MONOMOLECULAR ALKANE ACTIVATION ON AL- AND FE-CONTAINING ZEOLITES

by

Jang Ho Yun

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

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ABSTRACT

Zeolites are crystalline aluminosilicate materials with an open micro-porous three-dimensional framework structure and are used as a solid acid catalyst in oil refining and petrochemical industries, in processes such as fluidized catalytic cracking (FCC). FCC catalysts constitute more than 95% of zeolite catalyst consumption. Other zeolite-catalyzed processes include hydroxylation (e.g., phenol), alkylation (e.g., ethylbenzene, cumene), and epoxidation (e.g., propylene oxide). Even though synthetic zeolites have been used in the industry for decades, prospects are still bright for recent new challenges and applications.

Synthetic and post-synthetic modifications of zeolites can be used in the improvement of catalysts; the modification of zeolites can lead to new catalytic chemistry. Monomolecular conversion of alkanes proceeds through two reaction pathways: cracking and dehydrogenation. The protolytic mechanism of alkane activation, involving a formation of alkanium-like ions by a direct protonation from BAS, is the generally accepted mechanism for monomolecular hydrocarbon reactions in acid zeolite catalysts. The homolytic cleavage of C-C and C-H bonds of hydrocarbons, however, can occur through the formation of radical cations in modified zeolite catalysts. The main products (e.g., propene, hydrogen, ethylene, and methane) are similar to the products generated through a protolytic mechanism. Nonetheless, different selectivity patterns are observed between the cracking and the dehydrogenation pathways. In this thesis, we first investigated the effect of thermal treatments of SSZ-13 (CHA) with Si/Al ratios of 6 and 12 for the monomolecular propane conversion. The product-distribution and the kinetic analysis indicate that different types of active sites are generated by thermal treatments. In the case of SSZ-13 with Si/Al of 6, selectivity changed significantly with just a 50 K increase in the treatment temperature from 773 K to 823 K, but the activation energy did not change. SSZ-13 with Si/Al of 12 exhibited a gradual change in selectivity and activation energy with treatment temperature, indicating generation of different active sites.

Second, Fe³⁺ was isomorphously incorporated in the zeolite structure instead of Al³⁺ initially to compare the difference in acidity on alkane activation. The monomolecular propane reaction was studied over iron-silicate zeolites, and a mechanistic study was conducted using its reverse reaction (propene hydrogenation). H-[Fe]ZSM-5 and H-[Fe]beta show very high dehydrogenation selectivity (dehydrogenation-to-cracking ratio ~ 22), while H-[Al]ZSM-5 exhibits higher cracking selectivity than dehydrogenation selectivity by a factor of 2 to 3. The activation energies of the dehydrogenation of propane over H-[Fe] zeolites are lower than those over H-[Al]ZSM-5 (115 kJ/mol vs. 170 kJ/mol) a result which is inconsistent with the lower acidity of the iron silicate. A novel redox catalytic cycle was proposed and a mechanistic study with H-[Fe]ZSM-5 was explored to test the proposed mechanism. The Marcus theory for electron transfer and the ionization energies of the related molecules was used in a thermodynamic analysis of the reaction mechanism. The analysis verified that after formation of a propane radical cation, the energy barrier through a dehydrogenation pathway was lower than that through a

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cracking pathway, a result consistent with the observed high dehydrogenation selectivity over H-[Fe]ZSM-5.

In the next section, the monomolecular propane reaction is used again to investigate zeolites having only hydrogen-bonded acid sites. It is found that H-[Al(B)]Beta zeolites having only hydrogen-bonded acid sites, show lower activation energies and higher dehydrogenation selectivity than H-[A1]Beta zeolites. The hydrogen-bonded acid sites are expected to be located close to the oxygen atom in the framework, meaning that there is only narrow space near the acid sites. The constrained space leads to the formation of propyl cation intermediates predominantly, resulting in that the dehydrogenation pathway is favored than the cracking pathway.

In the last section of the thesis, the catalytic hydrodeoxygenation of furfural was examined using Ag-Cu bimetallic catalysts supported on SiO₂. Furfuryl alcohol is the main product of the reaction with a small amount of 2-methyl furan production on monometallic Cu/SiO₂. As the concentration of Ag increases in Ag-Cu bimetallic catalysts, the formation of 2-methyl furan increases and the formation of furfuryl alcohol decreases. The selectivity indicates that hydrogenation rates are enhanced by the addition of Ag. Since 2-methyl furan is a potential biofuel additive to gasoline, the Ag-containing catalysts can be promising for 2-methyl furan production.

This thesis main contribution has been a redox catalytic cycle that can explain the catalytic properties of thermally treated and iron-silicate zeolites for alkane conversions. The results of catalytic reaction and the mechanistic investigation are consistent with the existence of redox chemistry in those zeolites. This new zeolite chemistry and its further application can contribute to the resolution of emerging

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challenges in a petrochemical industry with the recent rise of shale gas by, for example, helping in the on-purpose propene production.

Chapter 1

INTRODUCTION

Zeolites have been investigated for over two centuries since stilbite and natrolite were named in 1756 by Axel Cronstedt and in 1803 by Martin H. Klaproth [1, 2]. Industrial applications of zeolites are primarily catalysis and gas purification in the petrochemical industry, but, zeolites have found applications in agriculture, horticulture, gas separations, domestic water treatment, and nuclear waste processing [3-6]. With the rise of shale gas, new challenges have emerged in oil refining and petrochemistry, such as the invigoration of gas-based infrastructure, emergence of coupled gas-fire power generation with intermittent renewables, disposal of fracturing fluids and produced (contaminated) water, requiring innovative science and new technologies [7-9]. Even though zeolites are not new materials, we expect that innovations in zeolite chemistry, structures and compositions can provide efficient and balanced solutions for the challenges mentioned above as major catalyst materials in the petrochemical industry.

This thesis investigates hydrocarbon conversions over zeolites with the ultimate goal of understanding the reaction mechanism at the molecular level. Most of the research is conducted using monomolecular propane conversion as a probe reaction and MFI-type zeolites. From the observation of the product distribution and the catalyst kinetic parameters, a reaction mechanism for hydrocarbon conversions over zeolites was proposed and evaluated. The cases studied in this thesis contribute to the elucidation of the nature of active sites, provide insight for hydrocarbon

conversions, and further improve industrial hydrocarbon chemistry and contribute to solving problems recently emerged, such as global warming through process efficiency enhancement and emission reduction.

1.1 Zeolites

Zeolites have a three dimensional framework structure (Figure 1.1) that is constituted by combining oxide tetrahedral such as SiO₄ and AlO₄. [10] Framework compositions can be varied by the isomorphous substitution of metal atoms, such as B, Fe, Ga, Mg, Mn, Ti, and Zn into the tetrahedral positions within the framework. Tetrahedra are the primary building blocks for zeolites. Tetrahedra can be combined in a finite number of ways to form different units, such as squares, pentagons, hexagons, and octagons, called secondary building units (SBU) [11]. The SBUs consist of n-ring structures, in which *n* is commonly 4, 5, 6, 8, 10 or 12. The linkage of SBUs can form cages and channels that are the essential elements of all zeolite structures. Due to the large diversity of zeolites structures reported, the zeolite frameworks have been codified into framework type-codes describing only the framework topology, but not framework composition, distribution of the tetrahedral atoms, or cell dimension. For example, the CHA abbreviation describes the topology of zeolites chabazite, AlPO-34, SAPO-34, SSZ-13, and ZK-14 [12]. The number of 'approved' framework types is over 210 according to the three-letter structure codes established by the International Zeolite Association [12].



Figure 1.1 Three dimensional zeolite framework structure (MFI).

As solid catalysts, different zeolites exhibit different selectivity because of the size of the differences in pores or channel dimensions [12]. Shape selectivity and the confinement effect of the zeolite micropores depend primarily on the size of pores [13-15]. For example, chabazite (CHA) has small pores formed by 8-membered rings, ZSM-5 (MFI) has medium pores (10-membered rings), and beta zeolite (*BEA) has large pores (12-membered rings) as shown in Figure 1.2. Different mechanisms of molecular shape selectivity can be distinguished based upon zeolite structure, reactant, transition states, and product kinetic diameters. The reactants selectively diffuse through the pore entrance toward the active sites when the pore size is smaller than some reactant molecules. Moreover, the products, which are larger than the size of pore exit, can be converted into smaller molecules to move outside of the pore (Figure 1.3).



Figure 1.2 Pore sizes within different zeolite frameworks.



Figure 1.3 Schematic illustration of shape selectivity: reactant, product, and transitionstate selectivity

The Si/Al ratio of a zeolite structure is a very important variable in the determination of the catalytic activity of zeolite materials. The minimum Si/Al ratio is 1 due to Loewnstein's rule, which establishes that no Al-O-Al bond exists in a zeolite [16]. Since an alumina tetrahedron (AlO₄⁻) has a negative charge while a silica tetrahedron (SiO₄) is neutral, a counter ion, such as H⁺ or alkali-metal ion (K⁺, Na⁺), must be presented to balance this negative charge. The site compensated by H⁺ form bridging hydroxyl group (Si–OH–Al) that are chemically and functionally Brønsted acid sites (BAS), as discussed in the next section. The number of the acid sites increases as the Si/Al ratio decreases in contrast to the acid strength which decreases in the presence of higher concentrations of framework Al [3]. The micropore volume increases as the Si/Al ratio decreases since Al-O bonds are longer than Si-O bonds (1.70-1.73 Å, 1.58-1.64 Å, respectively). The thermal stability of zeolites also depends on the aluminum content. Zeolites with high concentrations of Al are less thermally stable than zeolites with low concentrations of Al.

Acid-base reactions are the most common class of industrial chemical reaction, and acid base catalysis can be applied to every area of the chemical industry, including the oil refining industry. Since zeolites have high acidity, high surface area as well as the ability to do shape selective catalysis, they are used primarily as a solid catalyst in the oil refining and the petrochemical industries in reactions, such as hydrocracking, fluid catalytic cracking (FCC), aromatization and isomerization [17-19].

1.2 Propane Dehydrogenation, Opportunities from Shale Gas

Catalytic alkane activation, which directly converts alkanes to more valuable products, has been a topic of interest in chemistry and chemical industry [20-24] for

over a century. Dehydrogenation of alkanes is one of the important industrial alkane activation processes. Industrially, there are two dominant firms, Honeywell UOP and Lummus supplying this technology today. The Oleflex and Catofin processes, licensed by UOP and Lummus respectively, are catalytic dehydrogenation technologies for the production of light olefins from their corresponding paraffins [25-27]. The reactor design of the Oleflex process is based on moving bed technology, where the catalyst moves through the reactor with inter-reactor heaters. Coke is burnt off in the regenerator, and the cycle time is approximately 3 to 5 days through the reactors. Hydrogen is also fed in the reactor to reduce coke formation. However, this results in lower conversion and high compression cost. The Catofin dehydrogenation process is a route for the production of isobutylene, propylene or amylenes from isobutane, propane or isopentanes, respectively. The Catofin process uses adiabatic fixed-bed reactors, which swing (approximately 5-30 min cycle time) for storing the needed reaction heat between reaction and regeneration, and operating conditions that are selected to optimize the complex relationship between conversion, selectivity and energy consumption. Propene, which can be produced by dehydrogenation of propane, has been established as a major component of the global olefins business. The greatest volume of propene is generated as a by-product in steam crackers of naphtha and light hydrocarbons (propane) and through the fluid catalytic cracking (FCC) process.

Shale gas is natural gas that is found trapped within shale formation [28]. Shale is a fine-grained sedimentary rock that forms from the compaction of silt and clay-size mineral particles that we commonly call "mud". Over the past decade, the combination of horizontal drilling and hydraulic fracturing has allowed access to large volumes of shale gas that were previously uneconomical to produce [29]. Natural gas from shale has been the fastest growing contributor to total primary energy in the United States, and has led many other countries to pursue the development of shale deposits.

The availability of large quantities of shale gas will further allow the United States to consume a predominantly domestic supply of gas in the coming decades. According to the U.S. Energy Information Administration (EIA) Annual Energy Outlook 2011 [30], the U.S. possesses 2,552 trillion cubic feet (Tcf) of potential natural gas resources. Natural gas from shale resources accounts for 827 Tcf. At the 2009 rate of U.S. consumption (about 22.8 Tcf per year), 2,552 Tcf of natural gas is enough to supply approximately 110 years of use. Shale gas resource and production estimates increased significantly between the 2010 and 2011 Outlook reports predict that they are likely to increase further in the future [30, 31]. In 2012, prices went down to \$3/MMBtu (million British Thermal Unit) due to shale gas [32]. According to a 2013 Forbes magazine article, generating electricity by burning natural gas is cheaper than burning coal if the price of gas remains below \$3/MMBtu [33].

With substantial ethane fed ethylene production, the growth in propylene from typical steam crackers cannot keep pace with propylene demand and declining gasoline demand in Europe and North America limits the overall growth in propylene production from refineries. With low ethane prices due to the exploration of shale gas reserves, the low price of ethylene produced from this raw material has given ethanefed steam crackers in North America a feedstock advantage [34]. This has put naphtha-fed steam crackers at a disadvantage, with many of them shutting down or revamping to use ethane as feedstock. Consequently, the propene output rates from ethane-fed crackers are negligible. This, combined with the rise in propene demand,

has resulted in a tight propene market. New and novel lower-cost chemical processes for on-purpose propene production technologies are, consequently, of great interest to the petrochemical industry. Such processes include: metathesis, propane dehydrogenation (PDH), methanol-to-olefins/methanol-to-propene (MTO/MTP), high severity fluidized catalytic cracking (FCC), and olefins cracking. Among those, MTO/MTP and PDH stand out because they use low-cost raw materials. In the U.S., major companies are building PDH plants to take advantage of shale gas. In Middle East, the propane output is expected to be capable of supplying not only domestic needs, but also the demand from China, where many PDH projects are scheduled to go on stream within the next few years. The economic analysis presented that the estimated capital expenditures (CAPEX) for such a plant on the United States Gulf Coast is about USD 490 million. While China presented the lowest CAPEX, the USA presented the most advantageous operational margins, due to the rise of shale gas, which lowered propane prices.

Zeolites have been the main solid acid catalysts in petrochemical industry. Because of the exploitation of shale gas and change in propane dehydrogenation process, the importance of zeolites is being emphasized as catalysts for hydrocarbon processes and various approaches are being carried out to improve hydrocarbon chemistry in zeolite catalysts.

1.3 Activation of Hydrocarbon over Zeolite Catalysts

The actual details of the hydrocarbon activation mechanism of zeolites in various processes have not been completely established, although zeolites are used as the main catalyst component and as additive in petrochemical processes such as FCC.

Brønsted acid sites (BAS) are distorted tetrahedral structures of alumina-substituted zeolites with a longer Al–O(H)–Si bond than the other three Al-O-Si as shown in Figure 1.4. The BAS has been considered the main active site for hydrocarbon conversions over zeolite catalysts. The Brønsted acid form of a zeolite is obtained by exchanging the extra-framework cations with an ammonium solution, such as aqueous ammonium nitrate (NH₄NO₃), after any organic compounds used as the structure directing agents in as-made version of zeolite are burnt out by calcination. The acid site is formed by desorption of ammonia from such materials at elevated temperatures leaving proton on the zeolite surface.



Figure 1.4 Zeolite Brønsted acid sites.

1.3.1 Protolytic Mechanism of Alkane Activation

It is well known that Brønsted acid sites are significant in a number of hydrocarbon processes, such as alkylation of benzene with ethylene [35], disproportionation of toluene to form xylenes and benzene [36], alkane cracking and isomerization and many others [37-40]. In hydrocarbon conversion processes, the Brønsted acid sites donate a proton to an absorbed species forming alkanium or carbenium ions, species considered as transition states in alkane cracking reactions. The alkanium ion intermediates on Brønsted acid sites in zeolites play an important role in the activation of hydrocarbons, and it is the reason why it is called the protolytic activation of hydrocarbons.

Cracking of small alkanes, catalyzed by zeolites, can proceed via two mechanisms, both involving formation of alkanium ions: the bimolecular chain reaction, which involves *carbenium* ions that are further transformed by β -scission; and the *monomolecular reaction*, involving alkanium ions that are formed by the direct protonation of the alkane by the Bronsted acid sites of the catalyst [41-46]. The latter reaction, originally proposed by Haag and Dessau [47], is called "Haag-Dessau mechanism" or "protolytic mechanism" of alkane activation. The protolytic mechanism is favored at reaction temperatures of about 800 K over acid catalysts such as a zeolite. Medium pore zeolites, such as ZSM-5, are favored for the protolytic mechanism because the bimolecular reaction including hydride transfer is limited in the pores while the monomolecular reaction is readily allowed. The protolytic mechanism is kinetically significant only when the concentration of reactants and the conversion of reaction are very low.

To be specific, on Brønsted acid sites in zeolites as depicted in Scheme 1.1, the reaction of isobutane is initiated by protonation of C-H or C-C bonds [48]. First, pentacoordinated carbonium ions are formed on Brønsted acid sites in zeolites, and then this cation is decomposed into carbenium ions, which are t-butyl for dehydrogenation pathway and propyl for cracking pathway.

$$i-C_{4}H_{10} + HZ = \begin{bmatrix} CH_{3} \\ CH_{3} - CH_{3} \\ H - H \end{bmatrix}^{+} @Z^{-} \\ CH_{4} + C_{3}H_{7}^{+}@Z^{-}$$

Scheme 1.1 Initial protonation of C-H or C-C bonds of isobutane on Brønsted acid sites in zeolites

As the number of hydrogen atoms attached to the carbon atom, from which the hydride ion is abstracted, increases, the energy required for the formation of alkanium ion also increases. The high energy of formation decreases the stability of alkanium ions. For example, the tertiary carbenium ion is so stable that the formation of carbenium ion is easy and prevalent, while there is no formation of alkanium ion since the methyl carbenium ion is the least stable. In a zeolite, the charge separation, which exists when an alkanium ion is formed, may occur over the oxygen atoms so that the micropore in the zeolite surrounds the alkanium ion. In addition, cracking of heavy hydrocarbon is known to be faster than cracking of light hydrocarbon. For example, cracking of $n-C_{18}H_{38}$ is 20 times faster than cracking of $n-C_8H_{18}$ [49]. A longer chain length provides more chance to contact the hydrocarbon to the surface of a catalyst. It was reported that the heat of adsorption increases with increasing size of hydrocarbon due to an increase in the dispersion forces [50]. For example, the heats of adsorption of propane, n-butane, n-pentane, and n-hexane on H-MFI structure were -46, -58, -70, and -82 kJ/mol, respectively [50]. Adsorption equilibrium data for hydrocarbons on zeolites also support this explanation.

The reaction energies which cannot be measured directly can be estimated based on Born-Haber thermodynamic cycle. Thus, the activation barrier can be separated into enthalpy differences that independently reflect reactant and catalyst properties, such as the proton affinity (PA), the deprotonation energy (DPE), and the stabilization energy [51, 52]. The electrostatic stabilization of intermediates and transition states depends on acid strength, which is expressed as the deprotonation energy (DPE) and reflects solely the catalyst properties. H-MFI and H-FAU have similar DPE values estimated by QM-Pot methods [53], while [Fe]MFI exhibit higher DPE values than [A1]MFI by ~20 kJ/mol [51]. Differences in acidity between zeolites of different composition can be related to the observable activation energies and the product distribution of given reaction.

1.3.2 Redox Mechanism of Alkane Activation

The electron transfer from an organic molecule adsorbed into zeolite pores to the zeolite framework has been reported by numerous researchers [18, 54-58]. Moissette group has reported the spontaneous ionization of a number of molecules adsorbed on H-[A1]ZSM-5 and H-[Ga]ZSM-5 without pre-treatment by using molecules having small ionization potential. Examples are anthracene, biphenyl, 2,5-dimethylhexa-2,4-diene, and trans-stilbene [54, 59-64]. Our group has reported other sites that can extract electrons more readily than pristine zeolite by high temperature treatment above 873 K and by isomorphous substition of Al³⁺ for Fe³⁺ in the framework structure [65-67]. As a result of the spontaneous ionization, long-lived organic radical cations are formed.

The homolytic cleavage of C-C and C-H bonds of hydrocarbons can occur through the formation of radical cations at reaction temperatures above 700 K [68]. Similarly, hydrocarbon conversions can be initiated by electron transfer over sites that

can extract electrons from neutral molecules adsorbed in the zeolites. For example, a propane radical cation can be produced by extraction of one electron from the propane molecule, yielding pairwise propene and hydrogen (dehydrogenation channel) or ethylene and methane (cracking channel). After the generation of products in the zeolite pores, the electron is transferred back to the product molecules from the zeolite framework. These main products (propene, hydrogen, ethylene, and methane) are similar to the products generated through protolytic mechanism, however, show somewhat different selectivity between the cracking and the dehydrogenation channels. It has been reported that the dehydrogenation selectivity is enhanced for the propane conversion over [A1]ZSM-5 catalyst after thermal treatment at 1073 K [67]. This previous observation leads to the development of new plausible mechanism that can explain the structure of those sites and their role in hydrocarbon chemistry. The proposed redox catalytic mechanism for isobutane conversion over solid acid catalyst is illustrated in Scheme 1.2.



Scheme 1.2 Redox catalytic cycle for isobutane conversion over solid acid catalysts.

1.3.3 Transition State Theory

A transition state is an intermediate configuration on the reaction pathway between reactants and products, characterized by maximum value of potential energy. In transition state theory, the activated complex is considered to be formed in a state of
equilibrium with the molecules in the initial state, indicating the specific statistical and thermodynamic properties can be determined [69, 70]. Transition state theory has been successful in calculating the thermodynamic properties, such as standard enthalpy of activation, the standard entropy of activation, and the standard Gibbs energy of activation, for a particular reaction from the experimentally determined rate constant.

A catalytic reaction may consist of many elementary reaction steps. Since zeolites have a microporous structure, the coupling of reaction at the active centers with diffusion of the molecules through the micropores to and from the zeolite exterior is a key factor that needs to be understood. A characteristic time scale of a catalytic reaction event, such as proton activated isomerization of an adsorbed alkene molecule is 10^{2} s. However, the characteristic time of vibrational motion is 10^{-13} s, and diffusional time is 10^{-8} s, and adsorption time scale is typically 10^{-6} s. The time scale of desorption of a molecule is about 10^{-4} s or longer. The time scale of the protonactivated elementary reaction is 10^{-4} s due to high activation energies [71]. A longer time scale of reaction than the time of vibrational motion indicates that thermal energy exchange between reaction molecule and zeolite wall is fast, justifying the use of transition state theory with the following rate expression (Erying equation) [70]:

$$r_{TST} = \frac{kT}{h} \exp(\Delta S^{\ddagger} / R) \exp(-E_a / RT)$$
(1.1)

where, k is Bolzmann's constant, h is Planck's constant, ΔS^{\ddagger} is the activation entropy, and E_a is the activation energy for transition state, R is the gas constant. TST can then be used to understand the underpinning of catalytic chemistry in general.

1.4 Post Synthesis Modification of the Zeolite Structure

1.4.1 Thermal Treatment

The acid reactivity of zeolites is attributed to Brønsted acid sites. Assynthesized zeolites are not ready for direct usage as catalysts. After exchanging extraframework cations with ammonium ions, the material is calcined to decompose the ammonium into ammonia and a proton. Scheme 1. 3 represents the acid form of zeolites after decomposition of the ammonium ions at high temperatures over 723 K.

Additional post-treatments are required to modify the zeolite's physiochemical properties. For example, Zeolite Y (FAU) in acid form having even a low Si/Al ratio is not thermally stable, thus cannot be used at high temperature, especially the temperatures required for FCC process. In the process the FCC catalysts are recycled back and forth in the presence of steam between the reductive atmosphere in the reactor and the oxidative atmosphere in the regenerator. To increase the thermal stability of the zeolite before it is loaded into the FCC unit, it is steamed just enough to partially dealuminate the sample but not so much that the sample structure is compromised. Steaming also generates Lewis acid sites (LAS) that may enhance activity.



Scheme 1.3 Decomposition of ammonium ion (NH_4^+) to form BAS

1.4.2 Dehydroxylation at High Temperature

The Brønsted acid sites of zeolites decompose at high temperatures, usually above 873 K [72, 73]. The process of decomposition of hydroxyl groups from the initial structure is called dehydroxylation. For instance, in a FCC regenerator as shown in Figure 1.5, the catalysts are treated at temperatures in the range of 943 - 993 K, and dehydroxylation occurs under these conditions.

Dehydroxylation has been investigated by various spectroscopy techniques including ²⁷Al nuclear magnetic spectroscopy (NMR). Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS) [74-79]. The trigonal structure has not been detected by NMR while octahedral and pentacoordinated aluminum have been observed [78, 79]. For instance, bridged Si-OH-Al hydroxyl groups have an absorption band around the 3600 cm⁻¹ region of IR spectrum (Figure 1.5), and the intensity of this region decreases after zeolites are heated at elevated temperature above 873 K [80]. An IR peak at 3720- 3750 cm^{-1} is assigned to silanol groups [81]. The peak at 3666 cm⁻¹ is assigned to aluminum in partially extraframework positions. The aluminum in a threecoordination environment is often proposed as the origin of the peak at 3666 cm^{-1} [81]. CO adsorption studies have revealed that the peak at 3666 cm^{-1} is less acidic than the normal Brønsted acid sites and more acidic than the silanol group [81]. Extraframework aluminum [54], extra-lattice amorphous materials [82, 83], or the silanol group [84] have been considered for the assignment of the peak at around 3700 cm^{-1} .



Figure 1.5 FTIR spectra of OH stretching of BAS and silanol group heated at different temperatures



Figure 1.6 Schematic diagram of FCC process.

1.4.2.1 Heterolytic Dehydroxylation

It has been known that Lewis acid sites are generated as a result of dehydroxylation. Since it is difficult to characterize and identify the molecular structures of Lewis acid sites, the research about Lewis acid sites is still on-going and as of today there is no consensus as to the local structure of the Lewis acid sites. Three-coordinated aluminum units have been typically proposed as the source of Lewis acidity [82, 85]. Other non-framework aluminum moieties such as AlO⁺, Al(OH)⁺², Al(OH)⁺₂, Al(OH)₃, Al₂O₃ have also been suggested to be the true Lewis acids [86, 87]. The effect of Lewis acid sites on the catalytic activity and selectivity has been investigated and it has been revealed that the turnover rates of cracking and dehydrogenation are not related to the Lewis acid site concentration [52]. Instead, Lewis acid sites increase the reaction rate by enhancing the adsorption of reactants [38].

The heterolytic dehydroxylation of Brønsted acid sites is illustrated in Scheme 1.4 [57, 73], which in this case proceeds by dehydration [73, 88]. In the left side of this figure, the BAS are described as OH-groups. In this reaction, two moles of BAS react to give acid-base and positive-negative site pairs: one mole of aluminum in a trigonal structure (Lewis acid sites) and one mole of aluminum with a symmetric tetrahedral structure. The reverse of dehydroxylation can occur by inducing water from at the highest temperature of dehydroxylation to the temperature which water vapor can be present [89]. This heterolytic pathway has provided the idea that Lewis acid sites are important for the hydrocarbon cracking process at high temperature condition above 873 K.



