r_{CO} = \frac{\dot{V}\Delta C_{CO}}{m_{cat.}} \tag{7.1}$$

In Eq. 7.1, \dot{V} is the total volumetric flow rate (L h⁻¹), ΔC_{CO} is the change in CO concentration (mmol L⁻¹), and $m_{cat.}$ is the catalyst mass (g). Measured reaction rates are the net rate of the forward and reverse reactions; therefore, the observed rate must be transformed into the reaction rate for the forward reaction by using Eqs. 7.2-7.4. The equilibrium constant (K_C) is low (< 1) for the RWGS at the temperatures investigated, although the reverse reaction had a negligible contribution to the observed rates because of the low conversion (< 10%) under conditions at which the reactor was operated. Note that C_o (Eq. 7.4) represents the standard state (1 mol L⁻¹) and equals 1 since the reaction is equimolar.

$$r_{obs.} = r_{+} - r_{-} = r_{+}(1 - \eta) \tag{7.2}$$

$$\eta = \frac{[CO][H_2O]}{K_C[CO_2][H_2]} \tag{7.3}$$

$$K_C = \left(\prod_i C_{i_{eq.}}^{\gamma}\right) \frac{1}{C_o} \tag{7.4}$$

Experiments were designed to *i*) determine reaction rates in excess (i.e. nonequimolar) CO₂ or H₂, and *ii*) determine apparent kinetic parameters. In the first case, CO₂ and H₂ were fed to the catalyst—4.5% Fe/Al₂O₃ (43 mg) or 4.2% Fe - 3.4% K/Al₂O₃ (23 mg)—with the reactor temperature held at 753 K. The initial partial pressure of both CO₂ and H₂ was 15 kPa. After a break-in period of 15 h, the partial pressure of CO₂ was increased to 60 kPa, while the partial pressure of H₂ was held at 15 kPa. After another period of 3 h, the partial pressure of CO₂ was decreased to 15 kPa and the partial pressure of H₂ was increased to 60 kPa. Finally, both partial pressures were returned to 15 kPa. CO₂ conversion was quantified under the same conditions on a sample of magnetite (100 mg) and γ -Al₂O₃ (98 mg), but only with CO₂ and H₂ partial pressures of 15 kPa.

For the second case, kinetic parameters were determined with equimolar or near equimolar concentrations of CO₂ and H₂ on both 4.5% Fe/Al₂O₃ (45 mg) and 4.2% Fe – 3.4% K/Al₂O₃ (22 mg), and under large H₂ excess on 4.5% Fe/Al₂O₃ (42 mg) and 4.2% Fe - 3.4% K/Al₂O₃ (23 mg). With equimolar or near equimolar concentrations of CO₂ and H₂, the reaction was first performed for 15-16 h at a temperature of 753 K with reactant partial pressures of 15 kPa. The temperature was then lowered in 10 K increments to 723 K, with 5-6 GC injections (a period of about 60 min) taken at each temperature. After the period at 723 K, the CO₂ partial pressure was reduced to 10 kPa and increased in 2.5 kPa increments to a final partial pressure of 20 kPa. Finally, the CO₂ partial pressure was returned to 15 kPa and the H₂ partial pressure was lowered to 10 kPa and increased in 2.5 kPa increments. The basic outline of experiments conducted with excess H_2 was the same as that used for near equimolar reactant concentrations. Reactant partial pressures during the initial period were 90 kPa H₂ and 10 kPa CO₂. During the variable CO₂ partial pressure period, the H₂ partial pressure was 85 kPa and the CO_2 partial pressure was varied between 5 and 12.5 kPa in 2.5 kPa increments. To investigate the effect of H₂ partial pressure, the CO₂ partial pressure was kept at 10 kPa and the H₂ partial pressure was varied between 70-90 kPa in 5 kPa increments. At the end of the experiments, and several times during the middle of the experiments, reaction parameters were returned to a condition that had already been tested to determine if deactivation had occurred.

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The kinetic isotope effect (KIE) of H_2/D_2 was investigated on 4.5% Fe/Al₂O₃ (42 mg) and 4.2% Fe – 3.4% K/Al₂O₃ (24 mg). After pretreatment, the reaction began at a temperature of 753 K with CO₂ and H₂ partial pressures of 15 kPa. After 16 h, the temperature was lowered to 723 K and, after 1.5 h, H₂ in the feed was replaced by D₂.

7.2.7 Measurement of Reaction Rates with Intermittent CO₂ and H₂ Flows

CO formation rates were measured while alternating between CO₂ and H₂ gas flows. Catalysts were pretreated as described in Section 7.2.6, with a minor difference being the gas flow rates, which were 36 sccm helium and 4 sccm H₂. After pretreatment, H₂ flow was stopped and was replaced by 4 sccm of CO₂. After 20 min, CO₂ in the gas stream was replaced by H₂. This sequence was repeated three times. The reactor was then purged with helium for 20 min before CO₂ was readmitted to the gas stream. After 20 min, the reactor was again purged with helium before H₂ was readmitted to the gas stream. All sequences with a given gas composition lasted for 20 min, and the temperature of the reactor was held at 773 K throughout the duration of the gas switching portion of the experiment. The hydrodynamic behavior of the gas flow during the transient experiments was analyzed by switching the flow from 10% H₂/He to 10% CO₂/1% Ar/He. The response time of the inert Ar (m/z = 40) relative to those of the products formed was monitored to ensure that no artifacts were present.

Additional gas-switching experiments involving purge times of varying length with an inert gas were carried out on Fe/Al₂O₃ at 753 K. Following a reduction of the catalyst in 10 kPa H₂ for 2 h at 773 K, 15 kPa CO₂ was admitted to the reactor. After 20 min, CO₂ was replaced by 15 kPa H₂ for 20 min. Then, the reactor was purged with argon for 5 min. This sequence (CO₂ \rightarrow H₂ \rightarrow argon) was repeated several times, but each time the length of the inert purge was increased by 5 min. After the inert purge reached 20 min, the cycle was repeated a final time with a 5 min inert purge to monitor any effects from catalyst deactivation.

7.2.8 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) Measurements

Infrared spectra were collected with a Nicolet Nexus 470 spectrometer equipped with a mercury cadmium telluride (MCT) detector. A Praying Mantis accessory (Harrick Scientific) was used in conjunction with a HVC-VUV environmental chamber (Harrick Scientific) to collect diffuse reflectance spectra. Catalyst powder was held in the chamber on top of a wire mesh screen, and gases were delivered to the chamber by mass flow controllers. Potassium bromide was heated in the chamber to a temperature of 723 K under helium flow and used to collect the background spectrum. Potassium bromide was also used to dilute catalyst samples in a mass ratio of 8:1. Catalysts were pretreated by heating from room temperature to 773 K at a rate of 5 K min⁻¹ and holding at that temperature for 2 h in a flow of 30 sccm helium and 10 sccm H₂. The reactant gas in the feed was then switched between H₂ and CO₂ two times, in 30 min intervals, for a total of two periods in CO₂ flow. After the final period in CO₂ flow, the chamber was purged with helium. Infrared spectra presented are the average of 128 scans collected with a resolution of 2 cm⁻¹.

7.2.9 X-ray Absorption Near-Edge Structure (XANES) Spectroscopy

X-ray absorption spectroscopy (XAS) is a spectroscopic technique used to probe the geometric and electronic structures of materials. X-rays generated by a synchrotron are sent to interact with the atoms from the sample. As Figure 7.1 depicts, the incoming x-ray photons are of energy necessary to displace a K (1s) photoelectron

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from the core shell, which excites the atom and results in a core-level hole. To stabilize the atom, an outer shell electron drops down to the inner shell, and in the process emits X-rays which are characteristic of the element.



Figure 7.1. Illustration of electronic transitions for X-ray absorption.

X-rays of varying energies are directed at the sample, which generates an absorbance spectrum as shown in Figure 7.2. The spectrum consists of two parts: (1) X-ray absorption near edge structure (XANES) and (2) extended X-ray absorption fine structure (EXAFS). The large absorption edge in the XANES region results from the absorption of X-rays by the core 1s electrons. The location of the edge is related to the oxidation state of the element, with absorptions for lower oxidation states occurring at lower energies. Atoms with higher oxidation states require greater energy to excite the core electrons, because there are few electrons present and the nucleus can hold onto them tighter. Based on the location of the edge in the XANES spectrum, the average oxidation state of the material can be quantified. The oscillatory structure at higher energies in Figure 7.2 is the EXAFS region, and provides information about the atom's coordination environment.



Figure 7.2. Illustration of the XANES and EXAFS regions of the XAS spectrum.

XANES spectra were collected at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory on beamline X18A. Spectra of iron standards with known oxidation states (hematite and metallic iron) were collected after placing the materials on Kapton tape. *In situ* experiments were performed using the apparatus previously described by Paredis et al [36]. About 15 mg of catalyst was used in all experiments.

In situ experiments were performed after an initial reduction. During the experiments, gas flows consisted of either *i*) a continuous equimolar mixture of CO_2 and H_2 , or *ii*) alternating flows of CO_2 and H_2 . For continuous flow experiments, the temperature was increased from room temperature to 823 K under a gas flow consisting of 5 sccm H_2 and 5 sccm He. After a period of time in which the iron was

almost completely reduced to Fe^{2+} (see below), helium in the feed was replaced by CO_2 . For experiments in which the flow was alternated between CO_2 and H_2 , the temperature was increased to 773 K under a gas flow of 2 sccm H_2 and 8 sccm helium and held at that temperature until the iron was almost completely reduced to Fe^{2+} . Then, the catalyst was purged for 15 min with helium, and 2 sccm of CO_2 was added to the feed. The reactor was then purged with helium for another 15 min before 2 sccm of H_2 was added to the feed.

XANES data were analysed using the Athena extension of IFEFFIT software. All spectra were normalized by adjusting the pre- and post-edge line parameters in Athena so the regression lines passed through the middle of the data in their respective regions. Iron oxidation states and Fe³⁺/Fe_{tot} ratios were estimated by linearcombination fitting (LCF) analysis, assuming that the collected data are linear combinations of Fe²⁺ and Fe³⁺. The edge energies (E_o) for Fe⁰ and Fe³⁺ were determined from the standard materials to be 7111.9 eV and 7123.5 eV, respectively. These values correspond to the energies with the maximum first derivatives, and provide a linear relation that relates the oxidation state of iron to the edge energy in the spectrum. Then, the edge energies of spectra collected during the *in situ* measurements were determined and fit to the linear relation to quantify the amounts of Fe²⁺ and Fe³⁺ present in the samples.

7.3 Results

7.3.1 Elemental Composition and Dispersion of Iron in Supported Catalysts

Table 7.2 summarizes the elemental compositions and surface areas of catalyst samples. Iron loadings were between 0.9 and 9.1%, and were within 10% of their nominal values (see Table 7.1).

Material	Fe (wt%) ^a	K (wt%) ^a	Surface Area (m ² g ⁻¹) ^b
1Fe 3K	0.9	3.5	69.7
4Fe	4.5	-	79.0
10Fe	9.1	-	76.1
8Fe 3K	7.7	3.4	65.1
5Fe 1K	6.7	2.3	68.3
4Fe 4K	4.2	3.4	60.5
γ-Al ₂ O ₃	-	-	77.4

Table 7.2. Iron and potassium composition, and surface area, of catalyst samples.

^a Determined from elemental analysis (ICP-OES, Galbraith Laboratories)

^b Brauner-Emmett-Teller (BET) surface area from N₂ adsorption isotherm

^c All iron-containing materials supported on γ-Al₂O₃

The surface areas of all supported iron samples were 60-80 m² g⁻¹, with most samples having a surface area slightly below that of γ -Al₂O₃. In general, increasing potassium loading led to a reduction in surface area. A representative N₂ adsorption isotherm is shown in Figure 7.3.



Figure 7.3. N_2 adsorption isotherm for 10% Fe – 2.5% K/Al₂O₃.

Elemental mapping images (Figures 7.4 and 7.5) revealed a uniform distribution of iron and potassium, consistent with the absence of bulk iron diffraction peaks in the XRD patterns.



Figure 7.4. Elemental mapping images of 4.5% Fe/Al₂O₃. Iron highlighted (green, top left), oxygen highlighted (yellow, top right), and regular SEM image (bottom).



Figure 7.5. Elemental mapping images of 4.2% Fe - 3.4% K/Al₂O₃. Regular SEM image (top left), oxygen highlighted (yellow, top right), potassium highlighted (red, bottom right), and iron highlighted (green, bottom right).