Scheme 1.4 Heterolytic Brønsted acid site decomposition pathway

1.4.2.2 Homolytic Dehydroxylation

The heterolytic pathway of BAS decomposition has been the accepted dehydroxylation path for low-silica zeolites for decades [56, 73], although the molecular details of the structure remaining inside the zeolites are still unknown. In high-silica zeoites, the high energy is needed to decompose the BAS through the heterolytic pathway since the BAS are sparsely placed.

Our group recently examined the dehydroxylation of BAS of high-silica zeolites using mass spectrometry-temperature programmed desorption (MS-TPD) [73]. We found that the BAS of high-silica zeolites are decomposed to produce hydrogen and a small amount of water. The MS-TPD of two samples of ZSM-5 heated stepwise to 523 K, 798 K and 1023 K was carried out and a large amount of hydrogen is found when the temperature reached about 1023 K. The amount of hydrogen is also related to the Si/Al ratio. With a small Si/Al ratio (high aluminum), *less* hydrogen gas is produced. An electron hole pair generation for H-ZSM-5 calculated by hybrid quantum mechanics and a shell-model ion-pair potential approach also support our group's observation [90]. These results of the MS-TPD experiment and electronic structure calculation show that BAS of high-silica zeolites are decomposed by a redox process, not by dehydration.

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Also, it has been known that the acid form of zeolites treated at high temperature (under dehydroxylation conditions) react with molecules having small ionization potentials to form stable radical cations [56-58]. These radical cations have been studied frequently by the electron-spin-resonance (ESR) because they give excellent high-resolution ESR spectra [61]. Alkenes, polyaromatics, nitrogen-, oxygen-, and sulfur- containing organic molecules and others have shown to form radical cations in zeolite after heating at high temperatures.

Our group has proposed a new pathway to explain the decomposition of BAS of high-silica zeolites (Scheme 1. 5) and the formation of $[AlO_4]^0$ sites in zeolites [67, 73, 91]. A single electron hole is generated on one of the oxygen atoms surrounding aluminum atom by dehydroxylation. The active sites which are formed under the condition of dehydroxylation are considered nonacidic single-electron redox sites [55].

Scheme 1.5 Brønsted acid sites Homolytic Dehydroxylation

1.4.3 Isomorphous Substitution of Al³⁺

The isomorphous substitution of Al^{3+} for other heteroatoms, such as B^{3+} , Ga^{3+} , and Fe^{3+} provides new materials showing specific catalytic properties in oxidation and hydroxylation reaction related to the coordination state of the heteroatom [72]. As with Al-containing zeolites, isomorphous substitution with a trivalent element induces a negative charge that must be balanced by a cation. The acidic strength of BAS (Si-O(H)-M^{III}) depends on the nature of the trivalent heteroatom. The acidity sequence is

expected as follows: Al > Fe ~ Ga >> B. The isomorphous substitution has additional advantages, as well as the concerning acid catalyzed reaction. By isomorphous substitution, other kind of metals, which are well-known components of catalysts for other types of reaction (for example, iron as a famous catalyst component for oxidation reactions), can be introduced in zeolites. The catalytic properties can be changed by the degree of structural distortion caused by the incorporation of other metals having different ionic radii (Figure 1.6) and electronegativity. Especially, the tetrahedral sites in MFI-type materials have a great impact as new shape-selective industrial catalysts having tunable acidic strength. In addition, Fe is a famous material for oxidation reactions. Therefore, we focused on Fe-containing MFI zeolite in the work reported in the thesis.



Figure 1.7 Different ionic radii of tetrahedral Al and Fe sites.

1.4.4 Hydrogen-Bonded Acid Sites in Zeolites

¹H NMR studies concerning the geometry of BAS have been reported in literature [92-101]. One of interesting issues on the geometry of BAS is hydrogenbonded acid sites in zeolites. A hydrogen bond is not a true bond, but an attraction between the lone pair of an electronegative atom and a hydrogen atom attached to a second relatively electronegative atom [102] as shown in Scheme 1.6. It was reported by Haw [92] that hydrogen-bonded acid sites were detected in H-[A1]ZSM-5 by using ¹H NMR spectroscopy. The dehydrated [A1] zeolites exhibit two peaks. One peak is shown at 4 ppm, which is attributed to OH group (BAS), while another peak at 6.5 ppm is assigned to the hydrogen bonded acid sites [92]. Brunner et al. reported this new hydroxyl group at 7 ppm interacting with MFI zeolite framework [97] and Freude also reported two kinds of acid sites in H-[AI]ZSM-5 at 4.2 and 6.1 ppm [94]. Koller group also exhibited the hydrogen bonded acid sites at 6.1 ppm using ¹H-²⁷Al rotational echo adiabatic passage double resonance (REAPDOR) spectroscopy [98]. Beck and Haw again reported the hydrogen-bonded acid sites in zeolite beta using ²⁷Al irradiation [99], and Omegna et al. [101] supported the observation for zeolite beta. Muller et al. [100] also observed the hydrogen-bonded acid sites in zeolite beta using Cs-exchanged sample.



Scheme 1.6 Conceptual structure of hydrogen bonded acid sites.

Recently, Koller's group has synthesized BEA-type zeolite only having the hydrogen bonded acid sites without normal BAS. The samples have been prepared by post-synthetic modification of two different B-Beta samples; one is prepared by ion-exchange with a mixture of NH_4^+ and Ca^{2+} ions, and another is prepared by adding Ca^{2+} ions during synthesis. It is assumed that Ca ions located on Boron prevent from the exchange of Al for B. Ammonium exchange then lead to the formation of

hydrogen bonded acid sites. ¹H NMR of the prepared samples does not show the first peak at around 4 ppm. In addition, ¹H-²⁷Al REAPDOR shows that the 6.5 ppm proton line is coupled to ²⁷Al. The other proton lines are also observed at around 2 ppm, but they are assigned to silanol group and OH group formed near the remaining boron, respectively. The lines do not show dipolar coupling to ²⁷Al. From these observations, the authors concluded that a zeolite, which has only hydrogen bonded acid sites, is successfully prepared. The newly prepared samples, having only hydrogen bonded acid sites, are tested for the monomolecular propane reaction and compared the catalytic activity to other zeolites containing BAS.

1.5 Thesis Outline

The main objective of this dissertation is to investigate the structure, composition, and properties of active sites in zeolites after structural modification, and to reveal the reaction mechanism for hydrocarbon conversions over the zeolites which should involve to electron-transfer.

Chapter 2 reports the experimental procedures for synthesis of catalysts (mainly zeolite materials) and for sample treatments, and describes characterization techniques used in this dissertation. Synthesis recipes of zeolite type catalysts, which include aluminosilicate ZSM-5 ([AI]ZSM-5, MFI), iron-silicate ZSM-5 ([Fe]ZSM-5, MFI), all silica ZSM-5 (silicalite-1, [Si]ZSM-5, MFI), iron-silicate zeolite beta ([Fe]beta, BEA), and aluminosilicate SSZ-13 (CHA), and bimetallic Ag-Cu catalysts with different Ag/Cu ratios supported on SiO₂ are included. The characterization techniques include X-ray powder diffraction (XRD), N₂ adsorption, scanning electron microscopy (SEM), ultraviolet/visible light spectroscopy (UV/Vis), solid-state magic

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angle spinning nuclear magnetic resonance (MAS NMR), temperature programmed desorption (TPD), and temperature programmed reduction (TPR). The reactor setups and gas chromatography (GC) for analyzing product distribution after hydrocarbon reactions are also presented.

Chapter 3 discusses the effect of thermal treatment on propane conversion over SSZ-13 catalysts. The samples with different Si/Al ratios are thermally treated at various temperatures, which are higher than the temperature for normal calcination and thus can result in the structural modification. The propane conversion is used as a model reaction, and the changes in selectivity and activation energies are investigated.

Chapter 4 examines the catalytic activity of iron-silicate zeolites ([Fe]ZSM-5 and [Fe]beta) using propane conversion as a model reaction. The selectivity between the cracking and the dehydrogenation over [Fe] zeolites is compared to that over [Al] zeolites. Redox chemistry is used to explain high dehydrogenation selectivity over H-[Fe] zeolites.

Chapter 5 studies the reaction mechanism for propane conversion over [Fe]ZSM-5 using its reverse reaction, propene hydrogenation. The mechanistic relationship between the forward and reverse reactions is investigated and the energy changes along with the reaction coordinates, involving electron-transfer, are calculated to estimate the reaction mechanism for propane conversion over H-[Fe]ZSM-5.

Chapter 6 exhibits the propane conversion over the hydrogen-bonded acid sites in beta zeolite samples. Slower rates of reaction and higher dehydrogenation selectivity are observed over the hydrogen-bonded acid sites. Confinement effect of the reactants in zeolite pores can explain the different catalytic activity against beta zeolites having normal Brønsted acid sites.

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Chapter 7 covers selective hydrodeoxygenation of furfural on Ag-Cu bimetallic catalysts supported on SiO₂. The effect of Ag composition is investigated for the furfural conversion compared to that on pure Ag and Cu catalysts supported on SiO₂.

Chapter 8 summarizes the main findings and conclusions in this dissertation, and suggests possible approaches for the future research.

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Chapter 2

EXPERIMENTAL PROCEDURES

2.1 Introduction

The experimental procedures and techniques used through out my thesis are described in this chapter. First, the synthesis protocols of all the zeolites used in this research are presented. X-ray powder diffraction (XRD) is used to identify the crystalline structure of the various phases synthesized and to obtain unit cell volumes. N₂ adsorption isotherms are used to determine the microporous volume of the catalyst samples. Next, the techniques of scanning electron microscopy (SEM) and ultraviolet/visible light spectroscopy (UV/Vis), which are used to characterize the morphology and measure electronic transitions of the zeolite crystals and other solids, respectively, are described. A brief description of the technique of gas chromatography (GC), which is used to detect the products during the reactions, is also given. Lastly, the reactor setups and experimental protocols for thermal dehydroxylation and hydrocarbon conversions used in this research are reported.

2.2 Synthesis of Catalyst Samples

2.2.1 [Al]ZSM-5 (MFI)

[Al]ZSM-5 is most often prepared using an organic structure-directing agent (SDA) such as tetrapropylammonium hydroxide. Here, however, we use a completely inorganic synthesis gel to avoid the calcination step needed to remove the organic SDA in the typical ZSM-5 synthesis. This was done to avoid the potential effect of defect sites and other impurities that could be formed on the zeolite samples during the calcination steps. The all-inorganic synthesis of zeolites ZSM-5 is often the method used to prepare these zeolites in industry, mainly because it is inexpensive. This synthesis thus has the added advantage that the results can be directly applicable to ZSM-5 samples used in industrial catalytic reactors.

[A1]ZSM-5 samples with different framework composition (Si/Al ratios) are synthesized from the following molar batch compositions: x Na₂O: y Al₂O₃: 100 SiO₂: $z H_2O$ [1-3]. Three samples with high and low Si/Al ratios are used in this report. The sample [A1]ZSM-5(18) with a Si/Al ratio of ~18 is synthesized using a gel of composition 12 Na₂O: 2.86 Al₂O₃: 100 SiO₂: 3000 H₂O. The sample with a Si/Al ratio of 12.5 ([A1]ZSM-5(12), higher alumina content) is synthesized with a synthesis gel of composition 9 Na₂O: 4 Al₂O₃: 100 SiO₂: 3000 H₂O. The sample [Al]ZSM-5 with Si/Al ratio of 26 is synthesized with gel composition 16 Na₂O : $1.9 \text{ Al}_2\text{O}_3$: 100 SiO₂ : 3000 H₂O Colloidal silica (Ludox AS-40, 40wt% suspension, Sigma-Aldrich) and sodium aluminate (NaAlO₂, EM Science) were used as the silica and alumina sources. The reactant solutions are prepared in two polypropylene containers. First, the calculated amount of colloidal silica is mixed with a 5 M NaOH solution and DI water. Concurrently, sodium aluminate is mixed with a 5 M NaOH solution and DI water in a different container. After mixing for 1 hour separately, the solutions are combined. After one additional hour of continuous stirring, the final solution is loaded into a Teflon-lined Parr autoclave and heated in a convection oven at 463 K for 40 hours under rotation. The product is vacuum filtered, washed with DI water, and dried in air.

2.2.2 [Fe]ZSM-5 (MFI)

[Fe]ZSM-5 zeolites are synthesized using a procedure reported by Bruckner et al. [4] [Fe]ZSM-5 with different framework compositions are synthesized using the following molar batch compositions: 1) 30 Na₂O : 0.38 Fe₂O₃ : 30 SiO₂ : 5 TPABr : $1040 H_2O : 25 H_2SO_4$ for Si/Fe ratio of 26, 2) 30 Na₂O : 0.19 Fe₂O₃ : 30 SiO₂ : 5 TPABr : 1040 H₂O : 25 H₂SO₄ for Si/Fe ratio of 48. Iron (III) sulfate $(Fe_2(SO_4)_3 \cdot 5H_2O_1)$, reagent grade, Acros Organics) and sodium metasilicate (Na₂SiO₃·9H₂O, reagent grade, Sigma-Aldrich) are used for iron and silicon sources. The reactant solution is prepared in two containers. Iron sulfate (0.46 g for Si/Fe ratio of 26 and 0.23 g for Si/Fe ratio of 48), 5.5 g of concentrated sulfuric acid (H₂SO₄, 95-98%, Sigma-Aldrich), and 25 g of DI water are mixed in container 1. In a second container, 21.32 g of sodium metasilicate is dissolved in 40.85 g of DI water. The solution in the second container is then added slowly to the first container while stirring. Next, 3.33 g of tetrapropylammonium bromide ((C₃H₇)₄NBr, TPABr, 98%, Sigma-Aldrich) is added to the mixture until a uniform solution is obtained. The pale yellow final mixture is heated to a temperature of 443 K for 3 days under rotation in a Teflon-lined Parr autoclave. The zeolite samples are recovered by vacuum filtration, washed with DI water, and dried at room temperature for 24 hours. The samples are calcined in a horizontal quartz flow reactor (ID = 20 mm) with air (grade 0.1, Matheson) flow by increasing the temperature to 753 K at a rate of 2 K min⁻¹, and maintaining the final temperature for 4 hours. The synthesis and calcination protocols are illustrated in Figure 2.1.



Figure 2.1 [Fe]ZSM-5 synthesis and calcination procedures.

2.2.3 [Si]ZSM-5 (Silicalite-1, MFI)

All silica zeolite ([Si]ZSM-5 or silicalite-1) samples are prepared using the molar composition, 40 SiO₂ : 9 TPAOH : 1500 H₂O [5]. A solution of 13.2 g of 1 M tetrapropylammonium hydroxide (TPAOH, aqueous solution, Alfa Aesar) and 28.34 g of DI water is stirred for 0.5 hours. Then, 12 g of tetraethyl orthosilicate (SiC₈H₂₀O₄, TEOS, 98%, Sigma-Aldrich) is added to the solution and stirred until the solution becomes transparent to the naked eye. The final solution is transferred into a Teflon-lined autoclave and heated at 383 K for 3 days in a convection oven under static conditions. The zeolite is separated from the solution by centrifuge. The sample is calcined in a furnace under an air atmosphere by increasing the temperature up to 823 K with a ramp of 2 K min⁻¹, holding this temperature for 10 hours.

2.2.4 SSZ-13 (CHA)

SSZ-13 samples are synthesized using N,N,N-trimethyl-1adamantanammonium ion (TMAda⁺) as a structure directing agent (SDA). Two different methods are used to prepare the SSZ-13 samples with different Si/Al ratio. SSZ-13 with low Si/Al ratio (SSZ-13-6, Si/Al ~ 6) is synthesized using a procedure reported by Zones [6, 7]. In this procedure, 20 g of sodium silicate (Na₂SiO₃, Sigma Aldrich) and 0.64 g sodium hydroxide (NaOH, Fisher Scientific) are mixed with 48 g of deionized water at room temperature for 15 min. Next, 2 g of NH₄-Y zeolite (Zeolyst CBV-100) is added to the solution and stirred for 30 min. This is followed by the addition of 8.4 g of TMAdaOH (SACHEM Inc., 25% aqueous solution) to the solution and mixing for another 30 min in a covered container. The hydrothermal conversion of the synthesis solutions is carried out in Teflon-lined Parr autoclaves at a temperature of 413 K under rotation for 6 days. The zeolite samples are separated from the solution using vacuum filtration, washed using deionized water, and dried at room temperature. The as-synthesized zeolites are calcined in air at 823 K with 2 K/min heating rate for 8 h to remove the occluded TMAda⁺.

The synthesis method of SSZ-13 with high Si/Al ratio (SSZ-13-12, Si/Al = \sim 12) is also based on the report written by Zones [8] and by Eilertsen et al. [9] 13 g of tetraethyl orthosilicate (TEOS, Sigma Aldrich) and 26.4 g of TMAdaOH are mixed with 2.7 g of water at room temperature. The solution is stirred for 2 h and then 0.7 g of aluminum ethoxide (Al(C₂H₅O)₃, Sigma Aldrich) is added and mixed for additional 1 h. The resulting solution is then hydrothermally treated in Teflon-lined Parr autoclaves at 413 K under static condition for 6 days. Sample filtration, washing, drying, and calcinations are identical to those of SSZ-13-6 sample.

2.2.5 [Fe]beta (BEA)

[Fe]beta zeolite is synthesized using a procedure reported by Raj and Sivasanker [10]. The gel composition is 2.3 $(Na + K)_2O : 40 \text{ Si}O_2 : 0.5 \text{ Fe}_2O_3 : 1$ (TEA)₂O : 800 H₂O. Specifically, 0.62 g of sodium hydroxide (NaOH, Fisher Scientific), 0.46 g of potassium hydroxide (KOH, Fisher Scientific), and 74 g of tetraethylammonium hydroxide ((C₂H₅)₄NOH, TEAOH, 40 wt% solution, Sigma-Aldrich) are mixed, and the resulting solution is added to 24 g of fumed silica (CAB-O-SIL M-5, Cabot). The mixture is stirred until an optically clear solution is obtained. The silica solution is slowly added to a solution containing 2.45 g of iron sulfate dissolved in 40 g of DI water. The final solution is transferred into a Teflon-lined autoclave and heated in a convection oven at 413 K for 15 days. The sample is collected, washed, and dried in the same way as the [Fe]ZSM-5 samples. The sample, which is loaded on the semi-cylindrical shaped quartz container, is calcined in a horizontal quartz flow reactor (ID = 20 mm). The temperature is first increased to remove water with a ramp of 2 K min⁻¹ up to 753 K under 100 sccm of N₂ (ultra high purity grade, Matheson) flow. When the temperature reached 753 K, the N₂ flow is changed to an air flow (100 sccm) to burn organic materials, and the final temperature is kept for 8 hours with the air flow. The sample is cooled down to room temperature under air flow.

2.2.6 Ion Exchange Procedure

After calcination [Al] zeolite samples are ion exchanged twice in a 0.1 M solution of NH_4NO_3 at 353 K for 8 hours. For 1g of [Fe] zeolite samples, the samples are mixed with 500 ml of 0.1 M solution of NH_4NO_3 at room temperature overnight.

The samples are then filtered, washed with DI water, and dried in air at room temperature to obtain ammonium form of the zeolites (NH_4 -Zeolite). For sodium exchange, all the samples are ion exchanged three times in a 0.1 M solution of $NaNO_3$ at room temperature overnight. The steps following the ion exchange are the same to the ammonium exchange.

2.3 Characterization

2.3.1 Powder X-Ray Diffraction (XRD)

Synthesized samples were characterized using X-ray powder diffraction (XRD), which is a widely used characterization technique for polycrystalline materials. XRD analysis is based on observing the scattering intensity of an X-ray beam hitting a sample versus incident and scattered angle, and wavelength or energy. XRD provides information about the atomic structure of the crystal and the dimensions and symmetry of the periodic three dimensional lattice structure of the material. The elementary theory of X-ray diffraction is based on Bragg's Law as shown in equation (2.1).

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

where, d is the distance between atomic layers in a crystal, λ is the wavelength of the x-ray beam, and θ is the angle of the beam. Each peak in the diffraction corresponds to a particular reciprocal space vector in the sample crystal. The Miller indices (h, k, l) can be found by using equation as follows:

$$d_{hkl} = \frac{\mathbf{a}_1}{h} \frac{\left(h\mathbf{b}_1 + k\mathbf{b}_2 + h\mathbf{b}_3\right)}{|\mathbf{H}_{hkl}|}$$
(2.2)

where $(\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3)$ are the reciprocal vectors of the crystal, $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ are the unit cell vectors and \mathbf{H}_{hkl} is a vector perpendicular to the h, k, and l places. The indexing of all the peaks in a sample diffraction pattern can be accomplished by using Bragg's law and equation (2.2) [11].

XRD patterns are recorded on a Phillips X'Pert X-ray diffractometer using Cu K α radiation with $\lambda = 1.5406$ Å. The patterns are collected from 5 ° to 50 ° 2 θ using a step size of 0.02 ° and 2s per step. Figure 2.2 is an example of an XRD pattern of the H-[A1]ZSM-5 used in this study. By comparison to published patterns we establish that the sample is a pure H-[A1]ZSM-5 and that they do not contain any detectable impurities or amorphous material.



Figure 2.2 Sample XRD pattern for calcined H-[Al]ZSM-5

The refinement of the unit cell parameters of crystalline materials from observed XRD pattern was often carried out to assess the amount of framework heteroatoms present in the sample. The program UnitCellWin is used to refine the unit cell parameters by minimizing residuals in the experimentally determined Bragg position using a nonlinear least-square method [12]. The download of the program is available from http://www.ccp14.ac.uk/ccp/web-

<u>mirrors/crush/astaff/holland/UnitCell.html</u>. The samples were mixed an internal silicon standard (NIST standard, 10~20 wt%) to correct the peak positions before the refinement of the unit cell parameters.

2.3.2 N₂ adsorption

Physisorption of nitrogen is frequently used to determine surface area, pore volume, pore diameter, and pore size distributions of catalysts. The deposition of gas molecules on the material is measured over a range of pressure to form an adsorption isotherm. Different isotherms are obtained according to the type of adsorbent materials: microporous, non-porous with weak substrate, mesopores, and meropores with weak substrate, as shown in Figure 2. 3. Data for microporous nature of a material are obtained at low pressures (P/P₀ \leq 0.2) while the mesoporous data can be obtained at pressures (P/P₀) from 0.2 to 0.8.

Nitrogen adsorption isotherms are measured using a Micromeritics ASAP 2020 instrument at 77K. The surface area of a material is commonly found using the Brunauer, Emmett, and Teller (BET) equation [13]. The BET equation assumes the adsorption potential from one wall and the subsequent layers of adsorption are controlled by condensation [13, 14]. Since adsorption potential from both walls affect

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the adsorption in materials with micropores, the BET cannot be used for materials such as zeolites.



Relative pressure, P/P⁰

Figure 2.3 Basic types of adsorption isotherm: I) microporous, II) non-porous, III) non-porous with weak substrate, IV) mesoporous, and V) mesoporous with weak substrate.

Micropore volume, surface area, and mesopore volume of zeolites are determined by the deBoer t-plot method [15, 16]. The amount of gas adsorption within micropores increases rapidly in the low pressure regime, and they are filled much more quickly than the large pores (macro or meso). Slightly above the point where the micropores are completely saturated with adsorbate, there is a region where the adsorption within the large pores and on external surface is still linear with pressure and this can be extrapolated backwards to zero pressures to determine the amount of adsorbate contained within the filled micorpores. In the t-plot method, the statistical thickness of the adsorption layer is plotted to extrapolate the micropore volume. The statistical thickness is estimated from a semi-empirical formula, such as Harkins-Jura equation, which is commonly used for the analysis of zeolites. This equation is based on adsorption on nonporous Al₂O₃. The intercept is related to the micropore volume and the slope is related to the external surface area using following equations;

$$V_{mp}\left(cm^{3}/g\right) = \text{intercept} \times 0.001547 \qquad (2.3)$$

$$S_{ext}\left(m^2 / g\right) = \text{slope} \times 15.47 \tag{2.4}$$

where, V_{mp} represents the micropore volume and S_{ext} indicates the external surface area.

2.3.3 Scanning Electron Microscopy (SEM)

A scanning electron microscope (SEM, JEOL JSM 7400F) is used to obtain secondary electron images of the various catalyst samples. The SE detector collects emitted electrons by hitting the sample with an electron beam, and thus obtaining an image. The SEM has high resolution and penetrates the sample to a depth on the order of a micron. Energy dispersive X-ray spectroscopy (EDX), a peripheral attachment to the SEM, allows to identify particular elements which the sample has and their relative compositions. The EDX collects the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons, and displays the intensity of X-ray lines and element distribution map. The following example analysis (Figure 2.4) exhibits the SEM image for [Al]ZSM-5 and shows that the ZSM-5 structure contained Si and Al in approximately 94.89:5.11 (Si/Al ratio is 18.57).



Figure 2.4 (a) SEM image for ZSM-5 and (b) EDAX spectrum analysis

2.3.4 Ultraviolet/Visible Optical Spectroscopy (UV/Vis)

Ultraviolet visible optical spectroscopy (UV/Vis) is used to study molecular structure and dynamics through electronic transitions and vibrations in the ultra-violet and visible range (200 – 800 nm wavelength) of the electromagnetic spectrum. Molecules in the ground state absorb a specified range of ultraviolet and visible light to induce electronic transitions or vibrations and show an absorption spectrum [17]. The wavelength of the absorption bands depends on the atomic or molecular structure and composition, and the intensity of absorbance determines the concentration of the molecule or absorbing species. A schematic layout of UV/vis used in this study is illustrated in Figure 2.5(a) where the traditional transmission mode is presented. While UV/vis spectroscopy is a powerful tool to detect and identify organic species that absorb radiation in UV/vis energy range in the liquid phase, it is not applicable to directly obtain the spectrum of a powdered sample since transmission of the light through the powdered sample can be very low and limited due to light scattering. Instead of transmission, a diffuse-reflective method is used for powdered samples. To this end, an integrating sphere is used as shown in Figure 2.5(b). The most widely used theory of diffuse-reflectance is the Kubelka-Munk theory which assumes the radiation is composed of two oppositely directed radiation flux through a continuous medium. Using this theory, diffusive reflectance UV/vis spectra were translated by the Kubelka-Munk function:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S}$$
 (2.5)

where, R indicates the ratio of the diffuse reflectance of the sample to reference material (Spectralon made of polytetrafluoroethylene (PTFE) or barium sulfate), K an absorption coefficient, S the scattering coefficient of the powder.