7.3.2 TPR and TPDC of Fe/Al₂O₃ and Fe-K/Al₂O₃

TPR profiles for Fe/Al₂O₃ and Fe-K/Al₂O₃ are shown in Figure 7.6. Fe/Al₂O₃ shows a major reduction peak at 683 K, while Fe-K/Al₂O₃ shows a major reduction peak at 703 K. Additionally, the intensity of the reduction peak for Fe-K/Al₂O₃ is much greater than the peak for Fe/Al₂O₃, which likely indicates that a greater fraction of Fe is able to be reduced at lower temperatures with the addition of potassium. The reductions occur at temperatures below those of reaction conditions. Consequently, the iron should be in a reduced state (Fe²⁺) at the start of the reaction. There are additional

minor reduction peaks at 821 K and 983 K for Fe/Al_2O_3 and 844 K and 1051 K for Fe-K/Al_2O_3 which indicate the presence of additional iron species.



Figure 7.6. TPR profiles for Fe/Al₂O₃ and Fe-K/Al₂O₃.

Figures 7.7-7.9 show profiles for m/z signals of 15, 44, and 18 as a function of temperature during the TPDC experiments on Fe-K/Al₂O₃ and Fe/Al₂O₃. Figure 7.7 indicates that methane is released at 625°C and 849°C from Fe/Al₂O₃ and at 772°C from Fe-K/Al₂O₃, and confirms that carbides do form on these materials. However, the intensities of the methane peaks are very low, and thus only very small amounts of carbide are forming.



Figure 7.7. CH₄ (m/z = 15) desorption profiles during TPDC on Fe-K/Al₂O₃ and Fe/Al₂O₃.

Figure 7.8 shows that significant amounts of CO₂ were also released during the TPDC experiments. The CO₂ capacity appears to increase with the addition of potassium, as the peak intensity of CO₂ released from Fe-K/Al₂O₃ is much greater than that released from Fe/Al₂O₃. Additionally, CO₂ appears to be more strongly bound to Fe-K/Al₂O₃, as the desorption bands occur at much higher temperatures.



Figure 7.8. CO_2 (m/z = 44) desorption profiles during TPDC on Fe-K/Al₂O₃ and Fe/Al₂O₃.

Figure 7.9 shows that water is also released during the TPDC experiments. The amounts of water released from both materials are similar, and occur at nearly the same temperatures. The production of water indicates that that materials were oxidized during the reaction, and became re-reduced during the flow of H_2 .



Figure 7.9. H_2O (m/z = 18) desorption profiles during TPDC on Fe-K/Al₂O₃ and Fe/Al₂O₃.

7.3.3 Reaction Rates and Stability of Fe/Al₂O₃, Fe-K/Al₂O₃, and Bulk Iron Oxide

Bare γ -Al₂O₃ catalyzed CO formation with a rate of 3 mmol h⁻¹ g⁻¹, lower than the rates on all other samples by at least an order of magnitude (Figure 7.10). Bulk iron was loaded as magnetite (Fe₃O₄) and, after a short induction period, produced CO at a steady rate of 30 mmol h⁻¹ g⁻¹, which was the lowest specific rate on any of the iron-containing materials. The selectivity to CO on all of the materials under equimolar CO₂ and H₂ was always greater than 99%, with methane being the only minor side product. 4.5% Fe/Al₂O₃ catalyzed formation of CO with an initial rate of 50 mmol h⁻¹ g⁻¹, higher than the rate on bulk iron, but this sample deactivated at a nearly linear rate of 0.48 $\frac{\text{mmol h}^{-1}\text{g}_{cat.}^{-1}}{\text{h}}$. The initial rate of CO formation on 4.2% Fe –

3.4% K/Al₂O₃ was 140 mmol h⁻¹ g⁻¹, which is much higher than the rate on both bulk iron and 4.5% Fe/Al₂O₃, but deactivation occurred at an initial rate of 3.96 $\frac{\text{mmol }h^{-1}g_{\text{cat.}}^{-1}}{h}$ before gradually decreasing to 1.2 $\frac{\text{mmol }h^{-1}g_{\text{cat.}}^{-1}}{h}$.



Figure 7.10. CO formation rates on bulk Fe (loaded as magnetite), 4.5% Fe/Al₂O₃, and 4.2% Fe -3.4% K/Al₂O₃ at partial pressures of CO₂ and H₂ indicated in the legend. Other reaction conditions: T = 753 K, $F_{tot.} = 75$ sccm.

After an initial 800 min break-in period at a temperature of 753 K, both supported catalysts operated without further deactivation when the temperature was lowered by 30 K under nearly equimolar CO₂ and H₂ partial pressures (Figure 7.11). This was determined by measuring the CO formation rate at the very end of the experiment under the same conditions used during the break in period. Rates collected in the middle of the experiment, during which gas flow rates and temperatures were changed (lowered), were used to determine reaction orders and activation energies. Because the CO formation rate measured after the series of gas flow rate and temperature changes was the same as before the changes, the kinetic parameters extracted from the rate measurements are not corrupted by deactivation.

As shown in Figure 7.10, when the gas composition was changed to 60 kPa of CO₂ and 15 kPa of H₂, the rate of CO formation increased on both catalysts. The rate of deactivation on 4.5% Fe/Al₂O₃ increased to 2.58 $\frac{\text{mmol }h^{-1}g_{cat}^{-1}}{h}$ but remained linear. The 4.2% Fe - 3.4% K/Al₂O₃ catalyst also continued to deactivate under excess CO₂, but showed an exponential deactivation profile. When the gas composition was changed to 15 kPa CO₂ and 60 kPa H₂, the CO formation rate increased on both catalysts. The rate on 4.5% Fe/Al₂O₃ increased steadily with time on stream, whereas the rate on 4.2% Fe – 3.4% K/Al₂O₃ first increased rapidly to a maximum of 222 mmol g⁻¹ h⁻¹, exhibited stable activity for approximately 80 min, and then began to slowly deactivate at a rate of 1.5 $\frac{\text{mmol }h^{-1}g_{\text{cat.}}^{-1}}{h}$. The selectivity to CO decreased to 95% under excess H₂ on the 4.5% Fe/Al₂O₃ catalyst, with CH₄ being the main side product. On 4.2% Fe – 3.4% K/Al₂O₃, the selectivity to CO remained greater than 99% under excess H₂. Returning the gas composition to 15 kPa CO₂ and 15 kPa H₂ resulted in an initial rate of 116.8 mmol g^{-1} h⁻¹ on Fe-K/Al₂O₃ (compared to 103.6 mmol g^{-1} h⁻¹ observed at the end of the first period of flowing this gas composition). The rate decreased to 102.5 mmol g⁻¹ h⁻¹ over the course of one hour. Over Fe/Al₂O₃, returning the gas composition to 15 kPa of CO₂ and 15 kPa of H₂ resulted in a rate of 45.2 mmol $g^{-1} h^{-1}$ (compared to 43.7 mmol $g^{-1} h^{-1}$ observed at the end of the first period of flowing

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this gas composition), and the catalyst showed no deactivation over the course of one hour.



Figure 7.11. CO formation rates on 4.2% Fe -3.4% K/Al₂O₃ (top) and 4.5% Fe/Al₂O₃ (bottom) during experiments in which kinetic parameters were determined with near equimolar concentrations of CO₂ and H₂ in the feed. Temperatures are indicated in the figure, and the partial pressures of CO₂ and H₂ were 15 kPa.

7.3.4 Kinetics

After the initial break-in period, reaction rates on both catalysts were stable at a temperature of 723 K. This allowed for the determination of kinetic parameters without having to model the deactivation profiles. Table 7.3 summarizes these data at near equimolar concentrations of CO₂ and H₂ on 4.5% Fe/Al₂O₃ and 4.2% Fe – 3.4% K/Al₂O₃, and in large H₂ excess on 4.5% Fe/Al₂O₃.

Catalyst	Emeas (kJ mol ⁻¹)	Order in CO ₂	Order in H ₂		
~Equimolar CO_2 and H_2					
4.8% Fe/Al ₂ O ₃	46	0.37	0.58		
$4.5\%~Fe - 4.5\%~K/Al_2O_3$	69	0.21	0.54		
Excess H ₂					
4.8% Fe/Al ₂ O ₃	52	0.87	0.01		
$4.5\% \ Fe-4.5\% \ K/Al_2O_3$	23	0.65	0.53		

Table 7.3. Activation energies (E_{meas}) and reaction orders with respect to CO₂ and H₂.

Arrhenius plots are shown in Figure 7.12. Under near equimolar CO₂ and H₂ composition, the reaction order with respect to H₂ was nearly the same on both catalysts (0.58 and 0.54 on Fe/Al₂O₃ and Fe-K/Al₂O₃, respectively). In contrast, the reaction order with respect to CO₂ on 4.2% Fe – 3.4% K/Al₂O₃ was nearly half the order of that on 4.5% Fe/Al₂O₃ (0.37 and 0.21 on Fe/Al₂O₃ and Fe-K/Al₂O₃, respectively). Under excess H₂, the reaction rate on Fe/Al₂O₃ was nearly first order with respect to CO₂ and was independent of H₂ pressure. The activation energy increased by 6 kJ mol⁻¹ with respect to the value determined at equimolar concentrations of CO₂ and H₂. In contrast, the rate on Fe-K/Al₂O₃ under excess H₂ depended on the concentrations of both reactants (CO₂ reaction order = 0.65, H₂

reaction order = 0.53), and the activation energy of 23 kJ mol⁻¹ was significantly lower than the value of 69 kJ mol⁻¹ determined under equimolar CO₂ and H₂.



Figure 7.12. Arrhenius plots from conversion of CO₂ on 4.5% Fe/Al₂O₃ and 4.2% Fe - 3.4% K/Al₂O₃. Reaction conditions: T = 723-753 K, $P_{CO2} = 15$ kPa, $P_{H2} = 15$ kPa, $F_{tot} = 75$ sccm.

7.3.5 Kinetic Isotope Effect (KIE)

The reaction rate on 4.5% Fe/Al₂O₃ was considerably higher under CO₂/D₂ flow compared to CO₂/H₂ flow, indicating the occurrence of an *inverse* KIE (the average value of $r_{\rm H}/r_{\rm D}$ was ~0.65, see Figure 7.13). In contrast, the reaction rate on 4.2% Fe – 3.4% K/Al₂O₃ under CO₂/D₂ flow and CO₂/H₂ flow were nearly identical, with an average $r_{\rm H}/r_{\rm D}$ value of 1.03.



Figure 7.13. CO formation rates on 4.5% Fe/Al₂O₃ and 4.2% Fe – 3.4% K/Al₂O₃ while flowing H₂ (red circles) or D₂ (blue circles). Reaction conditions: T = 723 K, P_{CO2} = 15 kPa, P_{H2} or P_{D2} = 15 kPa, F_{tot.} = 75 sccm.

7.3.6 Gas-Switching Experiments

CO and H₂O were the main products formed during gas-switching experiments. On 4.5% Fe/Al₂O₃, CO was formed only when switching from H₂ to CO₂, whereas H₂O was formed when switching from H₂ to CO₂ and when switching from CO₂ to H₂ (Figure 7.14). However, when the catalyst was purged with helium before switching from H₂ to CO₂, water was not formed, even though CO was produced. The figure also shows that following the switch from H₂ to CO₂, which led to the formation of both products, the CO formation was observed slightly earlier than the H₂O formation.



Figure 7.14. Ion current at m/z = 18 (H₂O) and 28 (CO) during H₂/CO₂ switching experiments on 4.5% Fe/Al₂O₃ (top) and 4.2% Fe – 3.4% K/Al₂O₃ (bottom). Arrows with a label indicate a change in gas composition to the indicated gas. The catalysts were reduced in flowing H₂ for 2 h before the first admission of CO₂. Reaction conditions: T = 773 K, F_{He} = 36 sccm, F_{H2} or F_{CO2} = 4 sccm.

The potassium promoted catalyst showed a number of different properties in the gas-switching experiment (Figure 7.14). First, CO was produced when switching from CO₂ to H₂. Additionally, after flowing H₂ and purging the reactor with He, water was produced upon admission of CO₂. Concurrent with water formation, H₂ was observed as determined from the mass spectrometer signal at m/z = 2 (Figure 7.15).



Figure 7.15. Ion current at m/z = 2 (H₂), 18 (H₂O), and 28 (CO) during H₂/CO₂ switching experiments on 4.2% Fe – 3.4% K/Al₂O₃. Arrows with a label indicate a change in gas composition to the indicated gas. Reaction conditions: T = 773 K, F_{He} = 36 sccm, F_{H2} or F_{CO2} = 4 sccm. The figure is a modification of Figure 7.14.

The hydrodynamic behavior of the system was monitored by switching the gas flow from 10% H₂/He to 10% CO₂/1% Ar/He (Figure 7.16). The transient response curve of Ar (m/z = 40) appeared much faster compared to response curves of CO₂ (m/z = 44, 28) and CO (m/z = 28), indicating that the hydrodynamic behavior of the gas flow in the system did not affect our ability to accurately detect a kinetic response upon the gas switch [37]. It should also be noted that GC data collected during the gas-switching experiments verified the observations seen with the MS (results not shown), although only the MS data are presented because of the higher time resolution. The CO₂ contribution to the m/z = 28 signal was accounted for in order to identify the production of CO.