Figure 2.5 (a) The schematic layout of UV/vis spectroscopy, (b) optical geometry of the integrating sphere.

2.3.5 Gas Chromatography (GC)

Gas Chromatography (GC) is used for identifying chemical compounds in mixture of unknown compositions. GC passes a sample containing a mixture of compounds through a column, which is a thin tube, and electronically detects each component as it reaches, at different times, the end of a column.

For propane conversion, two detectors, a flame ionization detector (FID) and a thermal conductivity detector (TCD) are used. These are the two most common detectors for GC. FID is more sensitive to hydrocarbons than TCD, thus is generally used for identifying hydrocarbons. TCD is more frequently used for detecting hydrogen and inert gases. The GC instrument used for the propane reaction is GC model 2014 (Shimadzu) with two columns. One column is a MolSieve connected to a TCD detector and another column is a RT-alumina connected to a FID detector. The catalytic reaction rate were determined using a quartz tube plug flow reactor (ID = 5mm). Differential reaction conditions were used whenever possible to measure reaction rates without the assumption of a reaction rate expression model.

The GC instrument for the furfural conversion is GC model 2014 (Shimadzu) with one column, which is a HP-5 column (Agilent) connected to a FID detector. The furfural feed part and connection between the reactor to GC are heated at 483 K to prevent the effluent from being liquefied.

2.3.6 Solid-state Nuclear Magnetic Resonance (NMR)

²⁷Al and ²⁹Si NMR experiments were recorded on a Bruker AVIII-500 solidstate NMR spectrometer, operating 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 collected at a MAS frequency of 10 kHz, controlled to with +/- 2Hz using a Bruker MAS controller. ²⁹Si single pulse and cross polarization (CP) experiments were performed on each sample. For ²⁹Si single pulse MAS experiments, a 90 degree pulse with a width of 4.3 μ s was used and the recycle delay was 30 s. For ¹H-²⁹Si CP MAS experiment, 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 μ s, and the recycle delay was 5 s. For ²⁷Al MAS with and without proton high-power decoupling, a pulse with a width of 1.35 μ s was used and the recycle delay was 1 s.

2.3.7 Temperature Programmed Desorption (TPD)

TPD is one of the most frequently used techniques to characterize the acidity of materials. Here this technique is used to obtain information about the initial state (number and strength) of the acidic sites of the sample. The measurement is repeated then for the high temperature treated sample and by difference, we can quantify the effect of the treatment on the concentration of BAS. A 6.35mm diameter U-shape quartz flow reactor (Quartz Plus) is connected to a piping network integrated in a catalyst characterization system (Altamira Instruments, AMI-200ip). The reactor is installed in a clam-shell style furnace to control temperature. Temperature is measured using a K-type thermocouple and automatically controlled by the control software (Altamira Instruments, AMI-5200). A bed of quartz wool and quartz chips (Quartz Plus) are placed in the reactor, and 30 mg of ammonium-exchanged SSZ-13 sample is put on the bed. The corresponding TPD protocol for the high temperature treatment is presented in Table 2.1.
No	Ramp	Data	Treatment	Flow rate	Drogoduro		
110.	to	Nate	gas	Flow fate	rioceutre		
1	473 K	+10 K /min	Inert (He)		Dehydrate		
2	823 K	+20 K /min	Inert (He)		Desorption of ammonium		
3	373 K	-30 K /min	Inert (He)		Cool down		
	272 V		Ammonia	20	Regenerate ammonium exchanged zeolite by flowing		
4	3/3 K		(NH ₃)	20cc/min	NH ₃		
5	473 K	+10 K /min	Inert (He)				
	1073 K				Descention of an an a bid to an article		
6	(873,	+20 K /min	Inert (He)		tractment		
	823 K)				ueatment		
7	373 K	-30 K /min	Inert (He)		Cool down		
0	272 V		Ammonia	20/	Regenerate ammonium exchanged zeolite by flowing		
ð	3/3 K		(NH ₃)	20cc/min	NH ₃		
9	473 K	+10 K /min	Inert (He)				
10	823 K	+20 K /min	Inert (He)		Desorption of ammonium		

Table 2.1 Temperature-programmed desorption protocol corresponding to the high-temperature treatment of the zeolite samples.

In ammonia TPD, both BAS and LAS can be observed. BAS interact with ammonia to form ammonium ion, and LAS interact with the unpaired electrons on the nitrogen of ammonia. The ammonia in LAS is desorbed at lower temperatures than that in BAS. Different peaks can usually be observed in the TPD trace [18-20].

Ammonia TPD can provide useful information about the initial state of the acidic site of the sample. However, it is recognized that some limitations of ammonia TPD technique hinder a quantitative analysis of Brønsted acid sites densities [21, 22]. It was reported that ammonia adsorbs more strongly on CaO than on a USY zeolite [23]. In this sense, zeolites contain non-framework alumina or other species, for instance, Lewis acid sites, and ammonia can be adsorbed on such non-BAS. In addition, the observed the temperature peak maxima can be strongly affected by the conditions used for the measurement. The heat of adsorption can be estimated from

the temperature of the desorption peak using a simple kinetic model [21]. However, the desorption kinetics of crystalline materials are much complicated because of molecular interactions and readsorption [24]. The application of TPD is assumed that adsorption and desorption are in local equilibrium where diffusion limits the desorption process. However, this assumption is not valid since desorption and adsorption occur simultaneously with diffusion in these kind of microporous materials [21]. Therefore, using the TPD of ammonia experiment, strict quantitative analysis of the obtained profile is not possible.

2.3.8 Temperature Programmed Reduction (TPR)

TPR technique is used to determine appropriate reduction conditions for Ag-Cu bimetallic catalyst supported on SiO_2 and to study the interaction of s sample with a reducing agent [25]. The metal catalyst sample can be reduced to the metallic state in the presence of H₂ by increasing temperature slowly.

TPR experiments were also performed on the Altamira catalyst characterization system same as TPD experiments (Altamira Instruments, AMI-200ip). About 100 mg of sample was loaded into the U-shape quartz packed with quartz wool (Quartz Plus). The corresponding protocol for TPR is presented in Table 2.2. The effluent from the reactor passed through a TCD (Ar reference gas) to measure the consumption of H_2 as a function of temperature.

No.	Ramp	Rate	Treatment gas	Flow rate	Procedure
	to	ivate	Treatment gas	riow rate	Troccure
1	393 K	+10 K /min	$25\% O_2$ in Ar	20cc/min	
2	393 K		$25\% O_2$ in Ar	20cc/min	Dehydrate for 60 minutes
3	303 K	-5 K /min	Ar	20cc/min	Cool down
4	973 K	+10 K /min	5% H_2 in Ar	20cc/min	Reduction in H ₂

Table 2.2 Temperature-programmed reduction protocol for AgCu bimetallic catalyst.

2.3.9 Inductively Coupled Plasma Analysis (ICP)

Inductively coupled plasma (ICP) analysis can be used to measure the elemental composition of samples. Samples are first dissolved, and then sprayed into a high-temperature argon plasma (~10,000 K) where they are quickly vaporized. Collisions with Ar atoms within the plasma excite the atoms within the sample, and their subsequent relaxation results in the emission of photons at element-characteristic energies. The concentration of certain elements within the sample can be quantified by the intensity of these photons [26]. ICP was performed by Galbraith Laboratories (Knoxville, TN).

2.4 Reactor Design & Experimental Protocols

2.4.1 Thermal treatment of zeolites for catalysis

The samples were treated in a quartz plug flow reactor (ID = 5 mm). To support the sample in the center of the reactor, quartz wool was placed near the bottom of the reactor tube and quartz chips were located between quartz wool and the sample. The reactor was heated using a cylindrical furnace (C5232, Hoskins MFG. CO.) and the temperature was controlled using a temperature controller (NC 74000, Omega Engineering). The zeolites were first heated at 673 K for 2 h to remove water in the samples. To obtain acid catalysts, the samples were then heated at 773 K for additional 3 h (treatment 1). The dehydroxylated catalysts were prepared by heating the samples once again at dehydroxylation temperature (873, 973, or 1073 K) for 1.5 h (treatment 2). After treatments, the reaction temperatures varied from 733 K to 803 K. Treatment protocols are illustrated in Figure 2.6.



Figure 2.6 Temperature protocols for two treatments; 1) treatment 1 for acid catalyst and 2) treatment 2 for dehydroxylated catalyst

2.4.2 Thermal treatment of zeolites for naphthalene adsorption experiments

A total of ~0.25g of the ammonium-exchanged form of zeolite is put in a quartz vertical tube reactor (ID = 19 mm), designed to flow gas through the sample space. The reactor has a porous (4-15 μ m) fritted disc in the middle where the sample is placed (Figure 2.7). The reactor is heated by using a ceramic radiant heater (Omega

Engineering, OMEGALUX® CRFC). A gas manifold system allows an inert (Ar) and/or oxygen gas to flow through the reactor. The sample is first dehydrated at 473 K in an Ar gas for 2 hours, and then the ammonium ions are decomposed to form acid zeolites by heating the sample at 723 K in Ar for 4 hours.

After the sample treatment process, the samples are cooled down to room temperature in an inert atmosphere. A weighed amount of naphthalene (~0.005g, Sigma Aldrich, \geq 99.7%), corresponding to ~1 molecule per unit cell of zeolites, is mixed with the treated sample using a mortar and pestle in a glove bag (Glove bagTM Inflatable Glove Chambers) filled with dry argon. To create an inert atmosphere in the glove bag, the inert gas is repeatedly filled and purged into and from the glove bag. After this step, UV/visible spectra are measured at 0.5 nm of resolution over a wavelength range of 220 - 850 nm. These experiment steps are depicted in Figure 2.8.



Figure 2.7 Diagram of the reactor used for thermal treatment



Figure 2.8 Experimental protocol for detecting the generation of radical cations

2.4.3 Reactor Setup for Propane Conversion

The reactor, gas connection, and GC are connected as depicted in Figure 2.9. The reactant gases, including inert gases and alkanes, flow through the quartz tube reactor heated at the specified temperature. The temperature inside the reactor is monitored by a K-type thermocouple and changed by a temperature controller (NC74000, Omega Engineering). Ammonium form of catalysts on the quartz bed inside the reactor is heated to 473 K for dehydration, and then it is heated to 753 K to convert the ammonium form to the acid form of the zeolite. Additionally, the SSZ-13 samples are treated at 773 K (treatment 1) and 1073 K in an inert gas flow (treatment 2), respectively. After each treatment, the temperature is lowered to 700 K for the reaction with propane. The products, produced by contacting the reactant gas to the treated catalyst, are separated and recorded by GC.



Figure 2.9 GC system setup used to study propane dehydrogenation and propene (C3) hydrogenation processes.

2.4.4 Reactor Setup for Furfural Conversion

The reactor system is illustrated in Figure 2.10. The furfural is vaporized before contacting the catalyst by heating the gas line. The furfural feed is loaded in a 1 ml volume syringe (Gastight syringe[®], Hamilton) and controlled by using a programmable syringe pump (NE-1000, New Era Pump Systems. Inc.) with the rate of 0.1 ml/min. The stainless steel tube reactor (ID ~ 1.27 cm) is heated at the specified temperature using vertical tube furnace (Applied Test System Series 3210). The temperature inside the reactor is monitored by a K-type thermocouple and changed by a temperature controller (EZ-ZONE[®] PM-6, WATLOW). Approximated 50 mg of catalysts on the quartz wool bed inside the reactor is heated to 523 K in H₂ for

reduction, and then it is cooled down to the reaction temperature (483 K). The products are separated and recorded by GC. The pipe line between the reactor and GC is also heated at 483 K to prevent the effluent from being liquefied.



Figure 2.10 GC system setup used to study furfural conversion

2.5 Summary

The experimental methods and techniques used in this thesis were briefly described. MFI type zeolites ([A1]ZSM-5, [Fe]ZSM-5, [Si]ZSM-5) have been synthesized mainly, as well as CHA, *BEA types zeolites and Ag-Cu bimetallic catalyst on SiO₂. The important characterization techniques were illustrated, such as XRD, SEM, UV/Vis, TPD. GC and reactor setting, which are used to measure catalytic activity and selectivity, were also demonstrated.

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Chapter 3

EFFECT OF THERMAL TREATMENT ON THE CATALYTIC PROPERTIES OF SSZ-13 ZEOLITES FOR THE PROPANE REACTION¹

3.1 Introduction

In this chapter we demonstrated the catalytic properties of SSZ-13 zeolite samples treated at different temperatures for catalytic conversion of hydrocarbons. Understanding the effects of post-synthesis zeolite treatments, including high temperature, has been important for improving and modifying the catalytic properties [1-11] of zeolites in general. High-temperature treatment of zeolites, normally above 873 K, leads to the thermal decomposition of Brønsted acid sites (BAS), Si-O(H)-Al, by a process called dehydroxylation [12, 13]. The IR absorption band of the OH-groups of the BAS is detected in the range of 3600 – 3660 cm⁻¹ in the IR spectra of dehydrated samples [3, 14], and the concentration of the BAS can be estimated based on the relative intensity of this signal. It has been shown that samples treated at high temperatures have new chemical properties, including their ability to extract electrons from adsorbed species. For example, xanthene, iminostilbene, fluorene, 2,5-dimethylhexa-2,4-diene, biphenyl, and naphthalene [15-18] form radical cations upon adsorption on pretreated zeolites. It is also important to understand the properties of dehydroxylated zeolites because high temperatures are found in important industrial

¹ This work is being prepared for publication in 2014.

processes, such as in the regenerator of a fluidized catalytic cracking (FCC) unit or in the catalytic converters of automobiles.

In a dry inert atmosphere, there are two mechanisms by which the BAS dehydroxylation can proceed. In the heterolytic mechanism, the dehydroxylation proceeds through dehydration of BAS leading to the formation of water and Lewis acid sites (LAS), as illustrated in Scheme 1.4 [12, 13, 19]. In the homolytic mechanism (Scheme 1.5), the hydrogen atoms of the acid sites are lost as $H^{,}$, that is hydrogen atom, leading to the formation of an oxidized species on the zeolite surface. Nash et al. observed the production of hydrogen during dehydroxylation processes [19] corroborates that dehydroxylation could proceed through a homolytic mechanism in high-silica zeolites. The electron deficient sites formed by dehydrogenation of BAS (Scheme 1.5) can have redox properties that may impact the catalytic properties of the sample [19]. More detailed investigation of the sites generated after dehydroxylation has been difficult because these sites are EPR silent [16] and do not appear to have any well-defined UV/Vis or IR signature. We have shown that the sites that are generated after dehydroxylation have the ability to extract a single electron from a neutral organic molecule, such as naphthalene, forming radical cations [4]. In addition, long-lived electron-hole pairs are formed by migration of electrons from the zeolite framework to the radical cations. This observation suggests that the new sites could lead to a catalytic activation of adsorbed species by a redox mechanism instead of the typical protolytic mechanism.

The activation of small alkanes has been used frequently as a model reaction, because the cleavage of the C-C and C-H bonds in the hydrocarbon is a problem of both scientific and technological interest. Alkane activation on acid sites in zeolites

can proceed through bimolecular and monomolecular pathways. The bimolecular pathway involves hydride transfer between an alkane and an adsorbed carbenium ion when the concentration of surface species is high. In contrast, the monomolecular pathway (protolytic mechanism), involving the formation of alkanium-like ions, [20-28] is kinetically dominant at high temperatures (~773 K), low alkane partial pressure, and low conversion (<2%). The propane reaction rates and selectivity over H-ZSM-5 before and after dehydroxylation were investigated [3], showing comparable catalytic rates for propane activation but different selectivity and different activation energies [3]. In the monomolecular propane reaction, the reaction proceeds only through two channels, i.e., cracking and dehydrogenation. While acid catalysts have higher propane cracking selectivity than dehydrogenation by a factor of about three, the catalysts after dehydroxylation show similar cracking and dehydrogenation rates [3]. Reduced apparent activation energies for cracking (from 184 kJ/mol to 144 kJ/mol) and for dehydrogenation (from 187 kJ/mol to 127 kJ/mol) are also observed [3]. These changes indicate that the new sites catalyze the hydrocarbon conversion through a different reaction mechanism; a redox mechanism is a potential path for the reaction. Deuterium-labeled propane (C_3D_8) was used to evaluate the redox mechanism by measuring relative reaction rates of cracking and dehydrogenation ($r_{C_3H_8}/r_{C_3D_8}$) before and after dehydroxylation [3]. The relative reaction rate of cracking is not affected by the deuterium label, while that of dehydrogenation is increased from 1.13 to 3.5 [3]. This change in the relative reaction rate of dehydrogenation is consistent with radical cation chemistry [23]. The complexity of the ZSM-5 zeolite catalysts (12 distinctive tetrahedral sites) precludes complete understanding of the structure of the active sites.

The presence of 12 distinctive T-sites results in different turnover rates for the monomolecular propane conversions [29].

In this chapter, SSZ-13 (CHA) was used to activate propane because SSZ-13 has only one topologically distinct tetrahedron site and only four non-equivalent oxygen atoms [30, 31] in the structure (Figure 3.1). SSZ-13 is a promising solid catalyst for the methanol-to-olefins (MTO) process due to its unique shape-selectivity [32-37]. Adsorption capacity of SSZ-13 at ambient temperature and pressure also makes it as a promising adsorbent for CO₂ capture [38]. Copper exchanged SSZ-13 is a promising catalyst for selective catalytic reduction of NOx with ammonia. The Cu-SSZ-13 has high activity for NH₃-SCR and shows high nitrogen formation selectivity [39, 40]. In this chapter, we report the catalytic reaction rates and selectivity over SSZ-13 with different Si/Al ratios (6 and 12) after thermal treatments for the monomolecular propane reaction. The samples treated at different temperatures were characterized by XRD, N₂ adsorption isotherm, TPD, and ²⁷Al and ²⁹Si solid-state NMR. The product-distribution and the kinetic analysis indicate that different types of active sites are generated by thermal treatments. The catalytic properties of newly generated sites are also different for the samples with different Si/Al ratios. In case of SSZ-13 with Si/Al of 6, the selectivity changed dramatically with just 50 K of change in the treatment temperature from 773 K to 823 K, which is "normal" calcination temperature for acid zeolites prior to reaction tests. The activation energy does not change despite this drastic selectivity change. In case of SSZ-13 with Si/Al of 12, the selectivity and activation energy changed gradually with the treatment temperature, indicating generation of different active sites after thermal treatments. Further work is still necessary to establish the molecular structure of these new sites.



Figure 3.1 Equivalent tetrahedral sites in SSZ-13 structure [41]

3.2 Experimental Section

SSZ-13 samples with Si/Al ratios of 12 and 6 were synthesized, and the characterization techniques (XRD, SEM, N₂ adsorption, TPD, NMR) were employed to measure the properties of catalysts, as described in Chapter 2. The thermal treatment protocol, the propane reaction procedure, and the GC analysis are also demonstrated in Chapter 2.

3.3 Effect of Treatment on the Structure of the Zeolite Samples

3.3.1 XRD and N₂ adsorption

The XRD patterns for the samples with two different Si/Al ratios indicate that the calcined SSZ-13 samples (treatment 1) have high crystallinity (Figure 3.2) and are free of any crystalline and amorphous impurities. The full widths at half maximum

(FWHM) of the (-210) and (-311) reflections ($2\theta = 20.6^{\circ}$ and 30.7° , respectively) were 0.21° and 0.26° for SSZ-13-12 after treatment1. The FWHM of (-210) reflection did not change, while the (-311) reflection FWHM increased by approximately 11 % (from 0.26° to 0.29°) after treatment 2 (1073 K). However, the SSZ-13-12 sample was still highly crystalline after treatment 2 (1073 K), because structural damage and amorphous phase (background) other than slightly-broadened XRD peaks were not observed. Conversely, the XRD pattern of the SSZ-13-6 sample after treatment 2 showed reduced peak intensities and reveals the presence of a (minor) amorphous phase in the background, while the XRD pattern of the SSZ-13-6 treated at 873 K was still highly crystalline. The FWHM of the (-210) reflection ($2\theta = 20.7^{\circ}$) for SSZ-13-6 increased stepwise, i.e., from 0.18° to 0.19°, from 0.19° to 0.20°, and 0.20° to 0.24° as the treatment temperature increased from 773 K (treatment 1) to 873K, from 873K to 973 K, and from 973 K to 1073 K (treatment 2), respectively. The FWHM of the (-311) reflection $(2\theta = 20.7^{\circ})$ for SSZ-13-6 also increased from 0.26 to 0.29, from 0.29 to 0.31, and from 0.31 to 0.33. The effective particle size of crystal, calculated using the Scherrer equation [42], of the (-210) reflection for SSZ-13-6 decreased from 46.9 to 44.4, from 44.4 to 42.2, and from 42.2 to 35.1 nm as the treatment temperatures increased from 773 K (treatment 1) to 873K, to 973 K, and to 1073 K (treatment 2). For both samples, a slight shift is observed after treatment 2, indicating the change in the unit cell parameters.



Figure 3.2 XRD patterns of (a) H-SSZ-13-12 and (b) H-SSZ-13-6: calcined vs. thermally treated samples.

The micropore volumes of H-SSZ-13-12 and H-SSZ-13-6 after treatment 1 were 0.26 cm³/g and 0.28 cm³/g, respectively, showing good agreement with the expected values based on the chabazite structure and previous reports [43]. Table 3.1 shows that the volume of micropores in SSZ-13-12 decreased by 5% after treatment 2; there was no substantial structural damage even if the decomposition of BAS led to the minor reduction of the volume of the micropores. After heating the SSZ-13-6 sample to 873 K, the microporous volume did not decrease, but after heating the SSZ-13-6 samples to 973 K and 1073 K (treatment 2), there was significant reduction in the microporous volume, which is evidence of structural damage. XRD analysis and N₂ adsorption analysis show then that the sample with Si/Al ratio of 6 (SSZ-13-6) is less thermally stable and reveal some collapse of the crystalline structure at temperatures over 973 K. Consequently, the maximal treatment temperatures were 873 K for SSZ-13-6 sample and 1073 K for SSZ-13-12 sample.

Table 3.1 Micropore volumes (cm^3/g)

Treatment protocol	H-SSZ-13-12	H-SSZ-13-6
Treatment 1	0.257	0.275
Treated at 873 K	-	0.274
Treated at 973 K	-	0.192
Treatment 2	0.240	0.178

3.3.2 Ammonia TPD experiment

The thermal conductivity detector (TCD) signal profiles of ammonium desorption from the samples are illustrated in Figure 3.3. After treatment 2, the

amount of ammonia desorbed clearly decreases on SSZ-13-12 (Figure 3.3(a)); a large fraction of the Brønsted acid sites involved in ammonia adsorption was destroyed by heating to 1073 K. In addition, the position of the peak maximum in the signal profile shifted to a lower temperature from 742 K to 705 K. The temperature of the peak maximum is affected by the number of acid sites in the zeolite, the change in the zeolite structure, the carrier gas flow rate, or the amount of the sample [44]. Thus, the reduction of peak maximum temperature reflects a smaller number of acid sites after treatment 2. It has been also reported that ZSM-5 after thermal dehydroxylation at 1093 K exhibited much lower TCD trace than ZSM-5 treated at 823 K [3], similarly indicating a reduction in the number of BAS during dehydroxylation and the formation of non- or weakly interacting sites with ammonia. The sites produced in SSZ-13-12 sample by treatment 2 are then only mildly acid and do not strongly adsorb ammonia. For SSZ-13-6, the TCD signal of the sample treated at 873 K did not change after treatment at 873 K (Figure 3.3(b)). The amount of ammonia desorbed decreased after treatment 2 due to dehydroxylation or structural damage and the position of the peak maximum cannot be determined.



Figure 3.3 Ammonia TPD for (a) SSZ-13-12 after treatments 1 (black) and 2 (grey), and (b) SSZ-13-6 after treatment 1 (black), treated at 873 K (grey), and after treatment 2 (light grey)

3.3.3 Solid-State ²⁷Al and ²⁹Si MAS NMR Analysis

The local structure of aluminum species in zeolites can be determined using 27 Al MAS NMR measurements (Figure 3.4). The resonance band at around 60 ppm is assigned to the Al atoms in tetrahedral coordination, and the additional band around 0 ppm is normally assigned to *extraframework* Al in octahedral coordination [45-50]. Figure 3.4 shows that the NH₄-form of SSZ-13-12 has predominantly tetrahedral Al sites. Extraframework octahedral Al sites were generated in SSZ-13-12 sample after treatment 1, but this fraction decreased after treatment 2. A broad band was detected between 50 and 40 ppm in SSZ-13-12 after treatment 2. This broad band is related to extraframework penta-coordinated Al sites. The extraframework Al sites can be related to dealumination of the samples [47, 50]. SSZ-13-6 sample also showed the peak at 60 ppm in the NH₄-form, and a peak at around 0 ppm was generated after thermal treatments. The peak at ~ 60 ppm becomes quite broad and the fraction of extraframework octahedral Al sites increases after treatment 2.

²⁹Si MAS NMR spectra of NH₄-form and thermally treated samples are depicted in Figure 3.5. The three different resonances are assigned to the different Si(nAl) environments. The resonances at around -110 ppm, -104 ppm, and -98 ppm are related to Si4, Si3Al1, and Si2Al2 sites, respectively [45, 46, 51]. The Si/Al compositions of the crystalline framework can be estimated from the relationship;

$$Si / Al = \sum I_{Si(nAl)} / 0.25 \sum nI_{Si(nAl)}$$
 (3.1)

where $n = 0 \sim 4$, $I_{Si(nAl)}$ is the area of the peak for the Si environment. The estimated Si/Al ratios of SSZ-13-12 samples were 13.1, 12.1, and 12.2 for NH4 form of sample, the sample after treatment 1, and the sample after treatment 2, respectively (Table 3.2).

The Si/Al ratios show little reduction with increments in treatment temperature, but the ratios are in a reasonable range of batch composition of the synthesis procedure. The Si/Al ratios of the SSZ-13-6 sample after treatment 1 and after treated at 873 K were all 6.4, almost same as the ratio of NH₄-form SSZ-13-6. However, the Si/Al ratio for the SSZ-13-6 sample after treatment 2 increases to 10.9 (Table 3.2), indicating that framework Al atoms are lost after the treatment. From ²⁷Al MAS NMR measurements, the increase of Si/Al ratio of the sample after treatment 2 can be related to the generation of extraframework octahedral Al sites. At the same time, the increase in Si/Al ratio could be related to the structural damage of the framework of SSZ-13-6 sample because of low thermal stability.



Figure 3.4 ²⁷Al NMR of a) SSZ-13-12 samples; NH₄-form, treated at 773 K and 1073 K, b) SSZ-13-6 samples; NH₄-form, treated at 773 K, 873 K, and 1073 K.