Figure 7.16. Transient response curves for Ar (m/z = 40), CO₂ (m/z = 28, 44), CO (m/z = 28), and H₂O (m/z = 18) during gas switching experiments over Fe-K/Al₂O₃. Gas flow was switched from 10% H₂/He to 10% CO₂/1% Ar/He. Reaction conditions: T = 773 K, total flow rate = 40 sccm.

7.3.7 DRIFTS

Infrared spectra of the 9.1% Fe/Al₂O₃ and 7.7% Fe – 3.4% K/Al₂O₃ catalysts after pretreatment in H₂ showed only weak absorption bands (Figure 7.17). In the spectra of both materials, a small band at 3550 cm⁻¹ was visible, and on 7.7% Fe – 3.4% K/Al₂O₃, additional minor bands at 1379 and 1538 cm⁻¹ were also visible. The overall reflectance of the reduced materials increased dramatically after admission of CO₂, which is consistent with the change in color of the materials from dark grey to orange.



Figure 7.17. Diffuse reflectance infrared spectra collected *in situ* of 10Fe (top) and 10Fe5K (bottom). The catalysts were pretreated at a temperature of 723 K for 2 h in flowing H_2 , exposed to flowing CO₂ for 30 min, and reduced again in flowing H_2 .

The spectrum of 9.1% Fe/Al₂O₃ in Figure 7.17 shows bands at 3550-3750 cm⁻¹ from gas phase CO₂, and minor inflections at 1308 cm⁻¹ and 1595 cm⁻¹. On 7.7% Fe – 3.4% K/Al₂O₃, several new and intense bands formed at 1343, 1568, 2613, and 2904 cm⁻¹ after admission of CO₂ (the band at 1343 cm⁻¹ has a shoulder on the high energy side). The change in intensity of the bands during the course of a 30 min purge with inert gas was small (Figure 7.18). The IR spectra were collected at 723 K, since results from the packed-bed reactor experiments indicated that the materials are stable at this temperature (see Figure 7.11). Additionally, note that the actual bed temperature in commercial *in situ* spectroscopic environmental chambers, such as the one used in this work, is below the set point [38], [39]. Thus, it is highly unlikely that there were any changes to the materials caused by deactivation during the course of the DRIFTS experiments.



Figure 7.18. Diffuse reflectance infrared spectra collected *in situ* of 7.7% Fe - 3.4% K/Al₂O₃ after 30 min of CO₂ flow (purple) and after purging the chamber for 30 min with helium. The temperature was 723 K.

7.3.8 XANES Spectroscopy

XANES spectra were acquired during H_2/CO_2 gas switching experiments on 4.5% Fe/Al₂O₃ and 4.2% Fe – 3.4% K/Al₂O₃. The XANES spectra for the Fe-K/Al₂O₃ catalyst are shown in Figure 7.19. Before pretreatment, the position of the absorption edge energy and pre-edge energy were 7123 and 7114.5 eV, respectively. During heating under flow of H₂, the absorption edge energy shifted to 7119.5 eV by the time a temperature of almost 773 K was reached, and remained at that energy for the duration of the period in H₂ flow. When H₂ was replaced by CO₂, the position of the absorption edge energy shifted immediately to 7122.2 eV. The fraction of Fe³⁺, determined from a linear combination fitting analysis, was ~0.85 during pretreatment up to a temperature of nearly 773 K; at 773 K, no Fe³⁺ was observed within the detection limits of the technique. When CO₂ was admitted, the fraction of Fe³⁺

increased rapidly to ~0.65. Additionally, the existence of two isosbestic points at 7132 and 7143 eV indicates a transformation between the oxidized and reduced iron phases.



Figure 7.19. XANES spectra collected *in situ* (left) during a gas switching experiment on 4.2% Fe – 3.4% K/Al₂O₃ and fraction of Fe³⁺ (right) over the duration of the experiment. The catalyst was pretreated in H₂, and the H₂ flow was then stopped while CO₂ was added simultaneously. The catalyst was then re-reduced in H₂ after the period in CO₂. Reaction conditions: $T_{rxn} = 773$ K, P_{CO2} or $P_{H2} = 20$ kPa, $F_{tot} = 10$ sccm.

Analogous experiments with 4.5% Fe/Al₂O₃ showed that the reduction and

oxidation of the catalyst was both qualitatively and quantitatively the same as the

4.2% Fe - 3.4% K/Al_2O_3 catalyst (Figure 7.20).



Figure 7.20. XANES spectra collected *in situ* (left) during a gas switching experiment on 4.5% Fe/Al₂O₃ and fraction of Fe³⁺ (right) over the duration of the experiment. The catalyst was pretreated in H₂, and the H₂ flow was then stopped while CO₂ was added simultaneously. The catalyst was then re-reduced in H₂ after the period in CO₂. $T_{rxn} = 773$ K, P_{CO2} or P_{H2} = 20 kPa, F_{tot} = 10 sccm.

XANES spectra of 4.2% Fe – 3.4% K/Al₂O₃ collected during continuous flow of equimolar CO₂/H₂ are shown in Figure 7.21. Fe³⁺ was not detected after the initial pretreatment, but upon introduction of CO₂ the fraction of Fe³⁺ increased with time on stream until a steady value of Fe³⁺/Fe_{tot.} = 0.08 was reached. Changes in the XANES spectra can be seen both in the position of the absorption edge energy and of the white line; the absorption edge energy shifted slightly to higher energies upon admission of CO₂, and the intensity of the white line decreased. Isosbestic points at 7132 eV and 7143 eV appeared as they did during the XANES switching experiments, indicating again that the iron is converting between the oxidized and reduced states.



Figure 7.21. XANES spectra collected before and during flow of CO₂/H₂ on 4.2% Fe -3.4% K/Al₂O₃ (left) and fraction of Fe³⁺ determined form XANES spectra over the duration of the experiment (right). T_{rxn} = 823 K, F_{tot} = 10 sccm.

A different behavior was noted with 4.5% Fe/Al₂O₃ (Figure 7.22); with this catalyst, the position of the absorption edge energy did not change upon admission of CO₂, and the fraction of Fe³⁺ remained ~0 during the period of time during which CO₂ was fed.



Figure 7.22. XANES spectra collected before and during flow of CO_2/H_2 on 4.5% Fe/Al₂O₃ (left) and fraction of Fe³⁺ determined form XANES spectra over the duration of the experiment (right). T_{rxn} = 823 K, F_{tot} = 10 sccm.

Table 7.4 compares key properties and results of the Fe/Al₂O₃ and Fe-K/Al₂O₃ catalysts, and clearly shows that major differences exist between the two materials for nearly every experiment. Most significant are the inverse KIE observed on Fe/Al₂O₃ but no KIE observed on Fe-K/Al₂O₃, the observation of stable surface intermediates on Fe-K/Al₂O₃ but not on Fe/Al₂O₃, differences in kinetic parameters, and the production of H₂O on Fe/Al₂O₃ during the gas switch from H₂ to CO₂, but the production of CO and H₂O on Fe-K/Al₂O₃ during the same gas switch.

Experiment	Fe/Al ₂ O ₃	Fe-K/Al ₂ O ₃
KIE $(r_{\rm H}/r_{\rm D})$	0.65	1.03
Gas-switching (CO ₂ \rightarrow H ₂)	CO and H ₂ O produced	CO and H ₂ O produced
Gas-switching (H ₂ \rightarrow CO ₂)	H ₂ O produced	CO and H ₂ O produced
DRIFTS	No intermediate	Stable intermediate(s)
CO ₂ Reaction Order (~equimolar inlet)	0.37	0.21
H ₂ Reaction Order (~equimolar inlet)	0.58	0.54
E _{meas.} (kJ mol ⁻¹)	46	69
Ea ovidation state (standy state VANES)	~2	~2, with slow
re oxidation state (steady-state AANES)		oxidation

Table 7.4. Summary of experimental results on Fe/Al₂O₃ and Fe-K/Al₂O₃ catalysts.

7.4 Discussion

7.4.1 Stable Surface Species on Fe-K/Al₂O₃

Experiments in which gas flows were alternated between H₂ and CO₂ on 4.2% Fe – 3.4% K/Al₂O₃ (Figure 7.14) suggest that stable surface species form when the reduced catalyst is contacted with CO₂. After reduction in H₂ and upon admission of CO₂, CO and H₂O were produced. However, CO was also produced when H₂ was readmitted, even after an intermediate purge with helium. Thus, a stable carbon-containing intermediate must form during the period in CO₂ flow; the intermediate does not desorb or react in helium, and H₂ is required to decompose the intermediate and form products. It is possible that the CO released during the switch from CO₂ to H₂ on Fe-K/Al₂O₃ could result from the preferential adsorption of H₂ on iron, which causes desorption of CO from iron. However, no evidence was observed of adsorbed CO on Fe-K/Al₂O₃ or Fe-K/Al₂O₃ during the DRIFTS measurements. CO typically shows strong IR absorption bands around 2100 cm⁻¹ and 1830-1880 cm⁻¹ [40], but none of these bands were observed in our spectra. Additionally, the bond dissociation energies for Fe-CO complexes range from 145-274 kJ mol⁻¹ [41], while the bond

dissociation energy for Fe-H is 162 kJ mol⁻¹ [42]. The difference between these bond dissociation energy values indicate that the Fe-CO bond tends to be stronger than the Fe-H bond, and therefore CO will not likely desorb because of the introduction of H₂. In contrast to the potassium promoted sample, the 4.5% Fe/Al₂O₃ catalyst did not release CO upon switching gas flows from CO₂ to H₂, suggesting that stable intermediates do not form on this material.

DRIFTS spectra verified that observed stable intermediates form only on the catalyst containing potassium. After pretreatment in H₂, the maximum intensity across the IR spectrum decreased to ~50% on both materials (see Figure 7.17), a change consistent with the change in sample color from orange to grey and the reduction of Fe³⁺ to Fe²⁺, as also seen in the XANES spectra. Although the Fe/Al₂O₃ catalyst was oxidized by CO₂, as indicated by the overall increase in reflectance of the material and its change in color from grey to orange, only weak absorption bands were observed around 1308 cm⁻¹ and 1595 cm⁻¹. In contrast, when Fe-K/Al₂O₃ was contacted with CO₂, intense absorption bands formed that disappeared very slowly when CO₂ was removed from the gas stream (Figure 7.18). The formation of intense absorption bands on Fe-K/Al₂O₃, but not on Fe/Al₂O₃, are in agreement with the results from the gas-switching experiments and confirm the presence of a stable, carbon-containing surface species on the Fe-K/Al₂O₃ material.

The most intense bands on Fe-K/Al₂O₃ were observed at 1343 cm⁻¹ and 1568 cm⁻¹. A smaller band at 2904 cm⁻¹ is likely from the *v*CH vibration of a formate. The intense bands at 1300-1600 cm⁻¹ appear to be the superposition of bands from several different species. When the catalyst was purged with helium, two bands at 1651 cm⁻¹ and 1292 cm⁻¹ (identified from a difference plot of the spectra, see Figure 7.18) slowly

disappear, while the majority of the absorbing species remained unchanged. A shoulder at about 1380 cm⁻¹ is also visible, and might be paired with the band at 1550 cm⁻¹, both of which did not completely disappear after re-reduction in H₂. It is likely that the remainder of the band intensity comes from another species, with band centers around 1343 cm⁻¹ and 1568 cm⁻¹.

This analysis indicates that there are probably at least three surface species on the Fe-K/Al₂O₃ material, one of which is a formate. The formate ion exhibits characteristic IR vibrations at 1555 cm⁻¹ (asymm v_{CO}), 1376 cm⁻¹ (δ_{CH}), and 1348 cm⁻¹ (symm v_{CO}) on α -Fe₂O₃ [43]; IR bands were observed at 1568 cm⁻¹ and 1380 cm⁻¹ here and, together with the band at 2904 cm⁻¹, strongly suggest that formate is present on the catalyst surface. Other possible surface species that can form during exposure to CO₂/H₂ include bicarbonate, carboxylate, and carbonate. Carboxylates show IR vibrations at 1560 cm⁻¹ and 1340 cm⁻¹ on iron-oxide materials [43]. The bands we observed at 1550 cm⁻¹ and 1343 cm⁻¹ agree well with these previous assignments, and indicate that carboxylates may also form on the Fe-K/Al₂O₃ material. The bands at 1651 cm⁻¹ and 1292 cm⁻¹, which disappear during the helium purge, could potentially be assigned to bicarbonate (1655-1615 cm⁻¹ [asym v_{CO}], 1400-1370 cm⁻¹ [symm v_{CO}], 1300 cm⁻¹ [δ_{OH}]), carboxylate (1660-1560 cm⁻¹[v_{CO}]), or bidentate carbonate (1730-1660 cm⁻¹ and 1270-1230 cm⁻¹ on Al₂O₃) species, based on assignments from the literature [43].