Figure 3.5 ²⁹Si NMR of a) SSZ-13-12 samples; NH₄-form, treated at 773 K and 1073 K, b) SSZ-13-6 samples; NH₄-form, treated at 773 K, 873 K, and 1073 K

	Treatment	Si4	Si3Al1	Si2Al2	Si/Al ratio
	NH ₄ -form	0.73	0.24	0.03	13.1
SSZ-13-12	Treatment 1	0.68	0.31	0.01	12.1
	Treatment 2	0.66	0.32	0.02	12.2
	NH ₄ -form	0.42	0.52	0.07	6.2
887 12 6	Treatment 1	0.44	0.49	0.07	6.4
552-15-0	Treated at 873 K	0.44	0.49	0.06	6.4
	Treatment 2	0.69	0.30	0.02	10.9

Table 3.2 Normalized relative peak area from the ²⁹Si MAS NMR of SSZ-13 samples

3.4 Effect of Treatment Temperature on the Monomolecular Propane Reaction

3.4.1 Reaction Rates and Selectivity

The SSZ-13-12 samples were treated at five different temperatures; 773 K (treatment 1), and 823 K, 873 K, 973 K, and 1073 K (treatment 2). After being treated at temperatures above 873 K, the samples showed very high initial reaction rates of propane, an early period of deactivation, and then stabilization. In contrast, reaction rates were stable for the catalyst treated at 773 K only. For the samples treated at higher temperatures, reaction rates were recorded after the rates became stable. Conversions under 2% indicate that the reactions were performed under differential conditions; this is also verified by the stoichiometric ratio of methane to ethylene for cracking channel and of hydrogen to propylene for dehydrogenation channel. Figure 3.6 shows the reaction rates of the cracking and the dehydrogenation channels at the

reaction temperature of 773 K over SSZ-13-12 and SSZ-13-6 samples treated at different temperatures. The acid form of SSZ-13-12 (after treatment 1) showed higher reaction rates for the cracking channel (0.40 mol/s/g-cat $\times 10^7$) than for the dehydrogenation channel (0.17 mol/s/g-cat $\times 10^7$) and a cracking-to-dehydrogenation ratio of ~2.39 (Table 3.3).

The total reaction rates over the SSZ-13-12 samples treated at 823, 873, 973, and 1073 K were similar to the reaction rates observed over the SSZ-13-12 after treatment 1 (773 K), despite a slight increase in reaction rates over the sample treated at 823 K. Earlier reports [3, 4] and the TPD experiment reported above (Figure 3.3) have found that the number of BAS decreases by dehydroxylation. It is notable that reaction rates of SSZ-13-12 after thermal treatments are similar to the rates of the samples treated at low temperature. This implies that new active sites, different from BAS, can be generated and can catalyze the propane conversion. The change in cracking and dehydrogenation selectivity showed noticeable changes even though the total reaction rates over SSZ-13-12 samples treated at different temperatures barely changed. For the SSZ-13-12 samples, dehydrogenation selectivity increases step by step as the treatment temperature increased, and the reaction rates of the dehydrogenation channel become identical to the reaction rates of the cracking channel (0.32 mol/s/g-cat $\times 10^7$) at 973 K. It can be assumed that the proportion of sites different from BAS increases stepwise with treatment temperature, and that the mechanism of reaction changed beginning at the temperature of 973 K.



Figure 3.6 Reaction rates for cracking and dehydrogenation of propane at reaction temperature 773 K over SSZ-13-12 and SSZ-13-6 treated at different dehydroxylation temperatures.

Table 3.3 Cracking-to-dehydrogenation ratios at reaction temperature 773 K for SSZ-13-12 and SSZ-13-6 treated at different temperatures.

Treatment Temp., K	773 (Treatment 1)	823	873	973	1073 (Treatment 2)
SSZ-13- 12	2.39	1.88	1.35	1.00	1.03
SSZ-13-6	2.59	0.99	0.98	-	-



Figure 3.7 Log scale reaction rates for cracking and dehydrogenation of propane over a) SSZ-13-12 after the treatments 1 and 2 and b) SSZ-13-6 after treatment 1 and treated at 873 K.

SSZ-13-6 samples were treated at 773 (treatment 1), 823, and 873 K. The temperatures of 973 and 1073 K were not employed because of the samples low thermal stability as discussed above. The acid form of SSZ-13-6 (after treatment 1) also showed higher reaction rates for cracking (0.58 mol/s/g-cat ×107) than for dehydrogenation (0.22 mol/s/g-cat ×107), resulting in cracking-to-dehydrogenation ratios ~2.59 (Table 3.3). The SSZ-13-6 treated at 823 exhibited a little higher total reaction rate, and the SSZ-13-6 treated at 873 K showed similar total reaction rates, compared to that over the SSZ-13-6 after treatment 1 (773 K). The SSZ-13-6 samples showed very low reaction rates after treatment at 973 K and 1073 K (data not shown), as expected given that their structure was damaged by the treatment (see above).

The SSZ-13-6 samples showed drastic changes in selectivity with small change of treatment temperatures. After a pretreatment temperature of 823 K, the cracking-to-dehydrogenation ratio decreased from 2.59 to 0.99 with just 50-degree increase in the treatment temperature (Table 3.3). This drastic change in selectivity without apparent decomposition of BAS (as shown by the ammonia TPD experiments) cannot be explained at this time.

In Figure 3.7, the reaction rates of cracking and dehydrogenation over SSZ-13-12 and SSZ-13-6 were compared for pretreatment temperature of 773 K and for the respective highest treatment temperatures (1073 K for SSZ-13-12 and 873 K for SSZ-13-6). The cracking rates decreased slightly after thermal treatment for both samples, but dehydrogenation rates were significantly increased. Note that the change in selectivity after complete dehydroxylation is similar for both samples even if the treatment temperatures for SSZ-13-12 and SSZ-13-6 are different

3.4.2 Reaction Mechanism

The reaction rates and selectivity patterns suggest that the reaction mechanism on the pretreated SSZ-13 samples is different from the typical protolytic mechanism on the acid catalysts (treatment 1). An identical trend of selectivity change of the propane reaction over H-ZSM-5, before and after dehydroxylation, has been reported [3]. The formation of redox sites and Lewis acid sites has a role in the reactivity and selectivity of the zeolite samples [3] and that these sites have the ability to extract electrons from neutral organic materials, such as naphthalene [4].

A kinetic analysis of the data has been carried out by using following relationships:

$$r = k_3 \frac{K_1 P_{C_3 H_8}}{1 + K_1 P_{C_3 H_8} + K_4 P_{C_3 H_6} + K_4 P_{C_2 H_4}}$$
(3.2)

$$r = k_3 K_1 P_{C_3 H_8} = k_{app} P_{C_3 H_8}$$
(3.3)

Under the conditions for monomolecular propane reaction, such as low partial pressure, low conversion, and high reaction temperatures, the rate expression can be simplified to a first-order rate equation (Eq. 3.3). The apparent activation energies are reported in Table 3.4. For H-SSZ-13-12 after treatment 1, the activation energy for cracking is 170 kJ/mol, a little lower than that for dehydrogenation (174 kJ/mol). H-SSZ-13-6 after treatment 1 also exhibited higher activation energy for dehydrogenation (208 kJ/mol) than that for cracking (179 kJ/mol). A higher activation barrier is expected for dehydrogenation than for cracking because of the relative stabilities of the protonated C-H and C-C bonds in the propane molecule [30].

The difference of the activation energy ($E_{a,meas}$ for cracking $< E_{a,meas}$ for dehydrogenation) for the acid catalyst was consistent with previous reports. At the same time, the activation energy values showed good agreement with the experimental values for ZSM-5 samples [3, 23] and the values determined from the simulation of the propane reaction over the acidic chabazite [51, 52].

Traatmont	Measured activation energy, $E_{a,meas}$				
Tean K	SS	SZ-13-12	SSZ-13-6		
Temp., K	Cracking	Dehydrogenation	Cracking	Dehydrogenation	
773 (treatment 1)	170	174	179	208	
823	170	161	178	206	
873	165	158	179	198	
973	114	84			
1073 (treatment 2)	146	114			

Table 3.4 Measured activation energies (kJ/mol) for SSZ-13-12 and SSZ-13-6 treated at different temperatures.

The activation energy for SSZ-13-12 samples shows a stepwise decrease as the treatment temperatures increased (146 kJ/mol and 114 kJ/mol, for cracking and dehydrogenation, respectively), consistent with the change in selectivity. For the SSZ-13-12 after treatment 2, the activation energy for cracking was greater than that for dehydrogenation. The differences in activation energy indicate that different intermediates are generated during the propane conversion on the SSZ-13-12 sample after treatment 2 compared to the sample after treatment 1. The NMR and ammonium TPD experiments indicate that the selectivity change in SSZ-13-12 is related to decomposition of BAS, instead of formation of extraframework aluminum structures. In a previous report, different activation energies were also observed for propane

conversion over ZSM-5 before and after thermal treatments [3]. It was suggested that redox sites are generated in ZSM-5 after dehydroxylation, sites that can extract an electron from adsorbed neutral molecules [3]. Here, the activation energy for SSZ-13-12 was significantly lower after the treatment 2, as in the ZSM-5 case. We conclude that new sites must be generated by the thermal treatment and their effect increases as the treatment temperature increases because more BAS are decomposed. Consequently, the properties of the thermally treated catalysts lead to greater selectivity for the dehydrogenation channel in the propane conversion.

The proposed redox catalytic cycle over dehydroxylated SSZ-13-12 sample is depicted in Scheme 3.1. An electron is extracted from the propane molecule, resulting in the formation of a propane radical cation. The propane radical cation then dissociates into the propylene radical cation with hydrogen, or the ethylene radical cation with methane. The reaction cycle is completed after the electron is given back to the propylene or ethylene radical cations. Note that activation energy at the treatment temperature of 973 K is exceptionally lower than the values observed at other temperatures. It is possible that 1) some new sites, which have a different ability of the catalytic reaction than redox sites or LAS, were generated at 973 K but disappeared at 1073 K, and 2) some specific portion of the newly-generated sites may affect high dehydrogenation selectivity and the kinetics of the reaction.

The activation energies of SSZ-13-6 treated at 823 K were indistinguishable from those of SSZ-13-6 after treatment 1 (the acid catalyst). The activation energy of the dehydrogenation reaction decreased by \sim 10 kJ/mol (208 kJ/mol for SSZ-13-6 after treatment 1 to 198 kJ/mol for SSZ-13-6 treated at 873 K), while the values of the cracking reaction did not change. The change in selectivity with the same activation

energies in SSZ-13-6 samples can be related to thermal change in unit cell parameters of framework. When a sample is heated to remove the organic structure director, the unit cell volume increases at first and then starts to decrease with increasing temperature [53-55]. A confinement effect on selectivity of propane conversion (enhanced dehydrogenation) was also reported by Gounder [29, 56]. Contracted pores in the SSZ-13-6 samples likely lead to the cleavage of C-H bond rather than C-C bond of propane molecule. That leads to the enhanced selectivity toward dehydrogenation after thermal treatments without decomposition of BAS in the sample.



Scheme 3.1 Redox catalytic cycle for propane conversion over zeolite after high temperature treatment

3.5 Conclusions

Dehydrogenation can be enhanced over SSZ-13 (CHA) by high temperature thermal treatments. The structure-activity relationship of the SSZ-13 samples after thermal treatments is summarized in Table 3.5. Low thermal stability of SSZ-13-6 limited the pretreatment temperature to a maximum of 873 K. Therefore, thermal decomposition of BAS was not observed in the SSZ-13-6 sample at given treatment temperatures (823 and 873 K) even if the heterolytic mechanism is expected to be predominant due to locations of BAS close to each other. Instead, structural damage was observed for the samples after treated over 873 K. The reaction rates of the propane conversion were similar for the untreated catalyst and the thermally treated catalysts. However, SSZ-13-6 treated at 873 K showed higher selectivity in the dehydrogenation channel but identical kinetic parameters. The observed results indicate that the selectivity change is not a result of the generation of LAS or redox sites and the change in cell volume after thermal treatment may lead to the confinement effect, promoting C-H cleavage. Different measured activation energies were observed for the SSZ-13-12 sample treated at 1073 K despite of higher selectivity in dehydrogenation channel. The decreased activation energies and change in selectivity suggest the generation of different active sites other than BAS, in SSZ-13-12. After thermal treatments, LAS and the redox sites can be generated and could play an important role in the catalytic activity in the SSZ-13-12 sample. The observations in this work confirm the existence of different active sites other than BAS and their role of the catalytic activity in hydrocarbon conversion.

	SSZ-13-12		SSZ-13-6	
Structure change with	< 973 K	Partial dehydroxylation	< 973 K	Not changed
increase in treatment temperature	≥ 973 K	Dehydroxylation	≥ 973 K	Structural damage
Selectivity change	Gradually (773 to 973 K)		Drastically (773 to 823 K)	
Activation energy change	Decrease gradually		Not changed	
Assumed generated sites	Assumed enerated sites Redox sites (electron deficient sites) & Lewis acid sites		New sites or cell parameter change Structural damage (≥973 K)	

Table 3.5 Summary of effect of treatment temperatures on SSZ-13 samples

3.6 References

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Chapter 4

CATALYTIC DEHYDROGENATION OF PROPANE OVER IRON-SILICATE ZEOLITES²

4.1 Introduction

Zeolites contain tetrahedral Si⁴⁺ and Al³⁺ as framework atoms. In the acid form of aluminosilicate zeolites, the negative charge of the alumina tetrahedra ([AlO₄]⁻) is balanced by a proton (H⁺), forming a bridging hydroxyl group (Si-OH-Al) or Brønsted acid site (BAS). Other trivalent elements such as B³⁺, Fe³⁺, and Ga³⁺ can be used for isomorphous substitution of Al³⁺. Aluminosilicate zeolites are currently used for a number of industrially important Brønsted acid catalyzed reactions [1-6], and their Fecontaining counterparts are of interest for performing various reactions such as olefin oligomerization and isomerization of m-xylene [7-13]. Previous reports regarding the dehydrogenation of para- and ortho-ethyltoluenes have claimed that the reaction occurs on Fe atoms in the zeolite framework [12-14]. Kresnawahjuesa et al. reported that H-[Fe]ZSM-5 could catalyze olefin oligomerization, with less hydride-transfer and coke formation than H-[Al]ZSM-5 [8]. Propyl acetates were formed with high selectivity by acylation of propene over H-[Fe]ZSM-5 [7]. It was also reported that isomerization of m-xylene is catalyzed by BAS in Fe-containing zeolites, and the

 $^{^2}$ This chapter discusses the catalytic dehydrogenation of propane over iron-silicate zeolites, and it is based on a manuscript published at Journal of Catalysis in 2014.

conversion rates and selectivity are comparable to those exhibited by H-[Al] zeolites [10, 11].

The strength of acid sites can be measured using heats of adsorption of bases such as ammonia, pyridine, and acetonitrile. The heats of adsorption for ammonia and pyridine are similar for both H-[Fe] and H-[A1]ZSM-5 (145 kJ mol⁻¹ for ammonia and ~195-200 kJ mol⁻¹ for pyridine), and the heat of adsorption of acetonitrile for H-[Fe]ZSM-5 (95 kJ mol⁻¹) is slightly less than that for H-[A1]ZSM-5 (110 kJ mol⁻¹) [9]. These heats of adsorption suggest that the deprotonation enthalpy (DPE) of the H-[A1] zeolites and H-[Fe] zeolites is similar and the strength of acid sites is also similar. These reaction results over H-[Fe] zeolites with similar acidity than H-[A1] zeolites, lead to the question of whether typical protolytic chemistry, responsible for catalytic activity in the conversion of hydrocarbons over H-[A1] zeolites, is also the dominant reaction mechanism on H-[Fe] zeolites.

On the other hand, the measured DPE depends on the identity of the probe molecules and the proton location in the framework [15], and it leads to contradictory conclusions about the acid strength of H-[Fe]ZSM-5. A. Jones et al. recently reported that H-[Fe]ZSM-5 has higher deprotonation energy (DPE) than H-[A1]ZSM-5 by 23 kJ mol⁻¹ based on DFT calculation and CH₃OH dehydration reaction [16]. Since the rate constants of CH₃OH dehydration depend on acid strength and solvation by van der Waals interactions with the surrounding void environment, the rate constants can be the direct index of the acid strength of catalysts [16]. The results in their report would lead to higher activation energies for H-[Fe]ZSM-5 than H-[A1]ZSM-5.

Conversion of small alkanes has been used frequently as a model reaction because the cleavage of C-C and C-H bonds in hydrocarbons is a problem of fundamental scientific interest. Product distributions tend to be simple, and the results are easy to model and quantify. Alkane activation on acid sites in zeolites can proceed through bimolecular and monomolecular pathways. The bimolecular pathway involves hydride transfer between an alkane and an adsorbed carbenium ion when the concentration of surface species is high. In contrast, the monomolecular pathway (protolytic mechanism), involving the formation of alkanium-like ions [4, 17-21], is kinetically dominant at high temperatures (~773 K), low alkane partial pressure, and low conversion (<2%). The monomolecular alkane reaction proceeds through only two reaction pathways: cracking and dehydrogenation. Through the protolytic mechanism, H-[A1]ZSM-5 samples exhibit higher selectivity for cracking of propane than for dehydrogenation by a factor of about three [22]. In contrast, dehydrogenation selectivity is enhanced (cracking-to-dehydrogenation ratio ~1) in H-[A1]ZSM-5 after thermal dehydroxylation [22]. Lower apparent activation energies for cracking (from 184 kJ mol⁻¹ to 144 kJ mol⁻¹) and for dehydrogenation (from 187 kJ mol⁻¹ to 127 kJ mol⁻¹) are also observed [22].

In this chapter, we investigate the catalytic activity and selectivity for the monomolecular propane reaction over H-[Fe]ZSM-5 with different Si/Fe ratios (26 and 48) and over H-[Fe]beta zeolite (Si/Fe ratio, 15). The migration of Fe species from framework to extra-framework positions was monitored using UV/Vis spectroscopy and using the volume of the unit cell determined using XRD patterns. Conversion of propane resulted in a high selectivity to propene on H-[Fe] zeolites with lower activation energies when compared to H-[Al] zeolites. The results suggest that a redox mechanism is a plausible explanation for the hydrocarbon conversion on [Fe] zeolites reported here, as had been hypothesized earlier for dehydroxylated Al-containing

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zeolites [22, 23]. The viability of [Fe] zeolite for dehydrogenation of propane was examined and compared to chromia catalysts.

4.2 Experimental Section

4.2.1 Synthesis of zeolites

[Fe]ZSM-5 with two Si/Fe ratios of 26 and 48, [Fe]beta with Si/Fe of 15, [Al]ZSM-5 with Si/Al ratio of 26, and [Si]ZSM-5 (silicalite-1) were prepared using the same protocols described in Chapter 2. In addition, a chemical vapor deposition method (by subliming FeCl₃) was used to obtain iron clusters and/or iron oxide particles incorporated in the structure of the [Si]ZSM-5 samples [24, 25]. For the ionexchange with NH₄ cations, 1 g of the sample was mixed with 500 ml of aqueous solutions of NH₄NO₃ (0.1 M) and stirred at room temperature overnight. The samples were then filtered and washed with DI water three times. For sodium exchange the protocol was the same except that ~0.1 g of the zeolite (recovered from the reactor) was used for the ion exchange.

4.2.2 Characterization

Powder X-ray diffraction (XRD) patterns were collected on a Phillips X'Pert X-ray diffractometer using CuKα radiation. The samples were mixed with silicon standard (10-20 wt%) to correct the peak positions, and the UnitCellWin program was used to calculate unit cell volumes of the samples from the corrected XRD data as reported by Holland [26, 27]. Energy-dispersive X-ray (EDX) analysis was obtained on JEOL JSM 7400F scanning electron microscope (SEM) to measure the elemental

composition of the zeolites. The elemental composition was also measured with inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis (Galbraith Laboratories, TN). The micropore volumes of samples were determined from N₂ adsorption isotherms measured using a Micromeritics ASAP 2020 instrument. Before adsorption of N₂, the samples were degassed at 623 K for one day using an inhouse-built silica tube. UV/Vis spectra of the samples were collected by using UV/Vis spectroscopy (Jasco V-550) with a diffuse reflectance cell. Reflectance measurements converted to the Kubelka-Munk function:

$$F(R) = (1-R)^{2} / 2R = K / S$$
(4.1)

where, R is the ratio of the diffuse reflectance of the sample to that of a reference material (BaSO₄, Sigma-Aldrich), K is the absorption coefficient, and S is the scattering coefficient.

4.2.3 Measurement of Catalytic Rates

About 70 mg of zeolite was transferred to a quartz tube reactor (ID = 5 mm). To support the sample in the center of the reactor, quartz wool was placed near the bottom of the reactor tube and quartz chips were located between quartz wool and the sample. The reactor was heated in a cylindrical furnace (C5232, Hoskins Mfg. Co.). A temperature controller (NC 74000, Omega Engineering) and a thermocouple (type K, Omega Engineering) inserted in the quartz tube reactor were used to control temperatures of the reactor. The samples were first heated at 473 K for 2 hours to remove water and then heated at 753 K for 3 hours to obtain H-form samples under N₂

(ultra high purity grade, Matheson) flow of 100 sccm. The reaction temperature varied from 733 K to 803 K. The total flow rate of the reactant gas, containing 5 mole % of propane (research grade, Matheson) diluted in N_2 , was 80 sccm in all experiments. The reactor effluent was analyzed using gas chromatography (GC, Shimadzu 2014). A molsieve column was used for separation and eluted into a thermal conductivity detector (TCD) for H_2 and N_2 quantification and a RT-alumina column was connected to a flame ionization detector (FID) for hydrocarbons.

For the propane reaction at higher reaction conversions, the amount of sample was increased to 230 mg and the total flow rate decreased to 10 sccm, containing about 3~4 % of propane. The product distributions were analyzed using GC at reaction temperatures of 753 K and 803 K.

4.3 Iron Atoms in As-made, Calcined, and Steamed Samples

Bulk Si/Fe ratios of the H-[Fe]ZSM-5 were determined to be 26 and 48 (H-[Fe]ZSM-5 (26) and H-[Fe]ZSM-5 (48)) and Si/Fe ratio of H-[Fe]beta was 15 (H-[Fe]beta (15)) by ICP-AES analysis (Galbraith Laboratory, TN) and EDX spectroscopy. All the [Al], [Fe], and [Si] zeolite samples were highly crystalline based on XRD patterns, the XRD patterns showed excellent agreement with the structure types of MFI and BEA* (Figure 4.1). Table 4.1 displays the micropore volumes of the [Fe] zeolites and reveals that all the samples have micropore volumes within the ranges typically observed for these samples.



Figure 4.1 XRD patterns for a) as-synthesized silicalite-1, [A1]ZSM-5, and [Fe]ZSM-5 (MFI) and b) as-synthesized [A1]beta and [Fe]beta (BEA*). The samples are highly crystalline. The XRD patterns of [Fe] zeolites are consistent with the patterns for the structure type of MFI and BEA*.

Sample	Si/M ratio	Micropore volume (cm ³ g ⁻¹)	
H-[Fe]ZSM-5	26	0.119	
H-[Fe]ZSM-5	48	0.101	
H-[Al]ZSM-5	26	0.118	
H-[Fe]beta	15	0.204	

Table 4.1 Micropore volumes of [Fe] zeolites and [A1]ZSM-5

The UV/Vis spectra and the unit cell volumes of [Fe]ZSM-5 (26) were compared between as-made, calcined, and steamed forms of the samples to confirm the presence of Fe sites in the framework after calcination at 753 K. UV/Vis spectroscopy was used to help determine the location of iron atoms (in or out of the framework). Figure 4.2(a) shows the UV/Vis spectra of the as-made zeolite samples ([Fe]ZSM-5, [Fe]beta, [Al]ZSM-5, and [Si]ZSM-5). Four ligand field bands at 372, 410, 436, and 479 nm were observed for all [Fe]ZSM-5 samples, while no bands were detected for [A1]ZSM-5 and [Si]ZSM-5. [Fe]beta zeolite also showed ligand field bands at 374, 414, 440, and 481 nm. The four bands are attributed to the d-d transition of Fe^{3+} in tetrahedral coordination. The transitions at 372, 410, 436, and 479 nm for [Fe]ZSM-5 (at 374, 414, 440, and 481 nm for [Fe]beta) correspond to ${}^{6}A_{1}({}^{6}S) \rightarrow {}^{4}E({}^{4}D), {}^{6}A_{1}({}^{6}S) \rightarrow {}^{4}T_{2}({}^{4}D), {}^{6}A_{1}({}^{6}S) \rightarrow {}^{4}A_{1}{}^{4}E({}^{4}G), \text{ and}$ ${}^{6}A_{1}({}^{6}S) \rightarrow {}^{4}T_{2}({}^{4}G)$, respectively [28-31]. The spectral features confirm the presence of Fe³⁺ in the framework of zeolite, as has been reported previously [28-32]. An intense band was also observed at 220 nm (Figure 4.2(b)), which is attributed to a p-d charge transfer transition involving the framework oxygen anions and the iron cations in [Fe] zeolite [30, 31]. The unit cell volumes were determined based on the XRD

patterns of the samples (Table 4.2) [26, 27]. The unit cell volume of the as-made [Fe]ZSM-5 (26) was 5405 Å³, larger than those of the [Al]ZSM-5 (26) and [Si]ZSM-5 samples by reason of the larger size of tetrahedral Fe³⁺ cation (63 pm in radius) compared with tetrahedral Al³⁺ (53 pm) and tetrahedral Si⁴⁺ (40 pm) cations [33, 34].

Catalyst	[Si]ZSM-5 as-made	[Al]ZSM-5 (26)	[Fe]ZSM-5 (26) as-made
Unit cell volume $(Å^3)$	5357 ± 4	5382 ± 3	5405 ± 3
Catalyst	[Fe]ZSM-5 (26) calcined	[Fe]ZSM-5 (26) steamed	[Fe]ZSM-5 (26) after reaction
Unit cell volume $(Å^3)$	5412 ± 5	5350 ± 4	5382 ± 4

Table 4.2 Unit cell volumes of samples at different stage of preparation



Figure 4.2 a) UV/Vis spectra of as-made [Fe]ZSM-5 (26), [Fe]ZSM-5 (48), and [Fe]beta (15), b) UV/Vis spectra of as-made, calcined, and steamed [Fe]ZSM-5 (26).

A calcination process at 753 K was used for removal of the structure directing agent (SDA). The color of the sample changed from white to light yellow after the calcination step. The band at 220 nm in the spectrum of the calcined sample had almost the same intensity and position as those of as-made sample, but the spectrum showed a shoulder around 300 nm which is attributed to isolated octahedral Fe^{3+} complexes [31, 35]. The spectrum of the calcined sample still showed the four ligand field bands in the range of 350-550 nm even though the bands were overlapped with the shoulder around 300 nm (Figure 4.2(b)). The calcined [Fe]ZSM-5 had a larger unit cell volume (5412 Å³) than as-made [Fe]ZSM-5 (5405 Å³) because the structure directing agent (SDA) in the zeolite pores was decomposed. These results indicated that most of the Fe atoms remained in the framework structure after calcination while part of Fe migrated from framework to extra-framework positions.

Iron atoms can migrate from framework to extra-framework in Fe-containing zeolites during steaming process above a temperature of 873 K [13, 36-42]. Here [Fe]ZSM-5 and [Fe]beta zeolite samples were steamed by heating the samples at 973 K under air flow containing about 10% water. The sample became brownish in color after steaming at 973 K. In the UV/Vis spectrum of steamed [Fe]ZSM-5 (26), there was a broad absorption below 700 nm. The bands in the range of 350-550 nm were no longer observed. The intensity of the band at 220 nm was lower and the position of maximum absorption was shifted to a longer wavelength. The change in the position of this peak is caused by the migration of Fe atoms from framework to extra-framework positions in the zeolites [12, 31, 32]. The reduced and shifted (from 220 nm) peak indicates that the concentration of tetrahedral Fe³⁺ decreased after steaming and Fe species were formed in extra-framework positions. The aggregation degree of a

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transition metal oxide particle can be correlated to the absorption-edge energy as determined by the UV/Vis spectra [43, 44]. The absorption-edge energy was calculated from the position of the low energy rise in the graph of $\left[F(R_{\infty})hv\right]^2$ vs hv(Figure 4.3). The absorption-edge energies for as-made [Fe]ZSM-5 (26), calcined [Fe]ZSM-5 (26), and steamed [Fe]ZSM-5 were determined as 4.53 eV, 4.45 eV, and 2.70 eV, respectively. The band gap energy of bulk hematite (Fe_2O_3) is 2.0 eV [45]. The results suggest that aggregation of iron oxide occurs during the steaming process because the degree of aggregation increases with a reduction of the absorption-edge energy [43]. As shown in Table 4.2, the reduction in unit cell volume of the steamed [Fe]ZSM-5 (5350 Å³) indicated the removal of framework iron and the formation of extra-framework Fe species. It has been reported that when a sample is heated to remove the organic SDA, the unit cell volume increases at first and then starts to decrease with increasing temperature [46-48]. This result is consistent with the changes in unit cell volumes that were observed after calcination and after steaming. We conclude that large fraction of the tetrahedral framework Fe³⁺ ions remain in the framework after calcination while a majority of the Fe^{3+} ions migrate from the framework after steaming.



Figure 4.3 $[F(R_{\infty})hv]^2$ vs hv graph and the intercepts of a straight line fitted through the low energy rise in the graph.

4.4 Propane Conversion on Fe Sites in the Framework

[Fe]ZSM-5 (26) samples were used to investigate the role of framework and extra-framework Fe in the propane reaction. Highly reactive and quickly deactivating sites were initially observed for propane conversion over [Fe]ZSM-5 (26). (see Figure 4.4). The highly active sites were attributed to Lewis acid sites that could be extraframework species, as reported by Narbeshuber et al. [19, 49] In particular, isolated octahedral Fe³⁺ species generated after calcination could be these sites. After the initial deactivation period, the samples then showed catalytic activity for the propane conversion at a steady rate. The reaction rates and product distribution reported here were collected after this initial deactivation period.



Figure 4.4 Initial reaction rates of dehydrogenation over H-[Fe]ZSM-5 (26) at a temperature of 733 K.

The kinetic analysis was carried out using the following relationships:

$$r = k_3 \frac{K_1 P_{C_3 H_8}}{1 + K_1 P_{C_3 H_8} + K_4^{"} P_{C_3 H_6} + K_4^{'} P_{C_2 H_4}}$$
(4.2)

$$r = k_3 K_1 P_{C_3 H_8} = k_{app} P_{C_3 H_8}$$
(4.3)

Under conditions at which the zeolite surface is mostly empty, such as low reactant partial pressure, low conversion, and high reaction temperature, the rate expression can be simplified to a first-order rate equation (Eq. 4.3). Conversions under 2% indicate that the reactions were performed under differential conversion conditions, which is confirmed by the stoichiometric ratio of methane to ethylene for cracking channel and of hydrogen to propylene for dehydrogenation channel. The apparent activation energy was obtained using Arrhenius plots.

Rxn Temp. (K)	H- [Fe]ZSM-5	Na- [Fe]ZSM-5	Na- [Fe]ZSM- 5*	Steamed [Fe]ZSM-5	Na- Steamed [Fe]ZSM-5	H- [Al]ZSM-5
	Rea	ction rates of d	ehydrogenation	n, mol/s/g cat x	10 ⁷	
733	0.48 (0.02)	0.06	0.06	0.13	0.13	0.07 (0.21)
753	0.71 (0.03)	0.08	0.11	0.18	0.19	0.14 (0.44)
773	1.16 (0.05)	0.11	0.18	0.28	0.28	0.29 (0.83)
788	1.73 (0.07)	0.14	0.26	0.41	0.43	0.51 (1.31)
803	2.34 (0.10)	0.17	0.29	0.62	0.59	0.86 (2.08)
Activation Energy, kJ/mol						
	115±4 (110±5)	77±2	104±13	98±8	99±8	173±8 (160±2)
Average dehydrogenation-to-cracking ratios						
	22	-	26	17	21	0.36

Table 4.3 Kinetics of the monomolecular propane reaction (Si/M ratio of 26)

* Exchanged after reaction

Numbers in parenthesis () are rates of cracking

As shown in Table 4.3, the H-[Fe]ZSM-5 (26) sample had very high relative rates of dehydrogenation vs. cracking ($r_{dehydrogenation}/r_{cracking} \sim 22$), while the H-[A1]ZSM-5 (26) sample had higher rates of cracking ($r_{dehydrogenation}/r_{cracking} \sim 0.36$). The apparent activation energy for dehydrogenation over H-[Fe]ZSM-5 (26) was 115 kJ mol⁻¹ and was 173 kJ mol⁻¹ over H-[A1]ZSM-5 (26). A previous report also showed enhanced dehydrogenation selectivity and lower apparent activation energies for thermally dehydroxylated H-[A1]ZSM-5 compared to H-[A1]ZSM-5 [22]. The higher dehydrogenation rates and lower apparent activation energy are interpreted as

indicating that a different reaction mechanism for hydrocarbon conversion is operative in these samples. Sodium-exchanged [Fe]ZSM-5 (26) showed slower (but measurable) reaction rates (10-20%) compared to the rates observed over H-[Fe]ZSM-5 (26). This difference in reactivity indicates that the acid proton in H-[Fe]ZSM-5 (26) facilitates the electron transfer reaction (see below). The ability of H-Al-zeolites to extract electrons from adsorbed species has been observed numerous times [50-55] while, on the other hand, Na-exchanged zeolites show little (if any) electron transfer for the same species [22, 23, 50]. It is expected that the same trend will be observed for H-[Fe] zeolites vs Na-[Fe] zeolites. This should not be confused with Bronsted acid (protolytic) catalysis, which is inconsistent with the patterns of selectivity and apparent activation energies measured in the iron samples.



Figure 4.5 Log plot of reaction rates of dehydrogenation of propane over H-[Fe]beta (15), H-[Fe]ZSM-5 (26), and H-[Fe]ZSM-5 (48)

Rxn Temp. (K)	H-[Fe]ZSM-5 (26)	H-[Fe]ZSM-5 (48)	H-[Fe]beta (15)		
TOF of dehydrogenation, mol/s/(mol H^+) x 10^4					
733	1.15	0.99	1.43		
753	1.69	1.70	2.36		
773	2.79	2.76	3.01		
788	4.15	3.29	4.34		
803	5.63	5.30	5.97		
Activation Energy, kJ/mol					
	115 ± 4	114 ± 7	113 ± 2		

Table 4.4 TOF and activation energies over H-[Fe]beta (15), H-[Fe]ZSM-5 (26), and H-[Fe]ZSM-5 (48)

The catalytic reactions of propane were measured for the acid form of [Fe] zeolites with Si/Fe ratios of 15, 26, and 48 (H-[Fe]ZSM-5 (26), H-[Fe]ZSM-5 (48), H-[Fe]beta (15)) and an Arrhenius plot was used to compare the reaction rates over the various iron-silicate zeolites (Figure 4.5). The iron-silicate zeolites with higher iron concentration had higher reaction rates for propane dehydrogenation. H-[Fe]beta (15) had the highest reaction rates, and H-[Fe]ZSM-5 (48) had the lowest reaction rates. The measured activation energies were the same, within the experimental error, for all samples. Table 4.4 shows the turnover frequencies (TOF) and activation energies over H-[Fe]ZSM-5 (26), H-[Fe]ZSM-5 (48), and H-[Fe]beta (15). The TOF is nearly identical for all samples. This observation implies that i) the propane conversion mainly proceeds on isolated Fe sites in the framework, and ii) the pore size is not an

important factor in the propane reaction given that [Fe]beta zeolite (pore size of \sim 6.7 Å) has a larger pore dimension than [Fe]ZSM-5 (\sim 5.5 Å).

4.5 Propane Conversion on Extra-Framework Fe Species

Steamed [Fe]ZSM-5 samples were also examined for the propane conversion to understand the catalytic behavior of extra-framework Fe. The steamed [Fe]ZSM-5 sample showed 2 to 3 times higher reaction rates (0.28 mol s⁻¹ g cat⁻¹ x 10⁷ at 773 K) than Na-[Fe]ZSM-5 (0.11 mol s⁻¹ g cat⁻¹ x 10⁷ at 773 K), but showed only about 25% of the rate for H-[Fe]ZSM-5 (1.16 mol s⁻¹ g cat⁻¹ x 10⁷ at 773 K). The apparent activation energy was 98 kJ mol⁻¹, lower than that of H-[Fe]ZSM-5 (115 kJ mol⁻¹). The reaction rates and the measured activation energies indicated that the extraframework Fe species are catalytically active although the mechanism is unknown. After sodium-exchange of the steamed sample, similar reaction rates and activation energy than those of the steamed [Fe]ZSM-5 were obtained. Because the sodiumexchanged steamed sample did not show any differences when compared with the steamed sample, the steamed sample must have very few Fe atoms in the framework, and all the activity of the sodium-exchanged steamed sample and the steamed sample comes from the extra-framework species. [Si]ZSM-5 and FeCl₃ sublimated onto [Si]ZSM-5 did not exhibit any detectable catalytic reaction rates (data not shown).

It is concluded that H-[Fe]ZSM-5 has multiple active sites, consisting of Fe sites isolated in the framework and Fe species in extra-framework positions (both in and outside the zeolite pores). All sites showed very high dehydrogenation selectivity compared to H-[Al] zeolites, irrespective of whether the Fe atoms were in or out of the framework. However the catalytic activity of the Fe sites in the framework was higher than that of the extra-framework Fe sites.

4.6 Migration of Fe Atoms during Propane Reaction

After conversion of propane, the H-[Fe]ZSM-5 sample was recovered and exchanged with sodium to evaluate the possible migration of Fe atoms during reaction. The Na-[Fe]ZSM-5* (after reaction) sample had higher reaction rates than Na-[Fe]ZSM-5 (before reaction), as shown in Table 4.3. The reaction rates were lower than those of the Na-steamed [Fe]ZSM-5. This comparison indicates that a portion of the Fe atoms in the framework migrated to extra-framework positions during the propane reaction. The unit cell volume of [Fe]ZSM-5 after reaction is consistent with this explanation because the decreased values were still higher than the unit cell volume of steamed [Fe]ZSM-5. On the basis of the unit cell volume, we can estimate that about 50% of the Fe atoms migrated to extra-framework positions during reaction. Correspondingly, the reaction rates of Na-[Fe]ZSM-5. The high temperature and the reaction condition may have led to the migration of Fe atoms during the catalytic tests, a result that could be related to the initially highly reactive and quickly deactivating sites.

The reaction rates over sodium-exchanged samples (both Na-[Fe]ZSM-5 (26) samples before and after reaction, and Na-steamed [Fe]ZSM-5) were normalized to the number of extra-framework Fe species. The normalized number of extra-framework Fe species was calculated by subtracting the unit cell volume of Na-[Fe]ZSM-5 (26) sample before reaction from the unit cell volumes of three samples (Na-[Fe]ZSM-5 (26) samples before and after reaction, and steamed [Fe]ZSM-5).

Figure 4.6 shows that for these samples the reaction rates were proportional to the normalized number of extra-framework Fe species. The fraction of the total reaction rate associated with the extra-framework sites can be estimated from this relationship.



Figure 4.6 The reaction rates over sodium exchanged [Fe]ZSM-5, [Fe]ZSM-5 collected after reaction, and steamed [Fe]ZSM-5 at reaction temperature of 773 K, and the relative amount of Fe species in the extra-framework (Si/Fe = 26) as estimated from unit cell volume determinations.

4.7 Catalytic Properties at Higher Conversion

The reaction conversion over H-[Fe]ZSM-5 (26) increased to 5.2, 9, and 18 % at reaction temperatures of 753, 773, and 803 K, respectively. At 753 K, the conversion over H-[A1]ZSM-5 (26) was 5 %. The selectivity over H-[Fe]ZSM-5 (26) is compared with that over chromia catalysts in Table 4.5, since chromia catalysts are frequently used for the dehydrogenation of propane in industrial processes [56-58]. H-

[Fe]ZSM-5 (26) showed about 95 % selectivity toward propene at reaction temperatures between 753 and 803 K, while H-[A1]ZSM-5 (26) showed selectivity of about 25 %. Thus, H-[Fe]ZSM-5 (26) still showed high dehydrogenation selectivity when the reaction conversions were increased, and the selectivity values are comparable to the selectivity shown by chromia catalysts [51, 59]. In general, conversion over [Fe]ZSM-5 (26) was lower than those over the chromia catalysts under the conditions used here. Because the Fe atoms migrate from framework to extra-framework positions during the reaction, investigations of the reactivation of the catalysts are necessary before considering the use of [Fe] zeolites for dehydrogenation. Also note that rates have not been normalized per active site since we lack information about the site density in the chromia catalysts.

Sample	Reaction Temp. (K)	C ₃ H ₈ in feed (%)	Conversion (%)	Selectivity toward C ₃ H ₆
Cr_2O_3/Al_2O_3	0.50	20	26	-
$(6.15\% Cr_2O_3)$ [51]	8/3	20	26	/0
$CrOx/Al_2O_3$ (20% Cr) [59]	823	10	37	88
[Al]ZSM-5 (26)	753	4	5	25
	753	3	5.2	96
[Fe]ZSM-5 (26)	773	3	9	96
	803	3	18	95

Table 4.5 Dehydrogenation of propane at higher conversion

4.8 Reaction Mechanism

The high dehydrogenation selectivity (dehydrogenation-to-cracking ratio ~22) and low apparent activation energy (115 kJ mol⁻¹) for H-[Fe]ZSM-5 are very different from those of H-[A1]ZSM-5 (dehydrogenation-to-cracking ratio ~0.36 and activation energies 170-180 kJ mol⁻¹). It is then unlikely that the catalytic processes observed for H-[Fe]ZSM-5 proceed through a protolytic mechanism as is the case in H-[A1]ZSM-5. First, since the iron acid sites are slightly less acidic than the aluminum sites, the activation energy should be similar or higher than the activation energy for A1 acid sites and this is not the case. In Jones and Iglesia's paper, higher activation energy for [Fe]ZSM-5 is also expected vs. [A1]ZSM-5 based on CH₃OH dehydration and DFT calculation of DPE [16]. Second, if the mechanism is protolytic, after the transfer of the proton from the zeolite to the propane, the formed carbonium ion in Fe-zeolites is, to a first approximation, similar to the carbonium ion formed in A1-zeolites; and although some differences in selectivity are expected, they should be qualitatively similar, especially considering the high temperatures at which the experiments are conducted.

It is reasonable to suspect that the operating reaction mechanism on H-[Fe] zeolites is different from that on H-[Al] zeolites for this specific reason. There have been many studies about catalytic active sites on Fe-containing zeolites [32, 36-41, 60-70]. However, the Fe-containing zeolites in most studies were prepared by ion exchange, chemical vapor deposition sublimation, or steaming after hydrothermal synthesis, and thus the samples had mostly extra-framework Fe sites. Although the active sites in these Fe-containing zeolite samples remain a subject for further study, it is generally accepted that reactions over Fe-containing zeolites are catalyzed by the extra-framework Fe species: clustered iron species, iron oxides, and Fe²⁺ sites reduced

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from Fe^{3+} [32, 36-41, 60-70]. We have shown here that these species are active for propane conversion, but that they are not responsible for most of the observed reactivity.

It is possible to construct a catalytic reaction mechanism for H-[Fe]ZSM-5 based on a redox process. For example, early on McVicker et al. reported that hydrocarbon reactions can in fact proceed through radical intermediates over solid acid catalysts [71]. Generation of radical cations, which were suggested as major reaction intermediates, has been observed in the methanol-to-olefin conversion over zeolites [72, 73]. The radical-like route for hydrocarbon conversion is related to the oxidizing ability of the solid acid catalysts. In many cases this oxidizing ability leads to a spontaneous ionization of molecules with low ionization potential upon sorption in the pores of acid zeolites. The spontaneous formation of radical cations of 2,5-dimethylhexa-2,4-diene, trans-stilbene, and anthracene upon adsorption on H-zeolites has been reported [51-55].

Naphthalene was used here as a probe to evaluate the potential of redox chemistry in H-[Fe]ZSM-5. The experimental details are described in Chapter 2. It has been shown that [Al]ZSM-5 after dehydroxylation has the ability to extract (oxidize) a single electron from neutral naphthalene to form naphthalene radical cations [22, 23]. The post-dehydroxylated form of [Al]ZSM-5 also showed enhanced dehydrogenation selectivity (dehydrogenation-to-cracking ratio ~1) and a lower activation energy (127 kJ mol⁻¹). Figure 4.7 shows bands that can be assigned to naphthalene radical cations in H-[Fe]ZSM-5 while there are no such characteristic peaks in H-[Al]ZSM-5. The steamed [Fe]ZSM-5 did not generate the naphthalene radical cation either (data not shown) so extra-framework iron species seem to be inactive towards electron

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abstraction from naphthalene. This evidence for potential redox chemistry in H-[Fe]ZSM-5 is an important clue to the nature of the active sites.



Figure 4.7 UV/Vis spectra of naphthalene adsorbed in [Fe] and [Al]ZSM-5

The reaction mechanism depicted in Scheme 4.1 is proposed for the proane reaction over framework Fe-sites in H-[Fe]ZSM-5 and H-[Fe]beta. Here, an electron is extracted from the propane molecule at the framework Fe site when the propane contacts the sites, and a propane radical cation is formed. The propane radical cation is unstable and dissociates into the more stable propene radical cation [74-76] and molecular hydrogen. Because Na-[Fe]ZSM-5 show lower reaction rates than H-[Fe]ZSM-5, electron capture is presumed to be facilitated by the acid sites in H-[Fe]ZSM-5. The reaction cycle is completed after the electron is given back to the propene radical cation reforming the initial sites in H-[Fe]ZSM-5. This reaction mechanism is similar to that introduced for a thermally dehydroxylated catalyst in a previous report [22].



Scheme 4.1 Possible reaction mechanism in H-[Fe]ZSM-5

4.9 Summary

The catalytic properties of framework iron-containing zeolites were investigated using the monomolecular propane reaction. It was shown that the reaction proceeds with very high dehydrogenation selectivity and occurs via isolate framework Fe sites. The measured TOFs per framework iron atom were the same for the samples with different Si/Fe ratios (15, 26, and 48). Because there is an 80-90% decrease in reaction rates over the sodium-exchanged samples, it is concluded that framework Fe sites were the sites predominantly responsible for catalysis. The steamed [Fe]ZSM-5 showed lower reaction rates than those for H-[Fe]ZSM-5, indicating that the Fe sites isolated in the framework are the main channel for propane conversion on H-[Fe] zeolites. In other words, the monomolecular propane reaction is catalyzed on the Fe sites primarily in the framework and to a lesser extent outside the framework. Active sites in both framework and extra-framework positions showed very high dehydrogenation selectivity and low activation energies compared with those for H-[A1]ZSM-5. These results indicate that a reaction mechanism different from proton donation from the acid site could explain the observed properties of H-[Fe] zeolites. We propose a redox mechanism to explain the observed reactivity. The spontaneous formation of naphthalene radical cations upon adsorption on H-[Fe] zeolites at room temperature supports the notion that H-[Fe]-zeolites have redox properties that can lead to catalytic reactivity.

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Chapter 5

MECHANISTIC INVESTIGATION OF PROPANE DEHYDROGENATION AND PROPENE HYDROGENATION OVER H-[FE]ZSM-5 CATALYST³

5.1 Introduction

This chapter describes a mechanistic study of the propane dehydrogenation and propene hydrogenation reactions over H-[Fe]ZSM-5 zeolites. Alkanes are chemically inert because all their carbon atoms have four sigma bonds, a configuration requiring substantial amount of energy for C-H bond cleavage. Conversion of alkanes, therefore, usually proceeds under high temperature conditions and controlling production of desired chemicals is difficult. Mechanistic understanding of the alkane activation process can contribute to the systematic and practical control of alkane conversions. The dehydrogenation of alkanes is one of the most important industrial alkane activation processes and is thermodynamic difficult because it is endothermic and endergonic [1-3].

Industrially, chromium oxide catalysts have been used for decades for alkane dehydrogenation. Relative high yields are reported for dehydrogenation of alkanes at high temperature [4, 5]. However, there have been environmental concerns raised over the chromium oxide catalysts because the catalysts contain carciogenic Cr^{6+} . The increase in the amount of Cr^{6+} during the regeneration stage can result in an increase in the risk of lung cancer [4, 5]. Potentially, soil and water can be contaminated by

³ This work is being prepared for publication in 2014.
usage of chromium [6]. High oxidation states of chromium ion (Cr^{6+}) were found in chromium oxide catalyst after calcination [7], but reduced Cr^{3+} ions is in fact the active center for the reaction [8, 9]. Since the reduced Cr^{3+} ions are reoxidized to Cr^{6+} , a redox mechanism for dehydrogenation of alkanes has been proposed on chromium oxide catalysts [9-12].

In the previous chapter, we investigated iron-silicate zeolites for the catalytic monomolecular propane conversion [13]. The monomolecular propane conversion proceeds through only two reaction channels: cracking and dehydrogenation. The dehydrogenation-to-cracking ratios were about 22 over H-[Fe]ZSM-5, while the ratios were about 0.36 over H-[A1]ZSM-5. At higher conversion (20%) than what is typically used for the monomolecular reaction (< 2%), the dehydrogenation selectivity was still high (\sim 80%); that is comparable to the industrial chromium oxide catalysts. The activation energy of propane dehydrogenation over H-[Fe]ZSM-5 is 115 kJ/mol, significanly lower than that over H-[Al]ZSM-5 (173 kJ/mol). Jones et al. recently compared H-[Fe]ZSM-5 and H-[Al]ZSM-5 acid catalysis properties and determined that the deprotonation energy of the iron sample is higher by 23 kJ mol⁻¹. As a consequence acid catalyzed reactions by the iron zeolite should be slower and have higher activation energies than the aluminum forms.[14] The activation energy differences between Fe and Al zeolites in the propane reaction then indicate that the reaction proceeds through a non-protolytic mechanism in the iron samples. Enhanced dehydrogenation selectivity and lower measured activation energies were also observed for dehydroxylated aluminosilicate zeolites [15]. These results strongly suggest that the propane conversion over H-[Fe]ZSM-5 does not follow the typical protolytic mechanism for hydrocarbon conversion, the mechanism now accepted to

occur over the acid form of aluminosilicate zeolites [16-18]. The protolytic mechanism involves the formation of alkanium-like ions as reaction intermediates (Scheme 5.1(a)). A redox mechanism involving the formation of propane radical cations as the reaction intermediates, has been suggested by us for the propane conversion over H-[Fe]ZSM-5 (Scheme 5.1(b)). Through the redox mechanism [13], the tetrahedral Fe^{III} ion in the zeolite framework can be reduced to Fe^{II} as a result of extracting an electron from a propane molecule occluded in the zeolite channel. The tetrahedral Fe^{III} is oxidized back to the tetrahedral Fe^{III} after the formation of propene (dehydrogenation channel) or ethylene (cracking channel).



Scheme 5.1 Reaction mechanisms of dehydrogenation of propane (a) via alkaniumlike ion over H-[Al]-MFI and (b) via radical cation over H-[Fe]-MFI.

The presence of tetrahedral Fe^{II} in silicates and other oxides has been reported for synthetic glasses such as Na₂FeSi₃O₈, K₂FeSi₃O₈ [19], MFe_{0.5}Si_{2.5}O₆ (M=K, Na, Cs) [20-22], Fe₂SiO₄ [23, 24], and Rb₂FeSi₃O₈ [25], as well as for minerals such as staurolite (Fe_{1.5}Mg_{0.5}Al₉Si_{3.9}Al_{0.1}O₂₂(OH)₂ - 13.1 wt.% tetrahedral Fe^{II} site) [25]. These structures support the premise that a tetrahedral Fe^{II}O_{4/2} structure is chemically stable and could be formed during the reaction without destruction of the framework structure or migration of Fe atoms from the framework to extra-framework position. An example of the crystal structure of the synthetic iron-silicate glass [26] is depicted in Figure 5.1.



Figure 5.1 Tetrahedral Fe^{II} structures in synthetic leucite (K₂Fe^{II}Si₅O₁₂)

Further mechanistic investigations are required to confirm the hypothesis that a redox mechanism is operational for the propane conversion over H-[Fe]ZSM-5 and to develop better understanding of the potential of H-[Fe]ZSM-5 as a practical catalyst. To this end, investigation of reverse reactions has been shown to be useful in elucidating reaction mechanism. For example, fundamental investigations of the monomolecular propane dehydrogenation and the propene hydrogenation have been reported by Gounder and Iglesia [27-31]. On a separate problem, Chen and Bozzelli [32] reported a computational study of the kinetics and thermodynamics of the

benzene with OH· reaction. An elementary reaction mechanism premised upon the microscopic reversibility principle has been developed to model OH· radical reaction with benzene and experimental data. The reactant conversion, product yields at different reaction temperatures, reaction times, and initial concentrations, determined based on the model, were compared with experiment, showing better agreement than a model that omitted the reverse reaction. In early report by Savage et al. [33], the reverse reaction of n-alkylbenzene pyrolysis was used to study mechanisms and kinetics models for hydrocarbon pyrolysis. It was pointed out that the radical hydrogen transfer steps were an essential part of the mechanism to model the experimental data faithfully. Freund and Olmstead [34] have developed the mechanism of butylbenzene pyrolysis comprised reversible elementary reactions. The model predicted the reaction rates within a factor of two compared with experimental values [34]. Van Santen's group has reported various mechanistic studies of catalytic reactions, such as NH_x dehydrogenation and oxidation, considering the reverse reactions as well [35-37]. These reports point out that the microscopic reversibility is essential in the analysis of hydrocarbon reactions and clearly helps in the development reaction mechanisms. Propene hydrogenation is the reverse reaction of the propane dehydrogenation, and it is expected to proceed through the same elementary steps as the propane dehydrogenation, based on the microscopic reversibility principle [38].