IR bands in the 3600-3800 cm⁻¹ region of the spectra, which are associated with surface hydroxyl (–OH) groups, were not observed for the catalysts (see Figure 7.17). This is peculiar, as typically these bands appear very strongly in IR spectra. For instance, IR spectra of bare Al_2O_3 did reveal IR bands associated with –OH groups

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(spectra not shown). Thus, the observation of undetectable –OH groups for the catalyst samples is not an artifact, and suggests that the incorporation of iron and potassium into the sample has an effect on these groups.

7.4.2 Redox and Associative Pathways on Fe/Al₂O₃ and Fe-K/Al₂O₃

The associative pathway has often been proposed as the dominant mechanism for WGS [44]-[48]. However, in a recent review Burch et al. [49] concluded that the associative pathway typically accounts for less than 10-15% of the overall WGS reaction rate [50]-[52] and that formates are often only spectator species [38], [53]. The authors found that the associative pathway [49] can be dominant on low-activity materials such as MgO [44] and 0.2% Rh/CeO₂ [45], but that the vast majority of investigations in which an associative pathway was said to be dominant lacked the quantitative data necessary to validate the claim [46]-[48]. Steady-state isotopic transient kinetic analysis (SSITKA) and other advanced operando techniques have been applied to provide molecular-level insight on site coverage and reactivity of adsorbed reaction intermediates. SSITKA is often coupled with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and mass spectrometry (MS) to elucidate reaction mechanisms and differentiate between active reaction intermediates and spectator species, and has been applied in several instances to study the WGS and RWGS reactions. In a study of the RWGS reaction on 10% Cu/SiO₂, Yang et al. [54] used ¹²C/¹³C isotopic transient analysis with MS and IR to simultaneously measure the site coverage and residence time of adsorbed formate species. Their results showed that the formate removal rate was two orders of magnitude greater than the catalytic RWGS reaction rate, and thus the reaction has no influence on the formate surface
coverage. Using SSITKA-DRIFTS-MS, Burch and co-workers [34, 55] showed that surface carbonates were exchanged significantly faster than formates on 2% Pt/CeO₂, and thus formates observed by IR were actually not a major reaction intermediate. Finally, in a study of the WGS reaction on 2% Pt/CeO₂, Kalamaras et al. [56] used SSITKA-DRIFTS and SSITKA-MS to show that formates present on the catalyst could not be considered important reaction intermediates, and proposed that a redox mechanism is dominant relative to the associative mechanism.

Gas-switching experiments in which flows of H_2 and CO_2 are alternated (Figure 7.14) were used here to distinguish and quantify contributions from redox and associative pathways [57]. CO formation when the reduced form of both Fe/Al₂O₃ and Fe-K/Al₂O₃ catalysts are contacted with CO₂—even after the reduced catalysts were purged with helium to ensure the absence of H_2 — is evidence of a redox pathway. In the simplest form of the redox mechanism, gas-phase CO₂ adsorbs on a reduced site to form CO and an oxidized site (Eq. 7.5) which can then be re-reduced by gas phase H_2 to reform the reduced site (Eq. 7.6).

$$CO_2(g) + s_{red.} \rightarrow CO(g) + 0 \cdot s$$
 (7.5)

$$H_2 + 0 \cdot s \to H_2 O(g) + s_{red.} \tag{7.6}$$

During the gas-switching experiments, H₂O was produced during flows of only CO₂ or only H₂. This differs from what is expected in the traditional redox cycle (Eqs. 7.5 and 7.6), in which H₂O is only produced during the H₂ feeding period. Table 7.5 presents estimated initial rates of CO production on Fe-K/Al₂O₃ during each segment of the gas-switching experiments. The rate after the switch from H₂ to CO₂ can

tentatively be attributed to the rate from a redox reaction pathway, while the rate after the switch from CO_2 to H_2 can tentatively be attributed to the rate from an associative reaction pathway. The rates were calculated from the initial slopes of the concentration vs. time data in Figure 7.14, essentially modeling the system as a batch reactor (Eq. 7.7).

Material	Period	Rate after H ₂ → CO ₂ gas switch (µmol L ⁻¹ s ⁻¹ g _{cat.} ⁻¹)	Rate after $CO_2 \rightarrow H_2$ gas switch (µmol L ⁻¹ s ⁻¹ $g_{cat.}^{-1}$)	$(H_2 \rightarrow CO_2 Rate)/(CO_2 \rightarrow H_2 Rate) Ratio$
Fe/Al ₂ O ₃	1 st CO ₂	1.48		
	$2^{nd} \operatorname{CO}_2$	1.24		
	$3^{rd} CO_2$	1.15		
	4 th CO ₂ (after He purge)	0.47		
Fe- K/Al ₂ O ₃	1 st CO ₂	0.43	0.28	1.53
	$2^{nd} \operatorname{CO}_2$	1.07	0.26	4.19
	$3^{rd} CO_2$	1.48	0.26	5.63
	4 th CO ₂ (after He purge)	2.31	0.11	21.5
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Table 7.5. Estimated initial rates of CO production by redox and associative reactions during gas-switching experiments.

$$\frac{dc_A}{dt} = r_A \tag{7.7}$$

It is observed (Table 7.5) that the rates after the switch from CO_2 to H_2 decreased with each cycle, while the redox rates on Fe-K/Al₂O₃ increased with each cycle (even following the helium purge).

The presence of a stable, carbon-containing surface intermediate on Fe- K/Al_2O_3 , (see Section 7.4.1) may be evidence of an associative pathway. Apparently, potassium allows for a new reaction pathway to CO that involves a stable

intermediate. In the associative pathway, described generally by Eq. 7.8, CO_2 and H_2 adsorb on the catalyst surface to form a carbon-containing intermediate (i.e. formate, carbonate, or bicarbonate), which then decomposes in the presence of H_2 to form CO and H_2O .

$$CO_2(g) + H_2(g) \to CO_2 \cdot s + 2H \cdot s \to CO \cdot s + H_2O \cdot s$$
(7.8)

In summary, CO formed upon switching from H_2 to CO_2 is evidence supporting the redox mechanism, while the CO formed upon switching from CO_2 to H_2 is evidence in support of the associative mechanism. Both the redox and associative reaction pathways appear to contribute to the overall RWGS rate on Fe-K/Al₂O₃, while only the redox pathway is active on Fe/Al₂O₃. The ratios of the rates during CO₂ flow to H₂ flow for Fe-K/Al₂O₃ (Table 7.5) indicate that the redox pathway is the dominant contributor to the overall reaction rate.

7.4.3 Kinetics Parameters and Formulation of a Kinetic Model on Fe/Al₂O₃

There are few detailed kinetic investigations of the RWGS reaction over Febased catalysts to use as a basis of comparison for the measured kinetic parameters obtained from this study. Osaki et al. [58] reported an apparent activation energy of 78.2 kJ mol⁻¹ on 20% Fe/Al₂O₃, determined in the temperature range of 500-800 K. This value is significantly higher than the 46 kJ mol⁻¹ we obtained on 4.8% Fe/Al₂O₃. The reaction orders of 0.37 for CO₂ and 0.58 for H₂ obtained on Fe/Al₂O₃ under inlet conditions of 15 kPa CO₂ and 15 kPa H₂ (Table 7.3) appear to follow the power-law rate relation described by Eq. 7.9; that is, reaction orders are not independent. Additionally, under excess H₂ conditions the reaction orders of 0.87 for CO₂ and 0.01 for H₂ also follow this relation.

$$r = k_{app.} [CO_2]^n [H_2]^{1-n}$$
(7.9)

This relation between the reaction orders was also observed by Ginés et al. [59] on a CuO/ZnO/Al₂O₃ catalyst for $P_{H_2}/P_{CO_2} < 3$ (CO₂ order ≈ 0.3 , H₂ order ≈ 0.8), and by Kim et al. [57] on Pt/TiO₂ (CO₂ order = 0.831, H₂ order = 0.201) and Pt/Al₂O₃ catalysts (CO₂ order = 0.323, H₂ order = 0.702). The reaction orders of 0.21 for CO₂ and 0.54 for H₂ observed on the Fe-K/Al₂O₃ catalyst (15 kPa CO₂ and 15 kPa H₂, Table 7.3) do not obey the rate law of Eq. 7.9. Osaki et al. [58] observed reaction orders of 1.10 or CO₂ and 0.37 for H₂ on a 20% Fe/Al₂O₃ catalyst, indicating a stronger dependence on CO_2 partial pressure compared to H_2 pressure; this was the opposite from what we observed with our materials. Perhaps the secondary pathway on the Fe-K/Al₂O₃ catalyst has a lower or zero reaction order for CO₂ that leads to a lower observed reaction order compared to Fe/Al₂O₃ (or the amount of iron affects the reaction orders). Potassium is known to increase the adsorption capacity of CO₂ because of its basicity, which results in a much greater adsorption enthalpy. Evidence for the higher CO_2 adsorption capacity of Fe-K/Al₂O₃ relative to Fe/Al₂O₃ was seen by its ability to form carbon-containing intermediates in the absence of CO₂ during the DRIFTS and gas-switching experiments. The higher CO_2 coverage that results would lower the dependence of the reaction on the gas-phase concentration of CO₂.

As shown in Table 7.3, the activation energy $(E_{meas.})$ for the reaction on Fe-K/Al₂O₃ (69 kJ mol⁻¹) is significantly greater than that on Fe/Al₂O₃ (46 kJ mol⁻¹), even though Fe-K/Al₂O₃ showed higher catalytic activity. This is surprising, as normally the reaction rate increases with a decrease in the activation energy. The higher rate on Fe-K/Al₂O₃, despite its greater $E_{\text{meas.}}$, indicates that the pre-exponential factor is quite large in this case. According to Transition State Theory, a large pre-exponential factor indicates a slightly negative or even positive entropy of formation of the transition state (ΔS^{\ddagger}), and is characteristic of monomolecular reactions [60]. A monomolecular RDS typically involves the dissociation of a 'loose' activated complex; in this reaction it would likely involve C-O bond breaking. In contrast, the lower reaction rates observed on Fe/Al₂O₃ in spite of a lower $E_{\text{meas.}}$ indicate that the RDS is likely bimolecular and possibly involves C-H bond forming. As such, the ΔS^{\ddagger} will be much more negative for this reaction pathway, resulting in a smaller pre-exponential factor that reduces the rate constant [60].

We observed an inverse KIE on Fe/Al₂O₃, with a r_H/r_D ratio of ~0.65; this value is nearly the inverse of the typical r_H/r_D ratio of ~1.4 for a normal H/D KIE. Inverse H/D KIEs are typically secondary isotope effects that involve a change in bond hybridization, and result from a RDS involving C-H bond formation instead of C-H bond breaking [61]. An inverse KIE suggests that the activation energy decreases when D₂ is used instead of H₂, and that C-D bond formation is lower in energy compared to C-H bond formation. Therefore, the RDS for the reaction on Fe/Al₂O₃ seems to involve a hydrogen addition reaction, although it cannot be ascertained whether it is H addition to C or O; the expected value of the inverse KIE should be about the same for both. In general, isotope effects are such that $k_H/k_D > 1$ and $K_H/K_D < 1$, and therefore a switch from H₂ to D₂ would affect both of these ratios in opposite directions, leading to the possibility of a normal, inverse, or negligible isotope effect depending on the relative magnitudes of change for these two ratios [62]. The inverse KIE observed on Fe/Al₂O₃ suggests then that the *equilibrium* isotope effects are

dominant relative to the kinetic isotope effects, as the isotopic substitution changes the equilibrium of certain elementary steps.

In contrast, switching from H₂ to D₂ on Fe-K/Al₂O₃ had very little effect on the CO formation rate, as the $r_{\rm H}/r_{\rm D}$ ratio was observed to be 1.03. The absence of a significant KIE on Fe-K/Al₂O₃ indicates that the RDS does not involve the bond breaking or forming with H, implying that the incorporation of potassium into the catalyst alters the RDS of the reaction mechanism.

The gas-switching experiments with CO_2 and H_2 led us to conclude that a redox pathway is active on both Fe/Al₂O₃ and Fe-K/Al₂O₃ (see above). Based on this result, an initial model for the reaction pathway for both catalysts is given in Scheme 7.1. The mechanism shown is a classical redox pathway that includes steps for CO_2 adsorption, CO desorption, and H₂O desorption.

Scheme 7.1. Redox reaction pathway for CO formation.

1) $CO_2(g) + s \longrightarrow CO_2 \cdot s$ 2) $CO_2 \cdot s + s \longrightarrow CO \cdot s + O \cdot s$ 3) $CO \cdot s \longrightarrow CO(g) + s$ 4) $H_2(g) + O \cdot s \longrightarrow H_2O \cdot s$ 5) $H_2O \cdot s \longrightarrow H_2O(g) + s$

Using formation of CO on the surface (step 2) as the rate-determining step (RDS), a rate expression can be derived for formation of CO in the gas phase at differential conversion (Eq. 7.10).

$$r = \frac{k_2 K_1(P_{CO_2})}{\left(1 + K_1(P_{CO_2})\right)^2} \tag{7.10}$$

However, the rate expression in Eq. 7.10 does not show a dependence on the partial pressure of gas-phase H₂; that is, it is inconsistent with the experimentally determined reaction orders. Additionally the expression incorrectly predicts a negative reaction order with respect to CO_2 at high coverage. To incorporate H₂ into the rate expression, a 6th step can be included to allow for competitive adsorption by H₂, but the resulting rate expression still does not show a positive reaction order with respect to H₂ (Eq. 7.11).

$$r = \frac{k_2 K_1(P_{CO_2})}{\left(1 + K_1(P_{CO_2}) + K_6(P_{H_2})\right)^2}$$
(7.11)

The reaction pathway thus proposed in Scheme 7.1 (with and without the inclusion of competitive adsorption by H_2) is insufficient to properly model CO formation rates on either catalyst, as it does not agree qualitatively with the kinetics measurements.

Considering the inverse KIE that was observed on Fe/Al₂O₃, a different reaction mechanism can be proposed in which C-H bond forming is the RDS (Scheme 7.2). The model depicted in Scheme 7.2 is an associative mechanism involving the reaction of adsorbed CO₂ with dissociated H₂ to form a surface intermediate (step 4), which subsequently desorbs as CO (g) and H₂O (g) (step 3). This reaction scheme also incorporates competitive adsorption by H₂ (step 1) and H₂ dissociation on the surface (step 2). **Scheme 7.2.** Associative reaction pathway for CO formation based on the observation of an inverse KIE.

1)
$$H_2(g) + s \longrightarrow H_2 \cdot s$$

2) $H_2(s) + s \longrightarrow H \cdot s + H \cdot s$
3) $CO_2(g) + s \longrightarrow CO_2 \cdot s$
4) $H \cdot s + CO_2 \cdot s \longrightarrow COOH \cdot s + s$
5) $COOH \cdot s + H \cdot s \longrightarrow CO(g) + H_2O(g) + s + s$

Evidence for H_2 dissociation (step 2 in Scheme 7.2) was observed when H_2/D_2 mixtures were fed to the catalyst in either the presence or absence of CO₂ (Figure 7.23).



Figure 7.23. Ion current at m/z = 2 (H₂), 3 (HD), 4 (D₂), and 28 (CO) during flow of 7.5 kPa H₂, 7.5 kPa H₂ + 7.5 kPa D₂, and 7.5 kPa H₂ + 7.5 kPa D₂ + 15 kPa CO₂ on Fe/Al₂O₃. Arrows with a label indicate a change in gas composition to the indicated gas. Reaction conditions: T = 753 K, F_{tot} = 75 sccm.

HD formation was observed to occur quickly (on the same time scale as chemical conversion of CO_2 to CO), indicating that H_2 dissociation is reversible and not rate limiting. The intermediate formed in step 4 of Scheme 7.2 should not be observable by *in situ* IR spectroscopy because, by definition, its formation is *rate limiting* and it rapidly decomposes (recall that such intermediates were not observed on Fe/Al₂O₃ catalysts). The rate equation for CO formation according to Scheme 7.2 is presented in Eq. 7.12, assuming that step 4 is the RDS and that conversion levels are low.

$$r = \frac{k_4(K_1)^{1/2}(K_2)^{1/2}(K_3)(P_{CO_2})(P_{H_2})^{1/2}}{\left[1 + (K_1)^{1/2}(K_2)^{1/2}(P_{H_2})^{1/2} + K_1(P_{H_2}) + K_3(P_{CO_2})\right]^2}$$
(7.12)

Eq. 7.12 has both CO_2 and H_2 terms in the numerator, agreeing with the experimental results in which positive reaction orders were observed for both of the reactants. The fit of this equation is good for both catalysts (Table 7.6), with the only exception being that the fitted reaction orders for H_2 differ from the experimentally determined values (Figures 7.24-26).



Figure 7.24. Comparison of experimental and fitted data using kinetic models obtained from Scheme 7.2 on Fe/Al₂O₃ and Fe-K/Al₂O₃ as a function of temperature. Rate expressions used were Eq. 7.12 (Step 4 = RDS) or Eq. 7.13 (Step 5 = RDS).



Figure 7.25. Comparison of experimental and fitted data using kinetic models obtained from Scheme 7.2 on Fe/Al₂O₃ and Fe-K/Al₂O₃ as a function of CO₂ partial pressure. Rate expressions used were Eq. 7.12 (Step 4 = RDS) or Eq. 7.13 (Step 5 = RDS).



Figure 7.26. Comparison of experimental and fitted data using kinetic models obtained from Scheme 7.2 on Fe/Al₂O₃ and Fe-K/Al₂O₃ as a function of H₂ partial pressure. Rate expressions used were Eq. 7.12 (Step 4 =RDS) or Eq. 7.13 (Step 5 =RDS).

Table 7.6 shows that the H₂ reaction orders on Fe/Al₂O₃ and Fe-K/Al₂O₃ are 0.58 and 0.54, respectively, while the H₂ reaction orders fitted from the model are 0.50 for both catalysts. Note that the rate constant in the rate expression derived when step 4 of Scheme 7.2 is the RDS (Eq. 7.12) is a product of the elementary rate constant for step 4 (k_4) and the equilibrium constants of steps 1-3 (K_1 , K_2 , K_3). Equilibrium isotope effects are typically less than 1 [62], and therefore these terms are the likely cause of the inverse KIE that was observed experimentally. Only K_1 or K_2 can be the cause of the inverse KIE, though, since these steps involve H₂.

Material		Ea (kJ mol ⁻¹)	Order in CO2	Order in H2
	Experimental	46	0.37	0.58
Fe/Al ₂ O ₃	Fitted (Step 4 RDS)	46	0.37	0.50
	Fitted (Step 5 RDS)	45	0.38	0.59
	Experimental	69	0.21	0.54
Fe-K/Al ₂ O ₃	Fitted (Step 4 RDS)	70	0.22	0.50
	Fitted (Step 5 RDS)	71	0.22	0.98

Table 7.6. Measured and fitted kinetic parameters on 4.5% Fe/Al₂O₃ and 4.2% Fe – 3.4% K/Al₂O₃ using the associative reaction pathway illustrated in Scheme 7.2.

It is also possible that step 5 of Scheme 7.2 (decomposition of the surface intermediate) is the RDS on Fe-K/Al₂O₃, since stable carbon-containing intermediates were observed on this catalyst during the IR experiments. In this case, the rate expression shown in Eq. 7.13 is obtained.

$$r = \frac{k_5 K_1 K_2 K_3 K_4 (P_{CO_2})(P_{H_2})}{\left[1 + K_1 (P_{H_2}) + K_3 (P_{CO_2}) + (K_1)^{1/2} (K_2)^{1/2} (P_{H_2})^{1/2} + (K_1)^{1/2} (K_2)^{1/2} K_3 K_4 (P_{H_2})^{1/2}\right]^2}$$
(7.13)

It is unlikely that Step 5 is the RDS on Fe/Al₂O₃, since no carbon-containing intermediates were observed during the IR experiments; nonetheless, an attempt was made to fit the experimental data to the rate expression in Eq. 7.13 for this scenario. As Table 7.6 shows, the assumption that Step 5 is the RDS results in a better fit with the experimental data for Fe/Al₂O₃, as opposed to the case when step 4 was assumed to be the RDS and the H₂ reaction orders did not match well. The assumption of Step 5 as the RDS for the reaction on Fe-K/Al₂O₃ results in poor agreement between the fitted (0.98) and experimentally determined (0.54) reaction orders for H₂.

7.4.4 Evidence for a Redox-type Reaction Mechanism Involving a 'Hydrogen Pool' on Fe/Al₂O₃

The model depicted in Scheme 7.2 is consistent with the results from the KIE experiment on Fe/Al₂O₃, as well as part of the results from the gas-switching experiments (sections 7.3.6 and 7.4.2), in which only CO₂ (g) was required to form CO as according to the redox mechanism. However, the model in Scheme 7.2 is an associative mechanism, and is therefore inconsistent with the observed redox pathway determined by the gas-switching experiments to be the only working pathway on this catalyst. Likewise, although evidence from the gas-switching and DRIFTS experiments indicated that an associative pathway may occur on $Fe-K/Al_2O_3$ in addition to the redox pathway, its contribution, as quantified by the gas-switching experiments, was less than 40% of the overall reaction rate (Table 7.5), indicating that it is only a secondary pathway. Therefore, it is expected that a kinetic model derived from a redox reaction mechanism, which is the dominant pathway, should provide a better fit to the experimental data compared to an associative model. Consequently, a different model is proposed (Scheme 7.3). This model only addresses the reaction mechanism on Fe/Al₂O₃, because incorporation of potassium results in possibly two parallel reaction pathways; quantification of the kinetics of these processes is outside the scope of this thesis. The model for the reaction on Fe/Al₂O₃ is based on the idea that a 'hydrogen pool' exists within the catalyst; this pool is supplied continuously by dissociation of H₂ and provides the source of hydrogen atoms for H₂O produced during flow of CO₂ in gas-switching experiments. Formation of HD during flow of an equimolar gas mixture of H_2/D_2 indicates that dissociated hydrogen atoms (H*) reside on the surface and can inter-exchange to generate the HD (see Figure 7.23). It was found from the data in Figure 7.23 (in the presence of CO_2) that although the HD

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formation was reversible, it was not at equilibrium. That is, H₂ dissociation is a kinetically relevant step in the reaction mechanism. The H* atoms may generate hydroxyl (–OH) groups after they leave the metal site, but no evidence of this reaction was observed during the DRIFTS experiments. It could also be that the –OH groups formed are present in quantities too small to be detected by IR.

The proposed mechanism involving the 'hydrogen pool' is illustrated in Scheme 7.3. In Step 1, H₂ from the gas phase dissociates and forms $-O(H^*)$ — groups with oxygen atoms from the Al₂O₃ support or active iron phase, forming the 'hydrogen pool' on the catalyst. The H* atoms can reduce nearby Fe³⁺ sites, producing water and creating an oxygen vacancy in the process. In step 2, CO₂ travels to an oxygen vacancy located near two Fe²⁺ atoms, donates an oxygen atom to the vacancy thereby oxidizing two Fe²⁺ atoms to Fe³⁺, and leaves as CO. In Step 3, H* atoms from the 'hydrogen pool' migrate to the newly incorporated oxygen atom (O*) to form water and reduce the Fe³⁺ atoms back to Fe²⁺. Step 4 is then a repeat of Step 2, with CO₂ donating an oxygen atom to re-fill the oxygen vacancy and form CO.





Additional gas-switching experiments were performed to corroborate the general aspects of this proposed reaction mechanism (Figures 7.27-7.29). In these experiments, CO_2 was fed for 20 minutes, followed by H₂ for 20 minutes, and then the reactor was purged with argon; this cycle was repeated several times, with the purge time in argon varying each cycle from 5-20 minutes. As observed in the prior gas-switching experiments, CO was only produced for a brief time during the flow of CO_2 (Figure 7.27), because once all of the oxygen vacant sites are filled, CO production cannot continue. The amount of H₂O produced during flow periods of H₂ was consistent between each cycle (Figure 7.28); that is, the adsorbed O* species formed upon CO_2 reduction are stable at these reaction conditions. However, the amount of

 H_2O produced during the period of CO_2 flow decreased as the purge time in argon increased. After only a 5 min purge, the amount of H_2O produced during the period of CO_2 flow was much greater than that produced following a 20 min purge in argon. A 5 min purge in argon repeated at the end of the experiment confirmed that the decreased signal for H_2O production was caused by the increased purge time, and not by catalyst deactivation. Presumably, H* atoms from the catalyst surface desorb (as H_2) during the argon purge. This appears to be a slow process, because even following a 20 min purge, there were enough H* atoms on the sample to form small amounts of H_2O when CO_2 was administered.



Figure 7.27. Ion current at m/z = 28 (CO) during H_2/CO_2 switching experiments on Fe/Al₂O₃. Arrows with a label indicate a change in gas composition to the indicated gas. The catalysts were reduced in flowing H₂ for 2 h before the first admission of CO₂. Reaction conditions: T = 753 K, F_{tot} = 75 sccm, 15 kPa H₂ or 15 kPa CO₂.