The kinetics of the formation of a radical cation inside a zeolite pore often can be described, by Marcus Theory of electron transfer [39, 40], a theory that has been expanded to electro-chemical reactions at solid electrodes, as well as redox enzyme kinetics [41, 42]. It can replace Eyring transition state theory for two chemical species change in their charge with an electron jumping (redox reaction) without large

structural change [43]. The concept of *catalytic control* of electron transfer reactions, however, remains an undeveloped field [44]. Marcus theory points out that electron transfer rates can decrease as the driving force of electron transfer is increased depending of the magnitude of the reorganization energy of electron transfer (referred to as the Marcus inverted region). However, the reaction in the Marcus inverted region was only found 30 years after publication of original ideas in 1956 [45]. Experiments involving electron transfer usually satisfy the general trends, and rates increase as the driving force increases. Note that spontaneous electron transfer from hydrocarbons with low ionization energies adsorbed in zeolite pores to the zeolite framework has been reported in earlier investigations [46-48].

In this chapter, we investigate the kinetics of propene hydrogenation over H-[Fe]ZSM-5 and compare the results to the propane dehydrogenation and to both reactions over H-[A1]ZSM-5. The propene hydrogenation was investigated under hydrogen excess ($H_2/C_3H_6 > 2500$) to prevent the formation of undesired products, such as propene oligomers. The selectivity of propane conversion over H-[Fe]ZSM-5 is analyzed from a thermochemical perspective. Energy changes along the reaction coordinates were estimated based on the apparent activation energies for both propane dehydrogenation and propene hydrogenation, and on the ionization energies of propane and propene. The results indicate that in H-[Fe]ZSM-5, the main reaction channel proceeds through radical cation intermediates and not through alkanium-ion species.

5.2 Experimental Section

H-[Al]ZSM-5 with Si/Al ratio of 26 and H-[Fe]ZSM-5 with Si/Fe ratio of 26 were prepared and used in this chapter. The synthesis protocols are the same as those described in Chapter 2 and 4. The reactor and GC system used in this section are the same to those used in previous chapter. About 20mg of zeolite catalyst is transferred to a quartz tube reactor (ID = 5 mm). To support the sample in the center of the reactor chamber, quartz wool (~ 0.05 g) is placed near the bottom of the reactor tube and quartz chips (~1.6 mm diameter, Quartz Plus, Inc.) are placed between quartz wool and the sample. The reactor is heated in a cylindrical furnace (C5232, Hoskins Mfg. Co.), controlled by a temperature controller (NC 74000, Omega Engineering) and a thermocouple (type K, Omega Engineering) inserted in the quartz tube reactor located directly over the sample. The samples are first treated in flowing N₂ (100 sccm) by heating to 753 K with a rate of 2K/min for 3 hours to obtain acid form of the zeolites. The reactants flow into the reactor with dry N₂ as the carrier gas to vary the partial pressure of H₂ (0.2 ~ 1 bar) and C₃H₆ (5×10⁻⁵ ~ 4×10⁻⁴ bar). A high H₂/C₃H₆ ratio (>1000) is maintained at all times to avoid oligomerization reactions. The reactor effluent is analyzed using gas chromatography (GC, Shimadzu 2014). A molsieve column is used for separation and eluted into a thermal conductivity detector (TCD) for H₂ and N₂ quantification and a RT-alumina column is connected to a flame ionization detector (FID) for hydrocarbons. The temperature of the column is increased from 308 K to 393 K with a rate of 10K/min and the products are collected for 12 minutes.

5.3 Catalytic Hydrogenation of Propene versus Dehydrogenation of Propane

As shown in Scheme 5.2, the catalytic cycle of propane dehydrogenation includes the adsorption of propane in the zeolite channels (step 1), the formation of alkanium-ion-like transition state (step 2) as a rate-determining step, and the desorption of products to the exterior of the zeolite crystals (steps 3-5) [27]. The kinetic analysis of the monomolecular propane dehydrogenation can be carried out as follows:

$$r_{D} = k_{2}K_{1}P_{C_{3}H_{8}} = k_{D}^{app}P_{C_{3}H_{8}}$$
(5.1)

$$k_{D}^{app} = k_{2}K_{1} = \frac{k_{B}T}{h}K_{D}^{\ddagger} = \frac{k_{B}T}{h}e^{\left(\frac{\Delta S}{R}\right)}e^{\left(-\frac{\Delta T}{RT}\right)}$$
$$= \frac{ek_{B}T}{h}e^{\left(\frac{\Delta S^{\ddagger}}{R}\right)}e^{\left(-\frac{E_{a,D}^{app}}{RT}\right)} = A_{D}^{app}e^{\left(-\frac{E_{a,D}^{app}}{RT}\right)}$$
(5.2)

$$E_{a,D}^{app} = RT^2 \frac{\partial \left(\ln r_D\right)}{\partial T} = \Delta H_1 + E_2 = \Delta H_2^? - \Delta H_{H^+Z^-} - \Delta H_{C_3H_8(g)}$$
(5.3)

$$\Delta S_D^{app} = R \left[\ln \left(A_D^{app} \right) - \ln \left(\frac{ek_B T}{h} \right) \right] = \Delta S_2^{\ddagger} - \Delta S_{H^+ Z^-} - \Delta S_{C_3 H_8(g)}$$
(5.4)

where, r_D is the rate of propane dehydrogenation, $P_{C_3H_8}$ is the partial pressure of propane, k_D^{app} is the apparent dehydrogenation rate constant (first order), K_1 is the equilibrium constant relating intrazeolite propane concentration to gas or extra-zeolite propane pressure, k_2 is the intrinsic rate constant for the rate determining step. K_D^{\dagger} is the equilibrium constant for the formation of activated complexes. $E_{a,D}^{app}$ is the apparent activation energy (experimentally determined) and as can be seen in Eq. (3) is the enthalpy differences between intrazeolite intermediates and extrazeolite reactants. A_D^{app} is the pre-exponential factor and ΔS_D^{app} is the apparent activation entropy, the result of the entropy difference between the entropy of the transition state in the zeolite channel and reactants in a gas phase.

The propene hydrogenation reaction was conducted from 733 K to 803 K with excess H₂ gas (H₂/C₃H₆ > 2500). The temperature range was similar with the one used for propane dehydrogenation. Under these reaction conditions propane was produced as a major product with high selectivity (over 80%, Figure 5.2(a)), while ethylene and methane were formed in equimolecular ratios with low selectivity. It is reported that the minor products can be formed through monomolecular cracking of propoxide species [49, 50] or through interconversion of dehydrogenation transition states (C-H-H) to the cracking transition states (C-C-H) [15, 27]. The propane production rates correlate linearly with the partial pressures of H_2 and C_3H_6 (Figure 5.3): consequently, intrazeolite H₂ and C₃H₆ concentrations are equilibrated with their extrazeolite pressures and C₃ intermediates are kinetically relevant. The rate constants (k_{Al} , mol $(mol H^+)^{-1} s^{-1} (bar H_2)^{-1} (bar C_3 H_6)^{-1}$) at the reaction temperature of 773 K are defined to be the slope of the propane formation rates vs. the partial pressures of C_3H_6 and H_2 in this figure. The average rate constant is 0.036 $[mol (mol Al)^{-1} s^{-1} (bar H_2)^{-1} (b$ $(C_3H_6)^{-1}$] at 773 K, which agreed to within ~10% of each other (Figure 5.4). The kinetic analysis of the propene hydrogenation can be expressed as follows (based on the reverse direction of the catalytic cycle in Scheme 5.2):

$$r_{H} = k_{-2} K_{3}^{-1} K_{4}^{-1} K_{5}^{-1} P_{C_{3}H_{6}} P_{H_{2}} = k_{H}^{app} P_{C_{3}H_{6}} P_{H_{2}}$$

$$(5.5)$$

$$k_{H}^{app} = k_{-2}K_{3}^{-1}K_{4}^{-1}K_{5}^{-1} = \frac{k_{B}T}{h}K_{H}^{?} = \frac{k_{B}T}{h}e^{\left[\frac{\Delta S}{R}\right]}e^{\left[\frac{-\Delta T}{RT}\right]}(c^{\circ})^{-1}$$

$$= \frac{e^{2}k_{B}T}{h}e^{\left[\frac{\Delta S^{\dagger}}{R}\right]}e^{\left[\frac{-\frac{E_{a,H}}{RT}}{RT}\right]}(c^{\circ})^{-1} = A_{H}^{app}e^{\left[\frac{-\frac{E_{a,H}}{RT}}{RT}\right]}$$
(5.6)

$$(E_{a,H}^{app} = \Delta H^{\ddagger} + 2RT)$$

$$E_{a,H}^{app} = RT^{2} \frac{\partial (\ln r_{H})}{\partial T} = E_{-2} - \Delta H_{3} - \Delta H_{4} - \Delta H_{5}$$

$$= \Delta H_{-2}^{\ddagger} - \Delta H_{H^{+}Z^{-}} - \Delta H_{C_{3}H_{6}(g)} - \Delta H_{H_{2}(g)}$$
(5.7)

$$\Delta S_{H}^{app} = R \left[\ln \left(A_{H}^{app} \right) - \ln \left(\frac{e^{2} k_{B} T}{h} \right) \right]$$

$$= \Delta S_{-2}^{\dagger} - \Delta S_{H^{+}Z^{-}} - \Delta S_{C_{3}H_{6}(g)} - \Delta S_{H_{2}(g)}$$
(5.8)

where, r_{H} is the rate of propene hydrogenation, $P_{C_{3}H_{6}}$ and $P_{H_{2}}$ are the partial pressures of propene and hydrogen, k_{H}^{app} is the apparent hydrogenation rate constant (second order), K_{3} , K_{4} , and K_{5} are the equilibrium constants relating concentrations of intrazeolite transition state and reactants to extrazeolite reactants in a gas phase, k_{-2} is the rate constant for the reverse rate determining step. K_{H}^{\ddagger} is the equilibrium constant for the formation of activation complexes, relating the transition states to the gas phase. $E_{a,H}^{app}$ is the apparent activation energy and involves the enthalpy differences between intrazeolite intermediates and extrazeolite reactants. For second order reactions, the equation for the rate constant relating to enthalpy and to entropy needs to be modified as described in equation (5.6). c° is the concentration of the transition state complex in the standard state and is unit concentration having the same concentration unit as that used for the rate constant [51]. A_{H}^{app} is the pre-exponential factor and ΔS_{H}^{app} is the apparent activation entropy, the difference between entropy of transition state in the zeolite channel and reactants in a gas phase.

1.
$$C_{3}H_{8} (g) \xleftarrow{k_{1}}{k_{-1}} C_{3}H_{8}^{*}$$

2. $C_{3}H_{8}^{*} + H-[AI]Z \xleftarrow{k_{2}}{k_{-2}} C_{3}H_{8}^{+} [AI]Z + H_{2}^{*}$
3. $C_{3}H_{8}^{+} [AI]Z \xleftarrow{k_{3}}{k_{-3}} C_{3}H_{6}^{*} + H-[AI]Z$
4. $C_{3}H_{6}^{*} \xleftarrow{k_{4}}{k_{-4}} C_{3}H_{6} (g)$
5. $H_{2}^{*} \xleftarrow{k_{5}}{k_{-5}} H_{2} (g)$

Scheme 5.2 Set of elementary steps that define the catalytic mechanism for monomolecular propane dehydrogenation and propene hydrogenation with dihydrogen on H-[Al]ZSM-5.





Figure 5.2 (a) Selectivity to ethylene(C_2H_4) and propane(C_3H_8) and (b) their ratios formed during propene hydrogenation with varying H_2/C_3H_6 feed ratio at 773 K on H-[Al]ZSM-5 and H-[Fe]ZSM-5.





Figure 5.3 Dependence of C_3H_8 formation rates (773K) on C_3H_6 pressure and H_2 pressure on (a) H-[A1]ZSM-5 and (b) H-[Fe]ZSM-5. Rates are proportional to C_3H_6 pressure and H_2 pressure for both H-[A1]ZSM-5 and H-[Fe]ZSM-5.



Figure 5.4 Regression analysis and residues of the rate constants for propene hydrogenation over (a) [Al] and (b) [Fe]ZSM-5.

The propane dehydrogenation rates for the iron catalysts were examined and compared to H-[A1]ZSM-5. Scheme 5.3 shows that the catalytic cycle of propane dehydrogenation over H-[Fe] zeolites includes a *proposed* electron transfer step leading to the formation of radical cations (step 7), a step not present in Scheme 5.2 over H-[A1]ZSM-5. The rate-determining step is the formation of radical-like intermediates (step 8). Additional electron transfer from the zeolite to the propene radical cation is involved in step 9 and is not expressed separately because this step is much faster than the step 7. There is another possible reaction channel for the monomolecular propane conversion—the cracking of propane (Scheme 5.4)—from the formation of radical-like intermediates. In this second channel, the reaction would lead to the formation of an intrazeolite ethylene radical cation. However, cracking selectivity is very low over H-[Fe]ZSM-5 (~22 times lower than the dehydrogenation selectivity) [13] indicating that this reaction channel is energetically unfavorable (see below). The kinetics of monomolecular propane dehydrogenation over H-[Fe]ZSM-5 are analyzed using the following equations:

$$r'_{D} = k_{8}K_{6}K_{7}P_{C_{3}H_{8}} = k'_{D}^{app}P_{C_{3}H_{8}}$$

$$(5.9)$$

$$k_{D}^{\prime app} = k_{8}K_{6}K_{7} = \frac{k_{B}T}{h}K_{D}^{\prime \ddagger} = \frac{k_{B}T}{h}e^{\left(\frac{\Delta S}{R}\right)}e^{\left(-\frac{\Delta T}{RT}\right)}$$

$$ek T \left(\frac{\Delta S^{\prime \ddagger}}{R}\right)\left(-\frac{E_{a,D}^{\prime app}}{RT}\right) \qquad \left(-\frac{E_{a,D}^{\prime app}}{RT}\right)$$
(5.10)

$$= \frac{e\kappa_{B}T}{h} e^{(-\kappa_{-})} e^{(-\kappa_{-})} = A_{D}^{\prime app} e^{(-\kappa_{-})}$$

$$E_{a,D}^{\prime app} = RT^{2} \frac{\partial (\ln r_{D}^{\prime})}{\partial T} = \Delta H_{6} + \Delta H_{7} + E_{8}$$

$$= \Delta H_{8}^{\ddagger} - \Delta H_{ET,C_{3}H_{8}} - \Delta H_{H^{+}Z^{-}}^{\prime} - \Delta H_{C_{3}H_{8}(g)}$$
(5.11)

$$\Delta S_D^{\prime app} = R \left[\ln \left(A_D^{\prime app} \right) - \ln \left(\frac{ek_B T}{h} \right) \right]$$

= $\Delta S_8^{\ddagger} - \Delta S_{ET, C_3 H_8} - \Delta S_{H^+ Z^-}^{\prime} - \Delta S_{C_3 H_8(g)}$ (5.12)

where, the prime symbol is used to distinguish the kinetic parameters for H-[Fe]ZSM-5 from those for H-[A1]ZSM-5. K_6 is the equilibrium constant relating intrazeolite propane concentration to gas or extra-zeolite propane pressure, K_7 is the equilibrium constant relating electron transfer from reactant to zeolite, k_8 is the intrinsic rate constant for the rate determining step, and $E_{a,D}^{\prime app}$ and $\Delta S_D^{\prime app}$ are additionally related to the enthalpy and entropy changes by electron transfer ($\Delta H_{ET,C_3H_8}$ and $\Delta S_{ET,C_3H_8}$), respectively.

The propene hydrogenation was carried out under the same reaction conditions investigated for H-[A1]ZSM-5. Propane was produced over H-[Fe]ZSM-5 at much higher rate than ethylene as shown in Figure 5.2(a). The propane selectivity over H-[Fe]ZSM-5 was higher than that over H-[A1]ZSM-5 even when H₂/C₃H₆ ratios were below 2500 (Figure 5.2(b)). The reaction rate dependency with respect to the partial pressure of C₃H₆ and H₂ are also first order (Figure 5.3). The slope, average of rate constant (k_{Fe}) at 773 K is ~0.18 [mol (mol Fe)⁻¹ s⁻¹ (bar H₂)⁻¹ (bar C₃H₆)⁻¹], which also agreed to within ~10% of each other (Figure 5.4(b)). The kinetic analysis of propene hydrogenation over H-[Fe]ZSM-5 is addressed using the following relationships:

$$r'_{H} = k_{-8} K_{9}^{-1} K_{10}^{-1} K_{11}^{-1} P_{C_{3}H_{6}} P_{H_{2}} = k_{H}^{\prime app} P_{C_{3}H_{6}} P_{H_{2}}$$
(5.13)

$$k_{H}^{\prime app} = k_{-8}K_{9}^{-1}K_{10}^{-1}K_{11}^{-1} = \frac{k_{B}T}{h}K_{H}^{\prime ?} = \frac{k_{B}T}{h}e^{\left(\frac{\Delta S^{\prime \pi}}{R}\right)}e^{\left(-\frac{\Delta H^{\prime }}{RT}\right)}(c^{\prime \circ})^{-1}$$

$$= \frac{e^{2}k_{B}T}{h}e^{\left(\frac{\Delta S^{\prime \pi}}{R}\right)}e^{\left(-\frac{E_{a,H}^{\prime app}}{RT}\right)}(c^{\prime \circ})^{-1} = A_{H}^{\prime app}e^{\left(-\frac{E_{a,H}^{\prime app}}{RT}\right)}$$
(5.14)

$$E_{a,H}^{\prime app} = RT^{2} \frac{\partial \left(\ln r_{H}^{\prime} \right)}{\partial T} = E_{-8} - \Delta H_{9} - \Delta H_{10} - \Delta H_{11}$$

$$= \Delta H_{-8}^{\ddagger} - \Delta H_{ET,C_{3}H_{6}} - \Delta H_{H^{+}Z^{-}}^{\prime} - \Delta H_{C_{3}H_{6}(g)} - \Delta H_{H_{2}(g)}$$

$$\Delta S_{H}^{\prime app} = R \left[\ln \left(A_{H}^{\prime app} \right) - \ln \left(\frac{e^{2}k_{B}T}{h} \right) \right]$$

$$= \Delta S_{-8}^{\ddagger} - \Delta S_{ET,C_{3}H_{6}} - \Delta S_{H^{+}Z^{-}}^{\prime} - \Delta S_{C_{3}H_{6}(g)} - \Delta S_{H_{2}(g)}$$
(5.16)

where, K_9 , K_{10} , and K_{11} are the equilibrium constants relating concentrations of intrazeolite transition state and reactants to extrazeolite reactants in a gas phase, k_{-8} is the rate constant for the reverse rate determining step. The equilibrium constant relating electron transfer from zeolite to reactant is omitted in K_9 , and $E'_{a,H}^{app}$ and $\Delta S'_{H}^{app}$ also include the enthalpy and entropy changes due to electron transfer. The apparent activation energy and entropy for the propane dehydrogenation and propene hydrogenation over H-[A1]ZSM-5 and H-[Fe]ZSM-5 are listed in Table 5.1.

6.
$$C_{3}H_{8}(g) \xleftarrow{k_{6}}{k_{-6}} C_{3}H_{8}^{*}$$

7. $C_{3}H_{8}^{*} + H_{-}[Fe]^{(III)}Z \xleftarrow{k_{7}}{k_{-7}} C_{3}H_{8}^{**+} + H_{-}[Fe]^{(II)}Z$
8. $C_{3}H_{8}^{**+} + H_{-}[Fe]^{(II)}Z \xleftarrow{k_{8}}{k_{-8}} C_{3}H_{6}^{*+} H_{-}[Fe]^{(II)}Z + H_{2}^{*}$
9. $C_{3}H_{6}^{*+} H_{-}[Fe]^{(II)}Z \xleftarrow{k_{9}}{k_{-9}} C_{3}H_{6}^{*} + H_{-}[Fe]^{(III)}Z$
10. $C_{3}H_{6}^{*} \xleftarrow{k_{10}}{k_{-10}} C_{3}H_{6}(g)$
11. $H_{2}^{*} \xleftarrow{k_{11}}{k_{-11}} H_{2}(g)$

Scheme 5.3 Set of proposed elementary steps that define the catalytic mechanism for monomolecular propane dehydrogenation and propene hydrogenation with hydrogen on H-[Fe]ZSM-5. Note that there are two electron transfers: (1) at step 7, Fe is reduced and (2) at step 9, Fe is oxidized.

$$C_{3}H_{8}^{*} + H_{-}[Fe]^{(II)}Z + H_{2}^{*}$$

$$C_{3}H_{8}^{*} + H_{-}[Fe]^{(II)}Z + H_{2}^{*}$$

$$C_{2}H_{4}^{*} + H_{-}[Fe]^{(II)}Z + CH_{4}^{*}$$

Scheme 5.4 Illustration of the branching of the reaction network after the formation of the propane radical cation. Dehydrogenation and cracking pathways could be observed after the formation of propane radical cation.

	H-[Al]ZSM-5		H-[Fe]ZSM-5	
	Dehydrogenation of propane	Hydrogenation of propene	Dehydrogenation of propane	Hydrogenation of propene
E_a^{app} kJ mol ^{-1 a}	173	42	115	-14
ΔS ^{app} J mol ⁻¹ K ^{-1 b}	-96	-246	-155	-302

Table 5.1 Apparent activation energies and entropy changes for propane dehydrogenation and propene hydrogenation on H-[Al]ZSM-5 and H-[Fe]ZSM-5.

 $a \pm 4 \text{ kJ mol}^{-1}, b \pm 11 \text{ J mol}^{-1} \text{ K}^{-1}$

The rate constants of propane dehydrogenation $(k_D^{app}, \text{ mol s}^{-1} (\text{mol Al or Fe})^{-1}$ (bar C₃H₈)⁻¹) and propene hydrogenation $(k_H^{app}, \text{ mol s}^{-1} (\text{mol Al or Fe})^{-1} (\text{bar H}_2)^{-1} (\text{bar C}_3H_6)^{-1})$ over H-[A1]ZSM-5 and H-[Fe]ZSM-5 at various reaction temperatures are presented in Figure 5.5. The rate constants of the propane dehydrogenation over H-[Fe]ZSM-5 are higher than those over H-[A1]ZSM-5, and the rate constants of propene hydrogenation over H-[Fe]ZSM-5 are also higher than those over H-[A1]ZSM-5. The propane dehydrogenation apparent activation energies are 173 and 115 kJ mol⁻¹ over H-[A1]ZSM-5 and H-[Fe]ZSM-5, respectively (Table 5.1). The propene hydrogenation apparent activation energies are 42 kJ mol⁻¹ and -14 kJ mol⁻¹, respectively. Gounder reported that H-[A1] zeolites exhibit about 197 and 70 kJ mol⁻¹ of activation energies for propane dehydrogenation and for propene hydrogenation, respectively [27]. Even if our values are lower than the values reported by Gounder, they are still within a wide range (90~200kJ mol⁻¹) [17, 28] of activation energy for propane dehydrogenation reported in literature. Note that the activation energies of both reactions over H-[Fe]ZSM-5 are lower than those over H-[A1]ZSM-5. The different apparent activation energies for hydrogenation of propene support the hypothesis that the reaction mechanism of hydrocarbon conversions over H-[Fe]ZSM-5 is different from H-[A1]ZSM-5, as suggested earlier [13] because H-[Fe]ZSM-5 is a weaker acid than H-[A1]ZSM-5 [14] and the acid-catalyzed reaction would then have a *higher* activation energy in the iron samples.

The entropies of formation of the transition states are -96 and -155 J mol⁻¹ K⁻¹ for propane dehydrogenation over H-[A1]ZSM-5 and H-[Fe]ZSM-5, respectively. This is as expected because the formation of the transition state requires the loss of the translational degrees of freedom of the gas phase reactant. The much more negative value for the entropy of formation of the transition state on H-[Fe]ZSM-5 also suggests that these reactions are proceeding through different reaction mechanisms. The entropy of translation of propane in a classical ideal gas phase is calculated using Sackur-Tetrode equation.

$$S = k_B N \left[\ln \left\{ \frac{V}{N} \left(\frac{4\pi m U}{3Nh^2} \right)^{\frac{3}{2}} \right\} + \frac{5}{2} \right]$$
(5.17)

where, *V* is the volume of the gas, *N* is the number of particles in the gas, *U* is the internal energy of the gas, k_B is Boltzmann's constant, m is the mass of a gas particle, *h* is Planck's constant. The entropy of translation of propane is 167.9 J mol⁻¹ K⁻¹ at 773 K. The absolute value of entropy of formation of transition states over H-[Fe]ZSM-5 is closer to the entropy of translation of propane, indicating that the propane in H-[Fe]ZSM-5 loses almost all of the translational degrees of freedom. At this point is not clear why, in an electron transfer process, the transition state is so

'tight' [52]. The entropies of formation of the transition state are -246 and -302 J mol⁻¹ K⁻¹ for propene hydrogenation over H-[A1]ZSM-5 and H-[Fe]ZSM-5. It is expected that the entropies for the hydrogenation will be much more negative (in this case about twice as large) because they involve the loss of translational degrees of freedom of two gas phase molecules. The entropies of translation of propene and H₂ are 167.3 and 129.3 J mol⁻¹ K⁻¹, respectively, which support the expectation. The entropies for propane dehydrogenation and propene hydrogenation over H-[A1] zeolites reported by Gounder are -59 and -193 J mol⁻¹ K⁻¹ [27], which are also higher than our values because of the difference in the activation energies.

5.4 Propane Conversion over H-[Fe]ZSM-5

The difference of the apparent activation energy for propane dehydrogenation and propene hydrogenation is related to the enthalpy change in the reaction:

$$E_{a,D}^{app} - E_{a,H}^{app} = \Delta H_{C_3H_6(g)} + \Delta H_{H_2(g)} - \Delta H_{C_3H_8(g)} = \Delta H_{R(g)}$$
(5.18)

The transition states enthalpies, the enthalpy of adsorption into the zeolite pores, and the enthalpy of electron transfer cancel out. For both H-[A1]ZSM-5 and H-[Fe]ZSM-5, the differences between apparent activation energies for propane dehydrogenation and propene hydrogenation are 131 and 129 kJ mol⁻¹, (the same within experimental error), and are identical to the enthalpy for the stoichiometric propane dehydrogenation reaction (~130 kJ mol⁻¹ at the reaction temperatures investigated here, see Appendix B). It is also observed in Figure 5.5 that the extended lines to infinite temperature in Arrhenius plots all intersect at 931 K, the isokinetic temperature [53-56]. The isokinetic relationship satisfies the following relationships [53]:

$$\Delta H - T\Delta S = \text{constant} \tag{5.19}$$

The values for propane dehydrogenation and propene hydrogenation over H-[Al]ZSM-5 and H-[Fe]ZSM-5 using equation (5.19) are 255±2 kJ mol⁻¹. The isokinetic temperatures and the constants have the same values for both H-[Al]ZSM-5 and H-[Fe]ZSM-5 catalysts within experimental error. The activation energy differences and the isokinetic relationship support the premise that the forward and the reverse reactions over both H-[Al]ZSM-5 and H-[Fe]ZSM-5 are structurally related and proceed through the same elementary steps. Equilibrium constants were estimated using van't Hoff equation [43] and they were compared to the ratio of reaction constants for propane dehydrogenation and propene hydrogenation (Figure 5.6). The ratios of reaction constants obtained under the conditions of low concentrations of the reactants were consistent with the equilibrium constants for both H-[Al]ZSM-5 and H-[Fe]ZSM-5, even if the reaction conditions for both reactions are far away from equilibrium. This similarity verifies the reliability of the experimental reaction rates and turn over frequencies obtained in this investigation.