Figure 7.28. Ion current at m/z = 18 (H₂O) during H₂/CO₂ experiments on Fe/Al₂O₃. Arrows with a label indicate a change in gas composition to the indicated gas. The catalysts were reduced in flowing H₂ for 2 h before the first admission of CO₂. Reaction conditions: T = 753 K, F_{tot} = 75 sccm, 15 kPa H₂ or 15 kPa CO₂.



Figure 7.29. Ion current at m/z = 2 (H₂) during H₂/CO₂ experiments on Fe/Al₂O₃. Arrows with a label indicate a change in gas composition to the indicated gas. The catalysts were reduced in flowing H₂ for 2 h before the first admission of CO₂. Reaction conditions: T = 753 K, F_{tot} = 75 sccm, 15 kPa H₂ or 15 kPa CO₂.

It was also observed during CO_2 flow that H_2 was released from the catalyst (Figure 7.29). As was the case for the H_2O signal, the amount of released H_2 decreased monotonically as the purge time in argon increased prior to CO_2 introduction. This suggests that CO_2 forces dissociated H* atoms in the 'hydrogen pool' to re-combine and desorb as H_2 , while other H* atoms are simultaneously involved in attacking the oxidized Fe sites to produce H_2O and re-form the oxygen vacancies.

7.5 Conclusions

Packed-bed reactor studies indicate that incorporation of potassium into the Fe/Al₂O₃ catalyst resulted in a significant increase (~3 times) in the CO formation rate. Fe/Al₂O₃ and Fe-K/Al₂O₃ slowly deactivated under conditions of excess CO₂. Excess H₂ resulted in stable catalytic activity. Reaction rates depended more strongly on H₂ (orders 0.58 and 0.54 for Fe/Al₂O₃ and Fe-K/Al₂O₃, respectively) compared to CO₂ (orders 0.37 and 0.21 for Fe/Al₂O₃ and Fe-K/Al₂O₃, respectively) under near equimolar gas-phase composition. Gas-switching experiments on Fe/Al₂O₃ revealed that CO was formed only when switching from H₂ to CO₂, whereas H₂O was formed when switching from H_2 to CO_2 and when switching from CO_2 to H_2 . The results of the gas-switching experiments on Fe/Al₂O₃ suggest that a redox mechanism is active, since the order in which the reactants are adsorbed on the surface affects the products that are observed. On Fe-K/Al₂O₃, both CO and H₂O were produced when switching from H_2 to CO_2 and from CO_2 to H_2 , which suggests that an associative reaction mechanism may also be occurring. Evidence of carbon-containing surface intermediates on Fe-K/Al₂O₃—supporting the occurrence of an associative mechanism—was obtained using DRIFTS spectroscopy. IR bands associated with formate, and possibly carbonate, bicarbonate, and carboxylate, were observed in the presence of CO_2 and H_2 . No such IR bands were observed on the Fe/Al₂O₃ material, in agreement with the results from the gas-switching experiments, in which CO was not produced when switching from CO₂ to H₂. XANES spectra collected in situ showed that nearly all of the iron was reduced to Fe^{2+} under H₂ flow. In contrast, the majority of the iron is oxidized to Fe³⁺ under flow of CO₂. Under steady-state flow of an equimolar CO₂/H₂ gas mixture, the Fe atoms in Fe-K/Al₂O₃ slowly oxidized to Fe³⁺, while those in Fe/Al_2O_3 remained in a reduced state (Fe^{2+}). Isotope switching

experiments with H₂ and D₂ revealed an inverse KIE effect on Fe/Al₂O₃ ($r_H/r_D = 0.65$), but no KIE effect on Fe-K/Al₂O₃ ($r_{\rm H}/r_{\rm D} = 1.03$). The observed inverse KIE suggests that the RDS for the mechanism on Fe/Al₂O₃ involves hydrogen addition, while that on Fe-K/Al₂O₃ does not. It was also observed that H₂ dissociation and association occurs on the catalysts, as evidenced by the formation of HD under flow mixtures of H₂ and D₂. The H₂ dissociation leads to the formation of a 'pool' of surface H* atoms. Although the experimental evidence suggested that a redox mechanism is the only (on Fe/Al₂O₃) or dominant (on Fe-K/Al₂O₃) mechanism occurring, the rate expression obtained from the proposed redox mechanism (Scheme 7.1) did not show a dependence on H₂ pressure, making it inconsistent with the experimental results in which a clear dependence on H₂ pressure was observed. The associative model provided an excellent fit to the experimental reaction data, but did not explain other experimental results, which strongly suggested a redox mechanism. A third model (Scheme 7.3) is proposed that is based on the observations from the gas-switching experiments and involves a 'hydrogen pool'. This qualitative model illustrates how the reaction may proceed on the Fe/Al₂O₃ catalyst surface.

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Chapter 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Overview

As has been discussed throughout this dissertation, heterogeneous catalysis is an important branch of chemistry that can be applied in many ways to improve quality of life and the environment. In fact, 85-90% of the current chemical production uses catalytic systems to obtain the highest activities and selectivities possible [1]. Major challenges such as synthesizing alternative fuels, reducing harmful emissions to prevent pollution and climate change, producing pharmaceuticals, and creating processes that are safe to humans and the environment can all be addressed using the principles of catalysis. Going forward in the 21st century, it is of critical importance to understand at the atomic level how chemical reactions proceed so as to be able to design better materials which enhance catalytic activity and selectivity. This thesis improved the current molecular understanding of two important heterogeneously catalyzed gas-phase reactions: (1) NO oxidation on microporous materials and (2) the RWGS reaction on Fe/Al₂O₃ and Fe-K/ Al₂O₃. This chapter summarizes the major findings and conclusions from the preceding chapters, addresses unresolved issues, and proposes several possible directions for future research that build upon the work of this dissertation or are related to the chemistries and materials investigated.

8.2 Dissertation Summary

In Chapter 3, the reaction mechanism of catalytic low-temperature (T < 423 K) NO oxidation over several microporous materials (zeolites, MOFs, microporous carbons) was investigated. Reaction rates decreased with increasing temperature in this temperature regime, resulting in negative apparent activation energies (-24.9 kJ) mol^{-1} to -37.5 kJ mol⁻¹). For comparison, the homogeneous reaction only displayed a negative activation energy of -4.4 kJ mol⁻¹. Reactivity on the microporous catalysts was observed to be \sim 2-4 orders of magnitude greater than that for the homogeneous reaction. The activities of the materials at such low reaction temperatures is remarkable, especially since certain samples (siliceous CHA, microporous carbons) do not have any apparent active sites for catalyzing the reaction (per unit of volume). The fast catalytic rates were attributed to the occurrence of a homogeneous-like reaction within the catalyst micropores, in which the $[N_2O_4]^{\ddagger}$ transition state is stabilized by a physical confinement effect. Evidence for this hypothesis was shown by the fact that the catalyzed and homogeneous reactions exhibited the same reaction orders for NO and O₂ (2 and 1, respectively). Moreover, the more negative activation energies observed for the catalyzed reactions do not reflect a change in the reaction mechanisms, but rather a reduction in the energy required to form the transition state as a result of confinement. Transition state theory formalisms indicated very negative enthalpies of formation of the transition states (-33.7 kJ mol⁻¹ to -47.1 kJ mol⁻¹), which are favorable for the reaction to proceed. Additionally, negative entropies of formation (-272.2 J mol⁻¹ K⁻¹ to -304.8 J mol⁻¹ K⁻¹) were observed. These values are a result of the significant difference in entropy between the three reactants in the gas phase and the singular activated complex that forms within the micropores. The catalytic enhancements of the microporous materials indicate, however, that the

enthalpic gains outweigh the entropic losses associated with confinement. The higher activity of Na-SSZ-13 and H-SSZ-13 compared to the other materials indicates that electrostatic effects from extra-framework cations provide additional stabilization of the transition state to further enhance the reaction rate. Finally, the inhibition effect of NO₂ on reaction rates was experimentally investigated and quantitatively assessed using the integral reactor approach and Langmuir-Hinshelwood kinetic models. The presence of NO₂ in the feed stream was shown to negatively affect reaction rates with a reaction order close to -2.

Chapter 4 showed the occurrence of a new reaction regime for NO oxidation at temperatures greater than 423 K. Reaction rates increased with increasing temperature from 423-623 K on H-zeolites and Na-zeolites, but remained low and relatively independent of temperature on siliceous CHA. This observation indicated that zeolite composition plays a more important role in this temperature regime, and that framework aluminum atoms are necessary for activity. The inactivity of the siliceous zeolite indicated that the confinement effect responsible for the activity at low temperatures is no longer substantial at elevated temperatures because of the significant entropic barriers. Additionally, zeolite framework (CHA, MFI, BEA) had a substantial effect on NO oxidation rates, with activity among the acid-form zeolites being inversely proportional to the zeolite pore size. Activation energies scaled in the order of CHA < MFI < BEA. Application of transition state theory showed that the smaller pores provide significantly greater enthalpic stabilization for the activated complex that more than compensate for the large entropic costs. The activated complex at high temperatures was no longer $[N_2O_4]^{\ddagger}$ as it was a low temperatures, since rates were observed to be first order in NO and O₂. The new mechanism

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responsible for activity in this regime was investigated using *in-situ* FTIR spectroscopy. These studies revealed that NO⁺ is the only observable N_xO_y species present in significant concentrations on the alumino-silicate zeolites at high temperatures. Additionally, NO⁺ was not observed to form on the siliceous CHA, which indicated that it may have mechanistic importance since it only formed on the samples that showed activity. We proposed a plausible working model for the formation of NO⁺ at framework aluminum positions within the zeolite pores, and also showed that NO⁺ is in equilibrium with gas-phase NO. NO⁺ can desorb (as NO) from the site to leave behind an oxidized acid site (Si–O•–Al). NO oxidation activity was found to be directly proportional to the amount of NO⁺ present, and we therefore proposed a reaction mechanism for the high-temperature regime that involves NO⁺ as an intermediate. Finally, we identified the most probable rate-determining step that is consistent with the observed reaction ordered and observed reaction intermediates.

Chapter 5 discussed the NO oxidation reaction on Cu-zeolites at temperatures between 523 K and 823 K. Incorporation of copper into the zeolite frameworks resulted in substantially higher activity (by ~1-2 orders of magnitude) compared to the acid zeolites. Cu-ZSM-5 displayed higher rates than Cu-SSZ-13 and Cu-BEA. Additionally, the pretreatment conditions had a substantial effect on the reactivity of the Cu-zeolite samples. For all frameworks (SSZ-13, ZSM-5, BEA), pretreatment in a flow of 1% CO/He led to higher activity compared to pretreatment in 5% O₂/He, 1% NH₃/He, or 500 ppm NO + 500 ppm NH₃. Reaction orders also changed with different pretreatment conditions. Rates on Cu-zeolite samples pretreated in 5% O₂/He were observed to be first order with respect to NO and O₂ concentrations. For pre-reduced samples, the rate dependency on O₂ concentration changed to half order. Over Cu-

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SSZ-13, an investigation of Cu loading on reaction rates showed that rates normalized per gram of catalyst increased dramatically with increasing Cu loading up to ~1 wt%. Cu loadings beyond 1 wt% resulted in only slight increases in the rate. Meanwhile, rates normalized per mol of Cu (turnover frequencies) decreased substantially with increased Cu loading up to ~1 wt%, and were relatively independent of Cu loading at higher levels. UV-vis spectroscopy studies showed that Cu-zeolite samples contained Cu^{2+} following O₂ pretreatment and mostly Cu⁺ following CO pretreatment. DRIFTS spectra collected under *in-situ* conditions showed that different N_xO_y surface species formed depending on the Cu loading of the zeolite. A mechanism for the reaction on Cu-zeolites pretreated in 1% CO/He was presented and discussed.

Chapters 6 and 7 investigated the reverse water-gas shift (RWGS) reaction. This reaction was studied as part of a collaboration with the U.S. Army, and is the first part of a two-step CO₂ hydrogenation strategy to produce fuels from CO₂. Catalyst screening results presented in Chapter 6 showed that Fe/Al₂O₃ and Fe-K/Al₂O₃ catalyze the RWGS reaction with high activity and CO selectivity. Packed-bed reactor studies in Chapter 7 indicated that CO formation rates on Fe-K/Al₂O₃ were ~3 times greater than those on Fe/Al₂O₃. Both catalysts deactivated under equimolar gas compositions, but the rate of deactivation on Fe-K/Al₂O₃ was much greater. Conditions of excess CO₂ caused both catalysts to deactivate much more rapidly, while excess H₂ resulted in stable catalytic activity. Reaction rates depended more strongly on H₂ (orders 0.58 and 0.54 for Fe/Al₂O₃ and Fe-K/Al₂O₃, respectively) compared to CO₂ (orders 0.37 and 0.21 for Fe/Al₂O₃ and Fe-K/Al₂O₃, respectively) under equimolar gas-phase composition. Gas-switching experiments on Fe/Al₂O₃ revealed that CO was formed only when switching from H₂ to CO₂, whereas H₂O was formed when switching from H₂ to CO₂ and when switching from CO₂ to H₂. The results suggested that a redox mechanism is active on Fe/Al₂O₃, since the order in which the reactants are adsorbed on the surface affects the products that are observed. On Fe-K/Al₂O₃, both CO and H₂O were produced when switching from H₂ to CO₂ and from CO₂ to H₂, which suggests that an associative reaction mechanism may also be occurring. Evidence of carbon-containing surface intermediates on Fe-K/Al₂O₃ was obtained using DRIFTS spectroscopy to support the occurrence of an associative mechanism. IR bands associated with formate, and possibly carbonate, bicarbonate, and carboxylate, were observed in the presence of CO₂ and H₂. No such IR bands were observed on the Fe/Al₂O₃ material, in agreement with the results from the gasswitching experiments, in which CO was not produced when switching from CO_2 to H₂. XANES spectra collected *in situ* showed that nearly all of the iron was reduced to Fe^{2+} under H₂ flow. In contrast, the majority of the iron was oxidized to Fe^{3+} under flow of CO₂. Under steady-state flow of an equimolar CO₂/H₂ gas mixture, the Fe atoms in Fe-K/Al₂O₃ slowly oxidized to Fe³⁺, while those in Fe/Al₂O₃ remained in a reduced state (Fe²⁺). Isotope switching experiments with H_2 and D_2 revealed an inverse kinetic isotope effect (KIE) on Fe/Al₂O₃ ($r_{\rm H}/r_{\rm D} = 0.65$), but no KIE effect on Fe-K/Al₂O₃ ($r_{\rm H}/r_{\rm D}$ = 1.03). The observed inverse KIE suggests that the RDS for the mechanism on Fe/Al₂O₃ involves hydrogen addition, while that on Fe-K/Al₂O₃ does not. It was also observed that H₂ dissociation and association occurs on the catalyst, as evidenced by the formation of HD under flow mixtures of H₂ and D₂. This H₂ dissociation leads to the formation of a 'pool' of surface H* atoms. Although the experimental evidence suggested that a redox mechanism was the only (on Fe/Al₂O₃) or dominant (on Fe-K/Al₂O₃) mechanism occurring, the rate expression obtained from

the proposed redox mechanism (Scheme 7.1) did not show a dependence on H₂ pressure, making it inconsistent with the experimental results in which a strong dependence on H₂ pressure was observed. The associative model provided an excellent fit to the experimental reaction data, but did not explain other experimental results, which strongly suggested a redox mechanism. A third model (Scheme 7.3) was proposed that was based on the observations from the gas-switching experiments and also involved a 'hydrogen pool'. This qualitative model illustrates how the reaction may proceed on the Fe/Al₂O₃ catalyst surface.

8.3 Recommendations for Future Work

The studies presented in the preceding chapters have made important inroads towards identifying effective catalysts for the NO oxidation and RWGS reactions and understanding many of the important details regarding the reaction mechanisms. However, the scope of the reactions being studied is immense, and as such many questions still need to be addressed. The following sections of this chapter outline several possible directions for future research based on the findings from this dissertation. Some of the proposed ideas are meant to continue and support the work presented in this thesis, while others are less directly related but nonetheless are in a similar area of research.

8.3.1 Low-temperature NH₃-SCR

Cu-SSZ-13 and Fe-zeolites have proven to be excellent NH_3 -SCR catalysts with high hydrothermal stabilities, and as a result they are used for many industrial applications. However, the major drawback of these materials is that they only operate effectively at temperatures above ~473 K. Figure 8.1 shows NO_x conversion profiles during standard SCR over Cu- and Fe-SSZ-13 catalysts and highlights the poor activity of these materials at low temperatures [2]. For example, the NO_x conversion is only ~25% at 150 °C on Cu-SSZ-13, and it is not until ~200 °C when close to 100% NO_x conversion is achieved. On Fe-SSZ-13, no SCR activity is observed until ~200 °C, and only ~50% conversion is reached at 300 °C. During vehicle startup, when the working temperatures of these catalysts are not yet reached, only low levels of NO_x conversion occur, and thus a significant amount of NO_x emissions are released during this time. Going forward, it is essential that researchers identify catalysts which are effective across the broad temperature range at which stationary and mobile engines operate (298-1,000 K) to further reduce NO_x emissions and comply with increasingly stringent emissions standards. Now that catalysts with high activity and hydrothermal stability have been discovered and implemented commercially, greater efforts must be made by the R&D community in developing effective vehicle emissions control technologies or catalysts for operation in the low-temperature regime. As noted by Beale et al. [3], a third era of emissions control technology is currently emerging to address this concern. Era one was marked by the successful development of the "three-way" catalytic converter, and era two was marked by effective technologies for "lean-NO_x" conditions. Era three now provides the challenge of developing effective technologies that curb emissions at low exhaust temperatures, which will be common in the novel operating modes of future internal combustion engines [4].



Figure 8.1. NO and NH₃ conversions as a function of temperature during standard SCR on fresh Cu- and Fe-SSZ-13 samples [2]. Reproduced with permission from *Catalysis Today* (Elsevier).

It may turn out that, with further improvements, zeolites are capable of catalyzing low-temperature NH₃-SCR. Some preliminary work by Gao and coworkers that was presented in Beale et al. [3] has shown that modifications to the Cu-SSZ-13 lowered the "light-off" temperature (T_{50} , defined as the temperature at which catalytic activity reaches 50% conversion) from 174 °C to as low as 151 °C (Figure 8.2). It has not yet been disclosed as to what modifications were made to the base zeolite. This initial work is promising, although it is still not understood as to why the "light-off" temperature for NH₃-SCR is above 150 °C for state-of-the-art zeolites, and the underlying mechanistic reasons for this must be understood. More fundamental work is also needed on the importance of NO oxidation at low temperatures, as recent results from Yezerts et al. [5] indicate that the NO₂/NO_x ratio is strongly tied to the activity of the low-temperature NH₃-SCR reaction on Fe-SSZ-13. NO oxidation

catalysts that are effective at low temperatures (T < 423 K), such as the ones examined in Chapter 3 of this dissertation, may be particularly valuable in low-temperature SCR scenarios where it is imperative to increase the concentration of NO₂ in order to yield fast SCR conditions.



Figure 8.2. NH₃-SCR performance for Cu-SSZ-13 and a series of catalysts modified using the same Cu-SSZ-13 base catalyst (NH₃ = NO = 350 ppm, H₂O = 2.5%, O₂ = 14%, GHSV = 100,000 h⁻¹) [3]. Reproduced with permission from The Royal Society of Chemistry.

Pore size is another property of SCR catalysts that may need to be examined further to improve low-temperature performance. The small pore sizes of zeolites, in particular SSZ-13, benefit NH₃-SCR activity at high temperatures by preventing hydrocarbon absorption, but may adversely affect the NH₃-SCR activity of the samples at low temperatures. This is because water can readily absorb in the micropores in large amounts as the temperature is lowered. Therefore, the use of mesoporous materials with pores ranging in size from 2-50 nm may offer an advantage for these purposes. Examples of such materials include silica-alumina aerogels or mesoporous zeolites, which should possess comparable acid site densities, pore volumes, and surface areas to zeolites. I propose that a series of silica-alumina aerogels with varying pore sizes should be synthesized and tested for their SCR activities at temperatures less than 423 K. The materials should also have fairly high Si/Al ratios (Si/Al > 30) to minimize undesired water adsorption which may readily occur at lower temperatures. It may be possible that the acid sites present in these aerogels are sufficient to catalyze the reaction, and that metals like Cu and Fe do not need to be incorporated into the materials for the SCR reaction to occur. In fact, it has been documented that even H- and Na-zeolites can catalyze the reaction, though higher temperatures are needed [3]. Richter et al. [6] also showed that NH₄-MOR and NH₄-ZSM-5 were capable of catalyzing the SCR reaction to some degree at temperatures as low as 373 K.

Another class of materials other than zeolites that warrant further investigation for low-temperature NH₃-SCR studies are transition metal oxides and mixed transition metal oxide materials. Several of these materials have already shown some promising results. Kang et al. [7] showed that Cu-Mn mixed oxides exhibited NO_x conversion levels near 100% at 50°C. However, in the presence of SO₂ the conversion decreased significantly to 60% [7]. Long et al. [8] observed that Fe-Mn mixed oxide materials catalyzed 100% NO conversion at 100-180 °C. Additionally, Qi et al. [9] reported that NO_x conversions over MnO_x-CeO₂ catalysts exceeded 95% below 150 °C, and the presence of water and SO₂ only resulted in minor losses in activity. More recently, Zuo et al. [10] showed that Mn-ZrO_x mixed oxides are capable of catalyzing 100%

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NO_x conversion at 100 °C. The materials performed well in the presence of H₂O or SO₂, although activity decreased significantly in the combined presence of these molecules. All of these metal oxide materials display superior activity compared to zeolite catalysts at temperatures below 150 °C. Other mixed metal oxides with combinations of Mg, Ni, Cu, Co, Mn, Ce, or Cr should also be investigated.

8.3.2 Mechanism of NO⁺ Formation at High Temperatures, Characterization of NO⁺ Coordination, and the Use of NO⁺ as a Catalyst in Other Oxidation Reactions

An unresolved issue from the work in Chapter 4 concerns the route of NO^+ formation. The typical formation route for NO^+ at low temperatures is through dimerization of NO_2 to N_2O_4 , followed by heterolytic dissociation at acid sites to form NO^+ and NO_3^- . However, the equilibrium between NO_2 and N_2O_4 highly favors NO_2 at temperatures greater than 350 K, and therefore it is unlikely that N_2O_4 would be present under the conditions tested during our DRIFTS measurements. An alternative mechanism could involve NO and NO_2 , as illustrated in Eqs. 8.1 and 8.2.

$$Z^-H^+ + NO + NO_2 \rightleftharpoons H^+NO_2^- + Z^-NO^+ \rightleftharpoons HNO_2 + Z^-NO^+$$
(8.1)

$$Z^-H^+ + HNO_2 \rightleftharpoons H_2O + Z^-NO^+ \tag{8.2}$$

The mechanism of NO⁺ formation could be investigated using isotopic labeling experiments. For example, using a feed of N¹⁸O and N¹⁶O₂ we should observe the formation of $Z^-N^{18}O^+$ and $Z^-N^{16}O^+$ by the following mechanism:

$$Z^{-}H^{+} + N^{18}O + N^{16}O_{2} \rightleftharpoons H^{+}N^{16}O_{2}^{-} + Z^{-}N^{18}O^{+} \rightleftharpoons HN^{16}O_{2} + Z^{-}N^{18}O^{+}$$
(8.3)

$$Z^{-}H^{+} + HN^{16}O_{2} \rightleftharpoons H_{2}^{-16}O + Z^{-}N^{16}O^{+}$$
(8.4)

Additional isotopic studies using ${}^{16}O_2/{}^{18}O_2$ could be used to further confirm the proposed reaction mechanism from Chapter 4 for NO oxidation on H-SSZ-13 (reshown in Scheme 8.1).

Scheme 8.1. High-temperature reaction mechanism from Chapter 4 for NO oxidation on H-SSZ-13 (T = 423-673 K).

(A)	Z [·] + NO		Z-NO+
(B)	Z ⁻ NO ⁺ + O ₂		Z ⁻ NO ₃ ⁺
(C)	Z ⁻ NO ₃ ⁺ + NO		$Z^{-}NO_{2}^{+} + NO_{2}$
(D)	Z ⁻ NO ₂ ⁺	~	Z + NO ₂

For instance, ¹⁶O₂, ¹⁶O¹⁸O, and ¹⁸O₂ should form according to Eqs. 8.5 and 8.6. An equilibrium distribution of ¹⁶O₂, ¹⁶O¹⁸O, and ¹⁸O₂ should be expected if the reactions are fast. If the reactions are slow, then the forward and reverse rate constants could be determined for step (B) in Scheme 8.1. Additionally, N¹⁶O¹⁸O should be the expected product of the mechanism in Scheme 8.1 if steps (C) and (D) are fast and irreversible. This would provide further evidence that step (B) is the RDS, as was suggested in Chapter 4.

$$N^{16}O^{+} + {}^{18}O_2 \to N^{16}O^{18}O_2^{+} \to N^{18}O^{+} + {}^{18}O^{16}O$$
(8.5)

$$N^{16}O^{+} + {}^{18}O^{16}O \to N^{18}O^{16}O_{2}^{+} \to N^{18}O^{+} + {}^{16}O_{2}$$
(8.6)

It would also be interesting to characterize the NO⁺ site that forms at Brønsted acid sites in H-zeolites. As alluded to in Chapter 4, NO⁺ is likely coordinated to the

zeolite framework via a single oxygen atom based on the presence of an IR band at 952 cm^{-1} , which is attributed to the O_{lattice} -NO⁺ vibration [11]. Neutron powder diffraction experiments and analysis using Rietveld refinement would enable us to accurately refine the geometry of the NO⁺. This should be a relatively straightforward experiment, since SSZ-13 only has one T-atom in the structure. Additionally, at Si/Al ratios of ~6, there is only one Al atom per 6MR, and therefore there are only four oxygen atoms that serve as possible 'sites' where the NO⁺ can coordinate. This structural analysis will provide a well-defined molecular model, which is currently unavailable, that can be used for theoretical investigations using quantum chemical calculations. A detailed knowledge of NO⁺ is required because it may be an important intermediate in NH₃-SCR, since the nitrogen atom of NO⁺ has a formal oxidation state of 3+, which is equal but opposite in sign to that of the nitrogen in ammonium. Nitrite (NO₂⁻) is the only other N_xO_y species with nitrogen in a 3+ formal oxidation state, and is known to be an important intermediate in SCR that leads to N₂ and H₂O.