The relative energy changes along with the reaction coordinates were analyzed based on the kinetic and thermodynamic data for the propane dehydrogenation and propene hydrogenation over H-[A1]ZSM-5 (Figure 5.7(a)). First, the adsorption of propane in the pores of zeolite ZSM-5 has been modeled in Figure 5.7(a). The value of -46 kJ mol⁻¹, which was measured in earlier report [57], is used for the heat of

adsorption for propane in H-[A1]ZSM-5. The energy changes then reflect the apparent activation energy for the monomolecular propane dehydrogenation. The final products, propene and hydrogen in the gas phase, are obtained after desorption from the zeolite channels [58]. In the opposite direction, the apparent activation energy for the propene hydrogenation is indicated in the figure. Both reactions proceed through a common reaction intermediate, the alkanium ion over H-[A1]ZSM-5.



Figure 5.5 Arrhenius plot of rate constants and apparent activation energies of propane dehydrogenation and propene hydrogenation on H-[Al]ZSM-5 and H-[Fe]ZSM-5. Extrapolation of the fits to experimental data coincide at the isokinetic point.



Figure 5.6 Rate constant ratios of propane dehydrogenation to propene hydrogenation $(k_{meas,D}/k_{meas,H})$ on H-[Al]ZSM-5 and H-[Fe]ZSM-5.

For H-[Fe]ZSM-5, a radical cation is suggested as the reaction intermediate, but note that this is *not* the transition state. As shown in Schemes 5.2 and 5.3, the primary difference of the catalytic cycle over H-[Fe]ZSM-5 versus H-[A1]ZSM-5 is the electron transfer between the reactants and the zeolite. The ionization potential for the reactant is a factor that must be considered to explain the activation energy and the selectivity for propane conversion over H-[Fe]ZSM-5. In Scheme 5.5, approximated energy changes for the propane radical cation were estimated for the dehydrogenation and the cracking of the propane, and ethylene [59-62] —in the gas phase—were used for the estimation as well as the reaction enthalpies of propane dehydrogenation in gas phase. A negative energy change (-7 kJ mol⁻¹), indicating an exothermic reaction, is obtained for the dehydrogenation channel, while a positive energy change (24 kJ mol⁻¹, endothermic), was calculated for the cracking channel. Clearly, the positive energy change of the cracking channel indicates that this channel requires more energy than the dehydrogenation, that is, it is kinetically less favorable. Even considering that the products (CH_4 , C_2H_4) obtained via cracking channels are thermodynamically more stable than the products via the dehydrogenation channel (81 kJ mol⁻¹ vs 130 kJ mol⁻¹) in the gas phase, the higher activation barrier obtained using the ionization potentials for the cracking channel explains why the dehydrogenation channel is kinetically favored.

The approximate difference between the two energy changes for the cracking and the dehydrogenation is 31 kJ mol⁻¹ (see Scheme 5.5). Using a selectivity ratio (~22) of dehydrogenation to cracking for the propane reaction over H-[Fe]ZSM-5 [13], the difference between activation energies for the cracking and the dehydrogenation can be calculated as ~ 20 kJ mol⁻¹. The energy difference calculated in Scheme 5.5 (31 kJ mol⁻¹), which is even larger than the activation energy difference obtained using the experimental data, supports that kinetically a high dehydrogenation selectivity for the propane conversion over H-[Fe]ZSM-5 should be observed. (a) Dehydrogenation

e +	C_3H_8 ** \longrightarrow C_3H_8	-IE = -1071 kJ mol ⁻¹
	$C_3H_6 \longrightarrow C_3H_6^{++} + e^-$	IE = 939 kJ mol ⁻¹
	$C_3H_8 \longrightarrow C_3H_6 + H_2$	∆H ^o _R = 125 kJ mol ⁻¹
	C_3H_8 * \rightarrow C_3H_6 * H_2	∆E = -7 kJ mol ⁻¹
(b) Cracking	I	
e +	C_3H_8 ⁺ \longrightarrow C_3H_8	-IE = -1071 kJ mol⁻¹
	$C_2H_4 \longrightarrow C_2H_4^{+} + e^{-}$	IE = 1014 kJ mol ⁻¹
	$C_3H_8 \longrightarrow C_2H_4 + CH_4$	∆H ^o _R = 81 kJ mol ⁻¹
	$C_3H_8^{*+} \longrightarrow C_2H_4^{*+} CH_4$	$\Delta E = 24 \text{ kJ mol}^{-1}$

Scheme 5.5 Estimated energy changes associated with propane (a) dehydrogenation and (b) cracking via propane radical cation intermediate.



Figure 5.7 Enthalpy changes for propane dehydrogenation along the reaction coordinate of molecules in the gas phase and intrazeolite phase of (a) H-[Al]ZSM-5 and (b) H-[Fe]ZSM-5.

The approximated energy changes in the propane conversion through both cracking and dehydrogenation channels along with the reaction coordinates were reflected in the energy diagram shown in Figure 5.7 (b). The energy changes include

the heat of adsorption for propane in zeolites and the apparent activation energy for the monomolecular propane dehydrogenation. The radical cation intermediate is suggested for the reaction over H-[Fe]ZSM-5. After the formation of propane radical cations, the estimated energy change for the dehydrogenation and the cracking channels in Scheme 5.5 is illustrated for the purposes of this discussion. Then, the heat of adsorption (desorption) of propene in zeolites and the apparent activation energy for the propene hydrogenation are included for the dehydrogenation channel, while the heat of adsorption for ethylene in zeolites is adopted for the cracking channel. The final energy levels for the products are obtained based on the enthalpy of reaction in gas phase. This energy diagram explains why dehydrogenation rates should be much higher than cracking rates if radical cations are key reaction intermediates.

The reorganization energy of electron transfer is unknown for the propane conversion over ZSM-5 catalysts, but approximate calculation using Marcus equation can be carried out [41, 42, 44] (See Appendix C):

$$\Delta G^{\ddagger} = \frac{\left(\lambda + \Delta G^{\circ}\right)}{4\lambda} \tag{5.20}$$

where ΔG^{\ddagger} is the Gibbs free energy of activation, ΔG° is the standard Gibbs free energy accompanying the electron transfer reaction, and λ is the reorganization energy. ΔG^{\ddagger} was estimated as the sum of the apparent activation energy and the heat of adsorption of propane on H-[Fe]ZSM-5 zeolites (~161 kJ/mol) and based on this number the reorganization energies were estimated to be between 13.2 and 40.3 kJ mol⁻¹. This corresponds to ΔG° values from 80 to 121 kJ mol⁻¹. These calculations indicate that the propane electron transfer reaction is within the Marcus inverted region and consequently, molecules with lower ionization potentials than propane would show slower rates of reaction by this mechanism.

5.5 Summary

The propane conversion over H-[Fe]ZSM-5 catalyst was investigated based on mechanistic relationship between its forward (monomolecular propane dehydrogenation) and reverse (propene hydrogenation) reactions. The difference of the apparent activation energies of forward and reverse reactions is $\sim 130 \text{ kJ mol}^{-1}$, which is similar to the reaction enthalpy of the propane dehydrogenation. The extended Arrhenius plots of the rate constants intersect at 931 K, indicating the forward and the reverse reactions follow the isokinetic relationship. The ratios of the rate constants of the forward and the reverse reactions are also consistent with the equilibrium constants determined using the van't Hoff equation. From these observations, we can conclude that the propene hydrogenation proceeds through the same elementary steps as the propane dehydrogenation. A redox mechanism involving the formation of propane radical cations was proposed as the main reaction channel for H-[Fe] zeolite catalysts. The radical-like intermediates can be the kinetically-relevant step for hydrocarbon conversions over H-[Fe] zeolites. The energy change along with the reaction coordinates including the reaction enthalpy, the apparent activation energies, and the electron transfer in zeolite channels were investigated and compared for the cracking and the dehydrogenation, which are only two reaction channels for monomolecular hydrocarbon conversions. The cracking channel requires higher energy ($\sim 30 \text{ kJ mol}^{-1}$) than the dehydrogenation channel as a result of the approximation using the ionization potentials. This observation indicates why the

dehydrogenation channel is kinetically favored over the cracking channel in the propane conversion. The mechanistic insight for the hydrocarbon conversions and their selectivity over H-[Fe] zeolites can be established based on this case study. To the best of our knowledge, this is the first report of an electron transfer catalyzed alkane activation step on an acid zeolite.

5.6 References

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Chapter 6

PROPANE CONVERSION OVER HYDROGEN-BONDED ACID SITES IN ZEOLITES

6.1 Introduction

This chapter describes an investigation of the propane conversion over hydrogen-bonded acid sites in zeolites. The selectivity of the monomolecular propane reaction was interpreted based on the confinement effects in zeolites. This work, which is part of collaboration with Dr. Hubert Koller's group at the Institute of Physical Chemistry in the University of Münster (Germany) is a part of this dissertation, because we examined the catalytic properties of their specially prepared samples by using the monomolecular propane reaction.

A detailed knowledge of the local structure and bonding at the acid sites in zeolites is essential to develop a molecular explanation of the complex catalytic function of zeolites. In an attempt to elucidate the geometry of Brönsted acid sites (BAS), solid-state ¹H NMR spectroscopy studies have been reported in literature [1-10] because X-ray or neutron diffraction method cannot provide the exact local structures of BAS due to the disordered nature of isomorphous substitution of Al for Si in zeolites. Solid-state ²⁷Al NMR spectroscopy can also be used as the probing technique for the local structure of the Al sites. In a report about the ²⁷Al NMR spectroscopy of zeolites by Ernst [11], it is indicated that the observed signal is very broad due to a large nuclear quadrupole interaction with the electric field, an indication of the presence of distorted tetrahedral sites. The quadrupole interaction decreases when the
distortion is reduced by adsorption of probe molecules [12, 13] because the aluminum site becomes more symmetric. Therefore, the BAS in zeolite have been often observed by means of the adsorption of probe molecules.

Haw et al. [1] reported that hydrogen-bonded acid sites can be detected in H-[Al]ZSM-5 zeolites using ¹H NMR spectroscopy. The dehydrated [Al] zeolites exhibit two peaks. One peak at 4.3 ppm is attributed to OH group (BAS), while another peak at 6.5 ppm is assigned to hydrogen bonded acid sites [1], as shown in Figure 6.1. Brunner et al. also reported this new hydroxyl group at 7 ppm interacting with MFI zeolite framework [6] and Freude identified two kinds of acid sites in H-[Al]ZSM-5 at 4.2 and 6.1 ppm [3]. The Koller group also revealed the presence of hydrogen bonded acid sites at 6.1 ppm using ¹H-²⁷Al rotational echo adiabatic passage double resonance (REAPDOR) spectroscopy [7]. Beck and Haw again reported the hydrogen-bonded acid sites in zeolite Beta using ²⁷Al irradiation [8] and Omegna et al. corroborated this observation for zeolite Beta [10]. Muller et al. also observed the hydrogen-bonded acid sites in zeolite Beta on a Cs-exchanged sample [9]. In a report by Eckert et al., an O-O distance of ~284 pm, this is shorter than most of observed O-O distance, was suggested for the hydrogen-bonded proton with a chemical shift of 6.5 ppm in 1 H NMR spectrum [14]. Brunner et al. reported that the hydrogen-bonded proton is attributed to 3427 cm⁻¹ of IR frequency [15]. Quantum-chemical cluster calculations have been used to obtain complementary information about the local structure of acid sites and confirmed that ¹H chemical shift is sensitive to the hydrogen-bonded geometry [16, 17], supporting the presence of hydrogen-bonded acid sites.



Figure 6.1 ¹H MAS NMR spectrum of dehydrated H-[A1]ZSM-5 [7]

6.2 Synthesis of Zeolite Beta with Only Hydrogen-bonded Acid Sites

Zeolite beta can be synthesized over a wide range of Si/Al ratios (10 to ∞) [18, 19]. The studies on the mechanism of zeolite beta formation reported that three types of particles are observed in the aluminum containing solution while it is heated at 393 K: primary, secondary, and tertiary particles [20, 21]. The initial solution before heating contains the primary particles (< 3nm), and then the secondary particles (6-50 nm) grow at elevated temperatures. As the secondary particles grow larger over time, the tertiary particles (> 200nm) are made up by aggregation of the primary and the secondary particles. The tertiary particles change to be well organized zeolite beta after heating. The investigation on the effect of Al concentration showed that [[\equiv SiO]⁻ TEA⁺] ion pairs are substituted for [[AlO₂]⁻ TEA⁺] ion pairs are incorporated in the zeolite framework structure as tetrahedral structure of Al.

Koller's research group has synthesized BEA-type zeolites only having hydrogen bonded acid sites (that is without 'normal' BAS) as determined by ¹H NMR. The samples have been prepared by post-synthetic modification of two different B-Beta samples: one (sample 3) is prepared by ion-exchange with a mixture of NH₄ and Ca ions, and another (sample 4) is prepared by adding Ca ions during synthesis. It is assumed that Ca²⁺ ions are located on the boron sites to prevent the exchange of Al for B. Ammonium exchange then lead to the formation of hydrogen bonded acid sites. Sample 1 is B-Beta and sample 2 is Al-Beta prepared using 'standard' conditions, and they are used as reference materials.

6.2.1 B-Beta and Al-Beta

Synthesis protocols of borosilicates (B-Beta, sample 1) and aluminosicilate (Al-Beta, sample 2) beta zeolites are described in dissertation written by Koller's group [23]. The gel compositions of $1 \text{ SiO}_2 : 0.033 \text{ B}_2\text{O}_3 : 0.54 \text{ TEAOH} : 18 \text{ H}_2\text{O}$ and $1 \text{ SiO}_2 : 0.033 \text{ Al}_2\text{O}_3 : 0.54 \text{ TEAOH} : 18 \text{ H}_2\text{O}$ were prepared for samples 1 and 2, respectively. The as-synthesized samples were calcined in air at 823 K for 6 hours with a ramp rate of 2 K/min.

6.2.2 Al(B)-Beta Made From Calcined B-Beta by Ca²⁺ Ion Exchange (Sample 3)

The sample 3 was prepared by ion-exchange of B-Beta zeolite with a mixture of NH₄ and Ca ions as depicted in Figure 6.2.



Figure 6.2 Synthesis protocol of Al(B)-Beta (sample 3)

¹H NMR spectra of the prepared samples do not show the first peak at around 4 ppm (Figure 6.3) but clearly show a peak at 6.5 ppm for the hydrogen bonded sites. In addition, ¹H-²⁷Al REAPDOR shows that the 6.5 ppm proton line is coupled to ²⁷Al (Figure 6.4). Other proton lines are also observed at around 2 ppm, but they are assigned to silanol groups and a OH group formed near the remaining boron, respectively. The lines do not show dipolar coupling to ²⁷Al. From these observations, it can be concluded that a zeolite which has only hydrogen bonded acid sites is successfully prepared.



Figure 6.3 Deconvoluted ¹H NMR spectrum of sample 3



Figure 6.4 ¹H-²⁷Al dipolar interaction of sample 3

6.2.3 Al(B)-Beta Made From Calcined Ca,B-Beta (Sample 4)

A different sample, having only hydrogen-bonded acid sites (sample 4), was prepared by adding Ca^{2+} ions during the synthesis of borosilicate beta zeolite. Ca(NO₃)₂ was added to the gel for the synthesis of B-Beta as shown in Figure 6.5.



Figure 6.5 Synthesis protocol of Al(B)-Beta (sample 4)

The ¹H NMR and ¹H-²⁷Al REAPDOR (data not shown) exhibit the same features as shown for sample 3, indicating that sample 4 also has only hydrogen-bonded acid sites in the framework.

6.3 Propane Conversion over Zeolite Beta with Hydrogen-bonded Acid Sites

The reactor and GC system used in this section are the same used in chapters 3 and 4. The newly prepared samples (samples 3 and 4) having only hydrogen bonded

acid sites are tested for the monomolecular propane reaction and compared the catalytic activity to other zeolites (samples 2) having BAS.

First, the total reaction rates of propane conversion over all samples are compared in Figure 6.6, along with the reaction rates over H-[A1]ZSM-5 for comparison. The H-[A1]Beta (sample 2) and H-[A1]ZSM-5 exhibit almost the same reaction rates for the monomolecular propane reaction. In constrast, B-Beta (sample 1) presents very low reaction rates. It is well known that the acidity of B-Beta is very weak to show catalytic activity for hydrocarbon conversion [24-26]. Samples 3 and 4 show reaction rates that are intermediate between those over sample 1 and sample 2, indicating that their reactivity is lower than normal H-[A1]Beta sample, yet the samples still have catalytic properties for hydrocarbon conversion.



Figure 6.6 Reaction rates of propane conversion over five different samples: H-[Al]Beta (sample 2), H-[Al]ZSM-5, [B]Beta (sample 1), [Al(B)]Beta (sample 3), and [Al(B)]Beta (sample 4).

Next, the selectivity of propane conversion over beta zeolites with only hydrogen bonded acid sites was compared to that of [Al]Beta and [Al]ZSM-5 samples. The [Al]Beta and [Al]ZSM-5, which have 'normal' BAS, exhibited higher cracking selectivity than dehydrogenation selectivity by factor of 2 to 3. In contrast, the samples 3 and 4 showed the cracking-to-dehydrogenation ratios less than 1, that is, dehydrogenation selectivity is higher than cracking selectivity.

The activation energy of the cracking and the dehydrogenation channels over sample 2 ([A1]beta) is 177 kJ/mol and 159 kJ/mol. The activation energy of the cracking channel over sample 2 is similar to the values reported in earlier studies [27-29]. The activation energy of dehydrogenation is lower than that over [A1]ZSM-5, but they are within the wide variation in the reported dehydrogenation activation energy (95 ~ 200 kJ/mol) [27, 28, 30]. The activation energy of dehydrogenation over sample 3 decreased to 96 kJ/mol while the activation energy of the cracking channel is not changed. The activation energies of both cracking and dehydrogenation channels over sample 4 decreased to 150 and 55 kJ/mol, respectively, the decrease in value is more significant than the sample 3. The reduced activation energies for the dehydrogenation channel support enhanced dehydrogenation selectivity in Table 6.1. Unfortunately, it is unknown at this stage why sample 4 exhibits lower activation energies than the sample 3.

The changes in activation energies and selectivity indicate that the propane conversion proceeds over structurally different active sites as compared to the 'normal' BAS, in ways that are like the cases discussed in Chapters 3 and 4. B-Beta (sample 1) showed also very low cracking-to-dehydrogenation ratio, but its reaction rates are also very low (almost below detection levels).

Rxn. Temp. K	Sample 1 B-Beta	Sample 2 Al-Beta	Sample 3 Al(B)- Beta	Sample 4 Al(B)- Beta	Al-ZSM- 5
733	0.045	1.76	0.245	0.177	2.77
753	0.077	1.83	0.432	0.291	3.24
773	0.097	1.88	0.626	0.454	2.92
788	0.114	2.16	0.726	0.574	2.56
803	0.167	2.26	0.761	0.671	2.42

Table 6.1 Cracking-to-dehydrogenation ratios

Table 6.2 Apparent activation energies (kJ/mol) and entropies (J/mol/K)

Sample	$E_{a,crack.}$	$E_{a,dehyd.}$	$\Delta S_{crack.}$	ΔS_{dehyd} .
1 (B-Beta)	128	44	-	-
2 (Al-Beta)	177	159	-82.3	-110.8
3 (Al(B)-Beta)	177	96	-100.1	-200.0
4 (Al(B)-Beta)	150	55	-141.9	-258.2
5 (ZSM-5)	160	173	-104.1	-96.0

6.4 Confinement Effect on Selectivity of Propane Conversion

Gounder and Iglesia reported that for alkanes, the partial confinement effects are responsible for chemical reactions occurring via transition states with highly localized cationic centers within constrained environments [27, 31]. In their investigation on the monomolecular propane dehydrogenation over MOR zeolite, the cracking-to-dehydrogenation ratios were different over 8-MR and 12-MR locations. The propane cracking pathway only proceeded over the 12-MR location of MOR zeolite, while dehydrogenation pathway was favored over 8-MR location (cracking-todehydrogenation ratio was 0.63). This confinement effect can be used to explain the selectivity of propane conversion over hydrogen-bonded acid sites in beta zeolite samples.

Conceptually, it is expected that the hydrogen-bonded acid sites will be located in spatially confined environments as shown in Scheme 1.6 (Chapter 1) because the hydrogen bonding requires neighboring framework oxygen atom. The samples 3 and 4 contain exclusively hydrogen bonded acid sites without the 'normal' BAS. In the propane reaction over acid sites through the protolytic mechanism, the first step is the formation of an alkanium ion, and then from there the reaction proceeds via two pathways, either forming a methane and an ethyl cation (cracking) or a dihydrogen and a propyl cation (dehydrogenation) as shown in Scheme 6.1.

The experimental results suggest that in samples 3 and 4, the propane molecules cannot fully enter the zeolite "pockets" having hydrogen-bonded acid sites, while they preferentially react and remain in part within the zeolite channels having normal BAS. This can be envisioned as if the propane molecule can turn one end toward the catalytic sites: the proton can only attack C-H bonds of the contacted carbon. For the propyl cation formation, the primary carbon at the end of the C3 chain

would have to be stabilized by the zeolite to lower the transition state of propyl cation formation. On the other hand, the ethyl cation formation would require the central carbon of the propane molecule to be attacked breaking the C-C bond. The hydrogenbonded sites could, for geometric reasons, not provide enough space for this cracking pathway to proceed. Therefore, the C-H bond activation would be predominant over the hydrogen-bonded acid sites. On the contrary, the C-C bond activation can proceed over the normal BAS since there are better exposed and can attack the molecule at the C-H and C-C bonds. This explanation could be the reason why cracking is less favored in the hydrogen-bonded acid sites.

To verify the confinement effect, the activation entropies of the transition states were estimated in Table 6.2. Even if the activation energies of the cracking channel over samples 2 and 3 are the same (both 177 kJ/mol), the entropy of formation of the transition state over sample 3 has to have a lower value than sample 2. In addition, the entropy of the dehydrogenation over sample 3 and the entropies of both reaction channels over sample 4 exhibit very low values compared to the entropies obtained for sample 2. Much more negative entropy values for samples 3 and 4 indicate that the propane molecule in samples with only hydrogen-bonded acid sites lose more degree of freedom of translation. That is, it has to approach the active site with a very well-defined geometry. As was discussed in Chapter 5, the estimated entropy of translation of propane is 168 J/mol/K at reaction temperature of 773 K. The activation entropies of the dehydrogenation channel for the samples 3 and 4 are -200 and -258 J/mol/K, respectively, which are lower than the sample 2(-111 J/mol/K), H-[Al]ZSM-5 (-96 J/mol/K [29], -54~-59 J/mol/K [27, 32]), and H-[Fe]ZSM-5 (-155 J/mol/K [29]). In Gounder's report, the dehydrogenation selectivity is higher than the

cracking selectivity within 8-MR locations in MOR zeolites. However, their activation entropy values (-91 and -54 J/mol/K) are more positive than the activation entropy for cracking within 12-MR locations (-117 J/mol/K). Even if the size of 12-MR is simply larger than 8-MR, the stronger van der Waals force within 12-MR than 8-MR results in a more negative activation entropy and a tight fit. To conclude, the transition states for propane activation are highly constrained in the samples 3 and 4, and the tight fit leads to the enhanced dehydrogenation selectivity. Note that the H-[Fe]ZMS-5 exhibits higher dehydrogenation selectivity than samples 3 and 4 even if the entropy values of samples 3 and 4 are much more negative. H-[Fe]ZSM-5 sample does show confinement effects but instead proceeds through different reaction chemistry (redox mechanism). The propane conversion over samples 3 and 4 certainly proceeds through the protolytic mechanism, but their acidity is not as strong as the sample with the 'normal' BAS, resulting in lower rates of reaction and moderately high dehydrogenation selectivity.

The zeolite beta samples having only hydrogen-bonded acid sites without the 'normal' BAS were prepared and characterized using solid-state NMR spectroscopy. The catalytic properties of the hydrogen-bonded acid sites were investigated using the monomolecular propane reaction and compared to other zeolites (H-[Al]ZSM-5, H-[Al]beta zeolite). The total rates of reaction over the hydrogen-bonded acid sites are lower than those over the 'normal' BAS because of weak acidity and disadvantageous accessibility from the reactant molecule. However, the narrow space of the hydrogen-bonded acid sites lead that the propane conversion proceeds predominantly through the dehydrogenation channel.



Scheme 6.1 Proposed mechanism for propane conversion over H-Beta containing hydrogen-bonded acid sites.

6.5 Summary

The catalytic activity of hydrogen-bonded acid sites in beta zeolites was investigated using the monomolecular propane reaction. The rates of reaction over hydrogen-bonded acid sites are lower than those over normal BAS while the reaction proceeds with low cracking selectivity over hydrogen-bonded acid sites (cracking-todehydrogenation ratios ~ 0.63 for sample 3 and 0.45 for sample 4 at 773 K). To explain these observations it is noted that the hydrogen-bonds are expected to be located in constrained space close to framework oxygen. Therefore, the hydrogenbonded acid sites provide a very tight space for the formation of transition states of the cracking pathway. The activation entropy values (especially for the dehydrogenation channel) are much more negative than the other samples having the 'normal' BAS; - $200 \sim -250$ J/mol/K for hydrogen-bonded acid sites vs. -96 ~ -111 J/mol/K for 'normal' BAS. The reported topological information about hydrogen-bonds in zeolites and the estimated activation entropies for the transition states support the premise that the cracking pathway is less favored by the confinement effect of the hydrogen-bonded acid sites.