The unique ability of surface-bound NO⁺ cations formed at aluminum sites on H-zeolites to oxidize NO into NO₂ at high temperatures, which was described in Chapter 4, suggests that the system may be used for other oxidation reactions as well. The oxidation of CO, which is an important reaction in emissions control technology that uses expensive Pt- and Pd-based materials, could easily be investigated to test this hypothesis. To begin, the H-SSZ-13 sample could be 'activated' by using the procedure described in Chapter 4 to form NO⁺. Then, CO and O₂ can be introduced to the system. The oxidizing ability of NO⁺ for other oxidation reactions in addition to the NO oxidation reaction would signify the identification of a novel non-precious

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metal oxidation catalyst, and would offer further support for the proposed reaction mechanism in Chapter 4.

Finally, NO⁺ present in the H-zeolite could be used for the direct nitrosation of aromatic hydrocarbons [12, 13]. Direct nitrosation of methylated benzenes has been studied by Kochi and co-workers [14-16] using the nitrosyl ion salt NO⁺BF₄⁻. The process is illustrated in Scheme 8.2. We could investigate the same reaction using the zeolite-bound NO⁺ cation, which would regenerate the acid site as a result. If successful, this reaction could be used to improve the industrial production of aniline. Currently, aniline is produced from the hydrogenation of nitro-compounds, such as nitrobenzene. However, using a nitroso compound (such as the one shown in Scheme 8.2) in place of a nitro-compound would require less hydrogen and thus lower the production cost.

Scheme 8.2. Direct nitrosation of methylated benzene using nitrosyl ion salt NO⁺BF₄⁻.



8.3.3 NO_x Capture Using Microporous Carbons or Zeolites

We also observed evidence during the bench reactor studies that the microporous carbon materials studied for the NO oxidation reaction (see Chapter 3) may act as effective materials for trapping NO_x. During the reaction of NO and O₂ over the carbons at ambient temperatures, there was an extended period of time (~30)

minutes) before NO₂ was observed to exit the reactor as detected by IR spectroscopy (Figure 8.3). Outlet NO concentrations were also quite low during this initial period. The reaction was presumably occurring during this time of low outlet NO_x concentration, but all of the NO₂ was adsorbing within the pores of the materials. This prolonged period indicates a large amount of NO_x uptake by the materials. After ~30 minutes, the outlet NO₂ concentrations began to increase, but steady-state values were not reached until ~100-150 minutes, depending on the sample. It would be interesting to conduct further studies to examine how the NO_x uptake varies as a function of temperature or gas feed composition. Additionally, studies in which a gas stream of NO or NO₂ is passed over the sample would allow us to precisely quantify the amount of NO_x that these materials are capable of trapping. It is also possible that the zeolite materials, particularly the Na-samples, may be capable of adsorbing large amounts of NO_x at low temperatures, but further tests will need to be carried out. Some evidence for this was already seen in the IR experiments by the large amounts of N₂O₄ detected within the pores of the Na-SSZ-13 sample.



Figure 8.3. NO oxidation rates on microporous carbons. Reaction conditions: 1,000 ppm NO + 5% O_2 , catalyst mass = 100 mg, T = 298 K.

After running the reaction at 298 K, the flow was switched to He, and the sample was heated at a rate of 2 K min⁻¹ to 323 K (Figure 8.4). Large amounts of NO₂ that were trapped within the micropores (likely as N₂O₄) at low temperatures were released upon heating. It is likely that further heating to higher temperatures would have yielded even higher amounts of NO₂ release. Further investigation may show that these materials could be effective for trapping the large amounts of NO_x released during startup or cooler engine conditions. These materials could be placed upstream of the SCR unit, so that after the engine heats up the NO_x is released and passed downstream to the SCR catalyst for conversion to N₂ and H₂O. Pt and Pd loaded on porous supports are already used for similar applications [17]. These porous carbon

materials could present better a better economic option if they are able to exhibit comparable NO_x trapping ability.



Figure 8.4. NO₂ released from Carboxen 569 during heating from 298-323 K.

8.3.4 Miscellaneous Investigations Related to the NO Oxidation Reaction

This section presents several 'loose ends' related to the NO oxidation reaction that could be pursued with further research. First, it would be interesting to explore the abilities of other solid acid catalysts such as metal oxides over alumina, acidic polyoxometalates (i.e., heteropolyacids), or sulphated zirconia for their abilities to catalyze the NO oxidation reaction by a similar mechanism to the one proposed in Chapter 4. Additionally, it would be advisable to investigate whether or not Fe^{III}- or Ga^{III}-containing zeolites can also form NO⁺ and catalyze the reaction. Finally, our kinetic and mechanistic tests of catalyzed NO oxidation were carried out under very ideal conditions. The true effectiveness of the catalytic materials should be tested under more realistic engine conditions by examining the effects of impurities such as H_2O , sulfur (SO_x), CO, and hydrocarbons, which are typically present in fuels or the engine and can have considerable effects on the catalyst over time.

8.3.5 Improving Fe-K/Al₂O₃ Catalyst Performance and Stability for the RWGS Reaction

One of the major issues with the Fe-K/Al₂O₃ catalyst investigated in Chapter 7 is the fact that it slowly deactivates under equimolar gas flow of CO₂ and H₂ and rapidly deactivates under conditions of excess CO₂ at temperatures greater than 773 K. Since higher temperatures are required to increase the conversion of CO₂, it would be beneficial to identify a catalyst that does not require a high H₂/CO₂ ratio in order to exhibit stable activity, since H₂ is expensive and CO₂ is the desired reactant to convert. Addition of lanthanum oxide (La₂O₃) has been shown to help stabilize Al₂O₃ by preventing sintering and loss of surface area at high temperatures [18]. It would be worth investigating if adding lanthanum oxide could improve the stability of the Fe-K/Al₂O₃ catalyst, so that regeneration under conditions of excess H₂ is not necessary.

Additionally, other means of improving the activity or stability of the catalyst could be investigated by further exploring the catalyst composition. It was found that reactivity increased with increasing potassium loading up to 4.5 wt%, and increases in potassium loading beyond 4.5 wt% did not lead to substantial increases in activity or changes in selectivity. The effect of iron loading in potassium-promoted samples could be investigated further as well. The iron loading was investigated for Fe/Al₂O₃ samples and was varied from 1-10 wt%. RWGS activity was observed to increase with

higher amounts of iron within this compositional range, and an intermediate loading of ~4.5 wt% was chosen for investigations with potassium. However, the effect of iron loading in the presence of potassium was not investigated. It is likely that higher Fe loadings could increase activity but simultaneously decrease the stability if increased amounts of H₂O and CO form, which could potentially block the active sites of the catalyst. Deactivation of the catalyst could be linked to the slow oxidation of the iron from Fe²⁺ to Fe³⁺; evidence for this change was observed during the *in-situ* XANES measurements (see Chapter 7). Other promoters such as Cu, Zn, Zr, Mg, or Mn in addition to or in place of potassium would also be interesting to study for their effects on catalyst stability and activity.

8.3.6 Further Mechanistic Studies of the RWGS Reaction Using SSIKTA

As noted in Chapter 7, some inconsistencies arose between the experimental results and the proposed reaction models for the RWGS reaction catalyzed by Fe/Al₂O₃ and Fe-K/Al₂O₃. Much of the experimental work suggested that a redox mechanism was the only or dominant mechanism occurring, but the data agreed quantitatively with the proposed associative reaction mechanism. We did propose a third model, a non-traditional redox mechanism involving a hydrogen pool, which qualitatively agreed with our results, but more work must be done to ensure a quantitative agreement. The use of steady-state isotopic transient kinetic analysis (SSITKA) would aid greatly in being able to further explore the mechanism and confirm the findings presented in Chapter 7. SSITKA combines steady-state and transient techniques in order to obtain valuable information about the catalyst surface and reaction mechanism under realistic, steady-state conditions [19]. Figure 8.3.a illustrates a typical experimental setup. The experimental procedure begins by

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operating under steady-state conditions. Then, an isotopic transient (i.e. $H_2/^{12}CO_2/Ar \rightarrow H_2/^{13}CO_2/Kr$) is suddenly introduced, and the transient responses are monitored by MS. The inert gas is also altered during this switch to monitor the gas hold-up. Figure 8.3.b shows typical normalized transient curves for the decaying (P) and increasing (P*) responses of the products obtained after reaction of the unlabeled (R) and labeled (R*) reactants [20]. SSITKA also allows for the measurement of the average surface residence time (τ) and quantification of the most reactive surface intermediates that are converted into products [19].



Figure 8.5. a) Typical SSITKA experimental setup. b) Normalized transient curve for decaying response of the unlabeled product (P) including the inert response (I) and the increasing response of the labeled product (P*). c) Normalized transient response for decaying response indicating the graphic meaning of surface residence time (τ) [19]. Reproduced with permission from the American Chemical Society.

SSITKA is also frequently coupled with DRIFT spectroscopy in order to focus on the reactivity of surface species under reaction conditions (Figure 8.4). This experimental approach has been used in several instances to determine the role of formates in the WGS/RWGS reactions [20-22]. Formates are commonly observed in large amounts and hypothesized to be reactive intermediates in the associative mechanism, but the SSITKA-MS-DRIFTS investigations showed that they were simply spectator species or minor reaction intermediates of a slower secondary pathway [20-22]. This technique could be applied to our investigation of the RWGS reaction on Fe-K/Al₂O₃, in which various surface intermediates were observed to form, to discern which species have mechanistic importance and which are simply spectator species. The knowledge gained from such experiments would help us to improve our currently proposed reaction mechanism or suggest different models. We did make several initial attempts to perform SSITKA experiments in our laboratory, but these endeavors were unsuccessful, however, as we were unable to obtain high enough time resolution with the IR spectrometer available.



Figure 8.6. Schematic of IR-MS-SSITKA system used for operando investigations of catalytic reactions [23]. Reproduced with permission from *Catalysis Today* (Elsevier).

8.4 Dissertation Accomplishments

In summary, the work presented in this dissertation has made great progress in identifying and understanding the reaction mechanisms of heterogeneously catalyzed NO oxidation and the RWGS reaction. The major findings of each chapter are as follows:

- <u>Chapter 3</u>: Various types of microporous materials were shown to have remarkable abilities to catalyze the NO oxidation reaction at low reaction temperatures by physical confinement and electrostatic effects.
- (2) <u>Chapter 4</u>: At temperatures above 423 K, H- and Na-zeolites catalyze the NO oxidation reaction by a new apparent mechanism that involves NO⁺ species formed at Brønsted or charge-balancing sites within the zeolite framework.
- (3) <u>Chapter 5</u>: Cu-zeolites exhibit significantly higher NO oxidation activity compared to H-zeolites. Pretreatment conditions of Cu-zeolites have a substantial effect on NO oxidation rates, with pretreatment in 1% CO/He leading to higher reaction rates compared to pretreatment in 5% O₂/He, 1% NH₃/He, or 500 ppm NO + 500 ppm NH₃.
- (4) <u>Chapter 6</u>: A catalyst screening for the RWGS reaction showed that Fe-K/Al₂O₃ and Fe/Al₂O₃ effectively catalyze the reaction with high levels of activity and CO selectivity.
- (5) <u>Chapter 7</u>: Kinetic and mechanistic investigations of the RWGS reaction on Fe-K/Al₂O₃ and Fe/Al₂O₃ showed that a redox mechanism is the only reaction pathway on the Fe/Al₂O₃ catalyst, and is the predominant pathway on the Fe-K/Al₂O₃ catalyst. The potassium

promoter activates a secondary pathway for CO formation, which may be the so-called associative pathway.

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