6.6 References

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Chapter 7

FURFURAL HYDRODEOXYGENATION ON BIMETALLIC CATALYSTS

7.1 Introduction

This chapter discusses the catalytic hydrogenation of furfural with Ag-Cu bimetallic catalysts supported on silica (SiO₂). The biomass is fuel that is developed from organic materials, a renewable and sustainable source of energy. Global warming, which is the world most important issue, is mainly caused by increasing concentration of greenhouse gases produced by human activities [1-3]. The primary component of greenhouse gas emissions is carbon dioxide (CO_2) . Even though using biofuels also emits CO_2 , the net addition of CO_2 to atmosphere is low because the raw materials for biomass, which are plants and trees, need CO₂ to grow. With the global warming issue, the prospective of reduction of dependence on fossil fuels, improvement of rural economy, and creation of a major new industry led to search for an alternative ways of acquiring valuable chemicals and fuels, especially a renewable source of biomass [4, 5]. Over the last decade, a variety of approaches to converting six-carbon sugars, such as glucose and fructose into a chemical called hydroxymethylfurfural (HMF) have been investigated [6-11]. HMF represents renewable building blocks for the synthesis of polymers and industrial and household chemicals, and especially for furan-based biofuel [6, 12-17].

Furfural has received much attention by cellulosic ethanol producers and academic researchers. Furfural is almond-like scented, oily, colorless liquid that turns yellow to dark brown due to oxidation when exposed to air. It is used as a solvent for

refining lubricating oils, as a fungicide and weed killer and in the production of tetrahydrofuran, an important industrial solvent. In addition, furfural can serve as a building block for other potential transportation fuels including dimethylfuran and ethyl levulinate [18, 19].

The reaction channels and derivatives from furfural are depicted in Scheme 7.1. From the commercial point of view, the most important derivative of furfural has been furfuryl alcohol. This chemical has been used in synthesis of polymer, solvents, flavor and fragrance chemicals, and pesticide and pharmaceutical products, as well as in rocket fuels. Recently, 2-methylfuran (2-MF) has received much attention as important derivative of furfural because it is a versatile starting material used in the synthesis of many pharmaceutical, agricultural, industrial chemicals, and especially possible alternative biofuels [20]. 2-MF has excellent combustion stability, particularly in cold conditions, and has great thermal efficiency compared to gasoline, and emits lower aldehyde than gasoline and ethanol [21, 22].



Scheme 7.1 Reaction pathways for catalytic hydrogenation of furfural to various furfural derivatives.

Supported silver catalysts are good oxidizing catalysts, that are applied to the epoxidation of ethylene [23-25]. The catalytic reduction properties of the supported silver catalysts also have been used for the selective hydrogenation of unsaturated aldehydes to the corresponding alcohols [26-28]. Especially, Ag/SiO₂ catalysts are highly effective for selective hydrogenation, such as gas-phase hydrogenation of dimethyl oxalate to the corresponding alcohols [29, 30] and hydrogenation of chloronitrobenzenes [31]. In this chapter, we examined the effect of the incorporation of Ag into Cu/SiO₂ on the selective hydrogenation of furfural. The Ag-Cu bimetallic catalysts are expected to enhance the catalytic activity and stability for the hydrogenation of furfural to furfuryl alcohol and further to 2-MF.

7.2 Experimental Section

7.2.1 Catalyst Preparation and Reduction

The bimetallic catalysts with total 5 wt% of Ag-Cu are prepared using wet impregnation. The calculated amounts of silver nitrate (AgNO₃, Sigma Aldrich) and copper nitrate hydrate (Cu(NO₃)₂·xH₂O, Alfa Aesar, 99.999%) are dissolved in 5 ml DI water. 5 g SiO₂ (silica gel, Sigma Aldrich) is added to the mixture under stirring. The mixture is stirred overnight, and then dried at 383 K for 12 hours. The samples are calcined in air at 673 K using a 2 K/min heating rate for 5 hours. After calcination, the sample is reduced at 723 K with a ramp rate of 2 K/min for 5 fours under 50 sccm H₂ flow. The reduced catalysts are then passivated with 1% O₂ balanced with N₂ gas during cooling down to the room temperature. The reduction temperature was determined by a hydrogen TPR experiment.

7.2.2 Measurement of Catalytic Rates

About 50 mg of calcined sample is transferred into the house-built stainless steel tube reactor (ID ~ 1.27 cm). The sample is supported on 50 mg of quartz wool. The stainless steel tube reactor is heated at the specified temperature using vertical tube furnace (Applied Test System Series 3210). The temperature inside the reactor is monitored by a K-type thermocouple and changed by a temperature controller (EZ-ZONE[®] PM-6, WATLOW). The catalyst, which is loaded in the reactor, is heated to 523 K in H₂ for reduction, and then it is cooled down to the reaction temperature (483 K). The furfural feed rate is 0.1 ml/h and the flow rate of H₂ is 50 sccm (hydrogen excess). The reaction temperatures investigated vary from 463 K to 523 K. The products are separated and recorded by GC (Shimadzu 2014) equipped with HP-5

column (Agilent) and a flame ionization detector (FID). The pipe line between the reactor and GC is also heated at 483 K to prevent the effluent from being liquefied.

Carbon balance is estimated by proportion of total yield of all detected products over the conversion of furfural. For example, if the conversion of furfural is 20 % and the total yield of all detected products is 15 %, the carbon balance is 75 %. The carbon balance indicates how the furfural hydrodeoxygenation reaction is well controlled to produce desired products and how much undetected reactions (e.g., dimerization) proceeds.

7.2.3 Characterization

7.2.3.1 N₂ adsorption

The Ag-Cu bimetallic catalysts were characterized by nitrogen adsorption. The N₂ adsorption isotherms were measured at 77 K using Micromeritics ASAP 2020 analyzer. The BET surface area, pore volume, and average pore size are summarized in Table 7.1. The BET surface area, pore volume, and pore size tend to decrease with increasing concentrations of Ag.

	$S_{BET} (m^2/g)$	$V_{pore} (cm^3/g)$	D _{pore} (nm)
Cu/SiO ₂	444.6	-	-
Ag ₁ Cu ₃ /SiO ₂	435.7	6.28	57.6
Ag ₁ Cu ₂ /SiO ₂	432.2	4.69	43.4
Ag ₁ Cu ₁ /SiO ₂	429.8	4.23	39.4
Ag ₃ Cu ₁ /SiO ₂	413.6	4.46	43.1
Ag/SiO ₂	407.8	4.63	45.4

Table 7.1 Physicochemical properties of total 5 wt% Ag_xCu_y catalysts

7.2.3.2 Temperature Programmed Reduction (TPR)

The TPR experiments for the Ag-Cu bimetallic catalyst with different Ag and Cu concentrations have been carried out on Altamira catalyst characterization system (Altamira Instrument, AMI-200ip). The TCD signals are plotted in Figure 7.1 for the bimetallic samples. The maximum of the peak of TCD signal for the Ag₁Cu₃/SiO₂ sample is at 480 K, while the maximum of the peak for the Ag₃Cu₁/SiO₂ sample is at 380 K. The temperature of maximum of the peaks of TCD signal decreases with higher Ag concentrations, indicating that the presence of Ag increases reducibility of Cu in the catalysts. Note that there is only one peak in Ag₃Cu₁/SiO₂ and Ag₁Cu₃/SiO₂ catalysts, rather than two distinct peaks indicating that a close interaction between silver and copper exist and that the metal particles are formed after reduction are likely to be bimetallic and well distributed. In contrast, Ag₁Cu₂/SiO₂ and Ag₁Cu₁/SiO₂ catalysts have additional small peak at 550 K. There may be some portion of bulk metal oxides in the Ag₁Cu₂/SiO₂ and Ag₁Cu₁/SiO₂ catalysts.



Figure 7.1 TCD signals of the hydrogen reduction for Ag-Cu bimetallic catalysts with different concentrations.

7.3 Reaction Results

Total 5wt% Ag-Cu bimetallic catalysts supported on SiO₂ with Ag/Cu ratios of 0, 0.33, 1, 3, and ∞ were used to investigate the effect of Ag addition on the furfural conversion. First, the furfural consumption rates were plotted as a function of time to confirm that the catalyst is stable under the reaction condition (Figure 7.2). The decrease in the reaction rates with time is not very significant, and the sample's activity stabilizes by about 140 or 180 minutes on time of stream (TOS). Thus, after an initial period of rapid deactivation, catalysts are stable for the furfural hydrogenation reaction. Reaction rates and selectivity report below are taken after the catalytic activity has stabilized.



Figure 7.2 Furfural consumption rates as a function of time

The conversions on monometallic 1wt% Ag/SiO₂ and 1wt% Cu/SiO₂ were compared first (Figure 7.3). The conversions were about 5 and 12 % for monometallic 1wt% Ag/SiO₂ at reaction temperatures of 483 and 503 K, slightly higher than those for monometallic 1wt% Cu/SiO₂ (4.6 and 6.6 %). The carbon balance of monometallic 1% Ag catalyst supported on SiO₂ is not as good as the carbon balance of monometallic Cu catalyst, but their catalytic activity is not very different. 5 wt% Cu/SiO₂ catalyst shows 18 and 29 % furfural conversions, about five times higher than 1 wt% Cu/SiO₂. This indicates that the adsorption amount of furfural proportionally increases with the copper loading. The total conversions on monometallic 5 wt% Ag/SiO₂ (71 and 79 %) is more than five times larger than those on 1 wt% Ag/SiO₂, indicating that another effect occurs at higher silver concentration. Toy et al. reported [32] that the catalytic cycle for protodecarboxylation of aromatic carboxylic acids involves the interaction of substrate molecules with more than one Ag site in silver supported catalysts. Therefore, 10 wt% Ag/Al₂O₃ catalyst exhibits 216 h⁻¹ of turnover frequency (TOF) while TOF on 5 wt% Ag/Al₂O₃ is 19.6 h⁻¹. More than one Ag site can involve the furfural conversion when the concentration of Ag increases in Ag catalysts. The result on monometallic Ag/SiO₂ catalyst verifies the Ag content has catalytic activity for furfural conversion, even higher than the Cu contents.



Figure 7.3 Comparison of total conversions on 5 wt% Ag, 5 wt% Cu, 1 wt% Ag, and 1 wt% Cu.

Conversion and carbon balances for the various samples compared in Figure 7.4. The conversion of furfural on monometallic 5wt% Cu/SiO₂ (Ag/Cu = 0) is about 18 and 29 % at the reaction temperature 483 and 503 K, respectively. As the portion of

Ag content increases, the furfural conversions decrease, indicating the interaction between Ag and Cu reduces the furfural reactivity, or that Ag presents slower catalytic rates than Cu. As shown in Figure 7.2, monometallic Ag/SiO₂ catalysts exhibit higher reaction rates of furfural conversion than monometallic Cu/SiO₂ catalysts, contradictory to the trends observed on the Ag-Cu bimetallics. The decrease in total conversion by the addition of Ag to Cu/SiO₂ can be caused by the competition between Ag and Cu for surface sites. Even if Ag has similar or higher catalytic activity by itself, the priority seems to be given Cu for catalytic activity when Cu and Ag are combined. The interaction between Ag-Cu, which is not presented in this work, could also be the reason why the conversion decreased with the increase in Ag contents. The carbon balances are over 0.8 for all the samples, showing that mostly main products, such as furfuryl alcohol, furan, THF, and 2-MF, are formed during the reaction.



Figure 7.4 Total conversions of furfural on Ag-Cu bimetallic catalysts with different Ag and Cu contents

In Figure 7.5, furfural consumption rates are displayed in an Arrhenius plot. Total reaction rates increase with the reaction temperatures. The activation energy for monometallic 5 wt% Cu/SiO₂ catalyst was 34.4 kJ/mol, and as can be observed in the figure the activation energies decrease as the Ag content increases in the catalyst. However, the activation energy for 5 wt% Ag₃Cu₁/SiO₂ is 29.3 kJ/mol, which is still close to the activation energy for Cu/SiO₂ (34.4 kJ/mol). Therefore, it is difficult to distinguish if the decrease in the activation energy is result of adding Ag contents or it occurs accidently even if the activation energy for pure Ag/SiO₂ catalyst is very low (9.1 kJ/mol). Note that the activation energy for furfural consumption on Ag /SiO₂, as well as the rates of reaction, is also very different from other samples.



Figure 7.5 Furfural consumption rates and activation energies on Ag-Cu bimetallic catalysts with different Ag and Cu contents

The selectivity of the main four products was compared in Figure 7.6. The catalysts with monometallic Cu or low concentration of Ag exhibit very high furfuryl alcohol selectivity (~85%). The furfural alcohol was further hydrogenated to 2-MF, which selectivity is about (~10%). Advantageously, the selectivity toward furan and THF was very low as shown in Figure 7.6. For Ag/Cu ratios of 1 and 3, the selectivity toward furfuryl alcohol decreases and the selectivity for 2-MF increases slightly, while the furan and THF are not still observed. With increase in Ag concentration, the furfuryl alcohol selectivity continuously decreases and the 2-MF selectivity increases. The monometallic Ag catalyst exhibits similar selectivity for furfuryl alcohol and 2M-furan and still shows low selectivity for furan and THF. We can consider that the addition of Ag content enhances hydrogenation reaction, thus the selectivity for 2-MF increases while the selectivity for furfuryl alcohol decreases.



Figure 7.6 Selectivity of furfural conversion on Ag-Cu bimetallic catalysts with different Ag and Cu contents

Sitthisa and Resasco developed a method for conversion of furfural to furfuryl alcohol using a Cu catalyst supported on SiO₂[33]. The hydrogenation reaction was carried out in a continuous-flow quartz reactor under atmospheric pressure of hydrogen at temperatures between 483 and 563 K. The yield of 71% and 77% conversion of furfural is obtained. 2-methylfuran (2-MF) can be also obtained as byproduct. In contrast, furfural is converted to mainly furan by decarbonylation on Pd/SiO₂ catalyst, and the addition of Cu leads to formation of furfuryl alcohol by hydrogenation [34]. In their report, the furfural conversion on bimetallic Pd-Cu/SiO₂ and the addition of Cu makes electron back-donation from the metal to the carbonyl π^* orbital weaken, leading to higher furfuryl alcohol selectivity [34]. In like manner, the addition of Ag much weakens extent of electron back-donation from the metal to the π^* system, resulting in hydrogenation power stronger than monometallic Cu catalyst. In another report by Resasco group [33], the two possible mechanisms of furfural conversion on Cu/SiO₂ catalyst are demonstrated based on diffuse reflectance infrared Fourier transformation spectra (DRIFTS) and density functional theory (DFT) calculations. After formation of $\eta^{l}(O)$ -aldehyde binding mode by adsorption of furfural, there are possible two surface intermediates: 1) H atom attacks to C atom of adsorbed carbonyl group, resulting in alkoxide intermediate, and 2) H atom attacks to O atom, forming hydroxyalkyl intermediate (Scheme 7.2). Since the lower activation energy is shown for the later mechanism than the former one on Cu/SiO_2 catalyst, the formation of furfuryl alcohol is favored through the formation of hydroxyalkyl intermediate. This explanation can provide a clue for the reaction mechanism on both

monometallic Ag and bimetallic Ag-Cu catalysts. As shown in Scheme 7.2, the formation of 2-MF is expected through alkoxide intermediate by attacking to C atom by H atom. The addition of Ag can lead to the first mechanism, resulting in more 2-MF formation. In the case of monometallic 5 wt% Ag/SiO₂ catalyst, more than one Ag sites can produce synergetic enhancement effect on the reaction mechanism generating more 2-MF.

As mentioned in previous section, the formation of 2-MF is important because it is considered as possible alternative biofuel. The selectivity toward 2-MF from furfural obviously increases with the addition of Ag to the catalysts even if the reason why monometallic 5 wt% Ag exhibits that high conversions is not clear at this point. Further research is required to determine the exact role of Ag for the furfural hydrodeoxygenation reaction and to claim the Ag catalysts as promising catalysts for production of 2-MF from furfural.



H atom attacks at O atom

Hydroxylalkyl intermediate

Scheme 7.2 Possible mechanisms of furfural hydrogenation.

7.4 Summary

The catalytic furfural hydroconversion was investigated using Ag-Cu bimetallic catalysts supported on SiO₂. Total 5wt% monometallic and bimetallic catalysts with different Ag and Cu contents were prepared and studied the effect of adding Ag. Monometallic Ag/SiO₂ catalyst showed higher total furfural consumption rates than monometallic Cu/SiO₂ catalyst, while the Ag-Cu bimetallic catalysts exhibited lower rates than either pure Ag or Cu catalysts. Competition between Ag and Cu and strong interaction between Ag and Cu, which prevents the reaction, could be the reasons for the lower reaction rates. As Ag concentration increases in the bimetallic catalysts, the 2M-furan selectivity increases, indicating hydrogenation power becomes strong by adding Ag or the reaction proceeds through different reaction intermediates from that formed on Cu catalysts.

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Chapter 8

CONCLUSIONS

8.1 Dissertation Summary

This thesis investigates the hydrocarbon conversions over zeolites with the ultimate goal of revealing a reaction mechanism which is different from typical protolytic hydrocarbon conversion mechanism. The effect of thermal treatments of SSZ-13 with Si/Al ratios of 6 and 12 has been investigated for the monomolecular propane conversion in Chapter 3. The changes in selectivity and activation energies indicate that the different types of active sites are generated by thermal treatments, resulting in different catalytic properties for the samples with different Si/Al ratios. The selectivity over SSZ-13-6 has changed substantially with just an increase of 50 K in the temperature from 773 K to 823 K, which is a typical calcination condition. Activation energy does not change despite of this drastic selectivity change. It was concluded that the hydrocarbon conversion over thermally treated SSZ-13-6 proceeds through the protolytic mechanism after thermal treatment. Confinement effects by thermal treatment may cause the change in selectivity.

The selectivity and activation energy observed for SSZ-13-12 samples changed gradually with treatment temperature, indicating the generation of different active sites. A redox mechanism, involving the formation of propane radical cation intermediate, is suggested as an alternative reaction pathway for propane conversion over thermally treated SSZ-13-12 samples.
The monomolecular propane reaction was studied over iron-silicate zeolites in Chapter 4 and a mechanistic study was conducted based on microscopic reversibility principle in Chapter 5. The iron-containing zeolites show very high dehydrogenation selectivity (dehydrogenation-to-cracking ratio ~ 22) while typical Al-containing zeolites exhibit higher cracking selectivity than dehydrogenation selectivity by factor of 2 to 3. The activation energies of the dehydrogenation of propane over H-[Fe] zeolites are lower than those over H-[Al]ZSM-5 (115 kJ/mol vs. 170 kJ/mol). It is not possible to explain these observations by the typical protolytic mechanism for hydrocarbon conversions over zeolite catalysts. Instead, we proposed a redox catalytic cycle in this dissertation.

The mechanism was further investigated to verify the redox catalytic cycle using the propane dehydrogenation and its reverse reaction, propene hydrogenation over H-[Fe]ZSM-5 and contrasted to those over H-[A1]ZSM-5. The propane dehydrogenation and the propene hydrogenation have common elementary steps, and the difference of their activation energies correspond to the gas phase reaction enthalpy of propane dehydrogenation. The Marcus theory for electron transfer and the ionization energies of the related molecules were related to the thermodynamic analysis of the reaction mechanism. After formation of propane radical cation, a lower energy change through the dehydrogenation pathway than the cracking pathway explains very high dehydrogenation selectivity over H-[Fe]ZSM-5.

The monomolecular propane reaction is investigated using zeolites having only hydrogen-bonded acid sites in Chapter 6. The H-[Al]beta zeolite and H-[Al]ZSM-5, used as reference materials having normal BAS, exhibit similar rates of reaction, selectivity (cracking > dehydrogenation), and activation energy. The sample

of H-[Al(B)]beta, having only hydrogen-bonded acid sites, shows low reaction rates and lower activation energies than H-[Al]ZSM-5, and shows higher dehydrogenation selectivity (cracking-to-dehydrogenation ratios ~ 0.63 and ~ 0.45 at 773 K). It is noted that the hydrogen bonds are expected to be in constrained spaces coordinated to framework oxygen. The tight space leads to the formation of propyl cation intermediate predominantly, resulting that the dehydrogenation channel is favored than the cracking channel. The activation entropy values are very negative (-200 and -250 J/mol/K for zeolites having only hydrogen-bonded acid sites) compared to those for zeolites having 'normal' BAS (-111 and -96 J/mol/K), supporting the confinement effect because the propane molecule lose more degree of freedom of translation in zeolites having only hydrogen-bonded acid sites.

In the final section of this thesis, furfural conversion over Ag-Cu bimetallic catalyst supported on SiO₂ was examined in Chapter 7. Bimetallic catalysts with different Ag and Cu contents (5 wt% total) were prepared using the wet impregnation method. The furfuryl alcohol is the predominantly product from the hydrogenation of furfural; 2-methyl furan is produced by further hydrogenation over the Ag-Cu bimetallic catalysts and Ag monometallic catalyst. Compared to Cu/SiO₂, hydrogenation is much strong over Ag-containing catalysts, showing higher 2-methyl furan selectivity. The activation energy over Ag-Cu bimetallic catalysts are decreased with increase in concentration of Ag in the catalysts (from 34.4 for Cu/SiO₂ to 29.3 for Ag₃Cu₁/SiO₂). From these observations, the Ag contents enhance the hydrogenation of furfural conversion and decrease the activation barrier.

8.2 **Recommendations for Future work**

This dissertation has investigated the hydrocarbon conversion over SSZ-13 after thermal treatment, H-[Fe] zeolites, and zeolite beta having only hydrogen-bonded acid sites. The studies presented in the preceding sections have indicated that a redox catalytic cycle can explain observed catalytic properties for the propane conversion. There are many of unknowns about the mechanism of the redox catalytic cycle, the reaction intermediates, and the local structure of the active centers in the zeolites used in this dissertation. This section outlines possible directions for future research to support and expand the findings of this dissertation.

8.2.1 Characterization of Local Structure of Zeolites

Further studies are needed to elucidate the local structure of active sites in zeolites after high temperature treatment and iron-silicate zeolites. Neutron diffraction, electron spin resonance (ESR), X-ray absorption spectroscopy, Mössbauer spectroscopy are promising techniques for the future studies to probe the local structure in the samples under the reaction conditions.

8.2.1.1 Neutron Diffraction

Neutron diffraction is the application of neutron scattering to the determination of the atomic and magnetic structure of a material, especially crystalline solid. The technique is similar to X-ray diffraction but due to their different scattering properties, neutrons and X-rays provide complementary information [1]. It is necessary to carry out the diffraction experiments at elevated temperatures to examine the structural phase transitions. For example, it was reported that the measurement of the perovskitelike NaTaO₃ was carried out from room temperature to 933 K, exhibiting continuous phase transition from orthorhombic *Pbnm* at room temperature, orthorhombic Cmcm at 700 K, tetragonal *P4/mbm* at 835 K, and then to cubic *Pm*3m above 890 K [2]. The thermal expansion of the lattice parameters is also reported using neutron diffraction in the 373-1273 K temperature range [3]. In Chapter 3, the SSZ-13 samples treated at different temperatures were examined for hydrocarbon conversion, but it is still unknown why their selectivity and activation energies are different. Especially the case of SSZ-13-6, the dehydrogenation selectivity is enhanced even if the characterization techniques such as NMR, TPD, and XRD showed minor change in the structure. The confinement effect after the thermal treatment can be one of candidates for the selectivity change as we discussed in Chapter 6. The partial collapse of structure due to low thermal stability of SSZ-13-6 is also an important consideration. To attain a convincing explanation, it is required to observe the structural phase transition with increase in temperature and this can be done using high temperature neutron diffraction.

8.2.1.2 Electron Spin Resonance (ESR) Spectroscopy

Electron spin resonance (ESR) spectroscopy is a technique for studying materials with unpaired electrons. When an atomic or molecular system with unpaired electrons is subjected to a magnetic field, the electronic energy levels of the atom or molecule will split into different levels. The magnitude of the splitting is dependent on the strength of the applied magnetic field. The atom or molecule can be excited from one split level to another in the presence of an external radiation of frequency corresponding to the frequency obtained from the difference in energy between the

split levels. Such an excitation is called magnetic resonance absorption. The atom or molecule under investigation may be in different environments in an actual sample. The magnetic resonance frequency will hence be influenced by the local environment of the atom or molecule. The electron spin resonance technique is therefore, a probe for a detailed identification of the various atomic and molecular systems and their environments and all associated parameters.

ESR gives meaningful structural information even from ongoing chemical or physical processes, without influencing the process itself. Thus, it is used to complement other analytical methods in a wide range of application areas. ESR can provide the information about the active centers, the intermediate species, the activation processes of reactants, the surface reactions, and the study of the catalyst deactivation. The in-situ ESR can provide the information for the catalytic redox process under the reaction conditions [4, 5]. ESR measurements are carried out generally at temperatures of 77 K or below after stopping the reaction under study. In addition, short relaxation times of electron spins and exchange processes lead to a broadening of the ESR signals. Therefore, ESR spectroscopy is usually limited to this temperature range. Unfortunately, Fe^{2+} species have short relaxation times and requires low registration temperatures lower than 77 K, and the radical intermediates are frequently very reactive and too short-lived to be accessible by in-situ ESR at elevated temperatures. Thus, the ESR analysis should be measured for iron-containing zeolite after thermal treatment in the presence of reactants and quenching to low spectra recording temperatures. For iron-containing zeolites, Brueekner showed that 45% of the octahedrally coordinated Fe³⁺ species remains on the framework of

aluminophosphates and silicoaluminophosphates after calcination [6]. However, the assignment of the signals to certain iron species is still controversial.

The ESR can be measured for various H-[Fe]ZSM-5 samples (as-made, calcined, steamed, Na-form, and collected after reaction) as the unit cell volumes were compared for those samples in Chapter 4. The nature of active center in H-[Fe]ZSM-5 for hydrocarbon conversion, the reaction intermediates, and further activation mechanism can be revealed on condition that the sample does not change much during chilling after the reaction.

8.2.1.3 Mössbauer Spectroscopy

Mössbauer spectroscopy can provide very precise information about the chemical, structural, magnetic and time-dependent properties of a material. It is based on the Mössbauer effect, which is recoilless gamma ray emission and absorption. Nuclei in atoms undergo a variety of energy level transitions associated with the emission or absorbing of a gamma ray. The energy levels are related to their surrounding environment. Nuclei in solid crystal can emit or absorb a gamma ray, and the gamma ray emitted by one nucleus can be resonantly absorbed by a sample containing nuclei of the sample isotope, and this absorption can be measured [7, 8].

The observed Mössbauer parameters are a chemical shift, quadrupole splitting, and magnetic splitting. The chemical shift describes a shift in the resonance energy of a nucleus due to the transition of electrons within its s orbital. The chemical shift does not change with temperature, however small changes are generally attributed to second-order Doppler effect. Quadrupole splitting reflects the interaction between the nuclear energy level and surrounding electric field gradient. Magnetic splitting is a result of the interaction between the nucleus any surrounding magnetic field. These three parameters can often be used to identify a particular compound by comparing it to known spectra (e.g. Mössbauer Effect Data Center) [9]. As a result, the Mössbauer spectroscopy can characterize the oxidation state, coordination number of atoms, cation ordering, and site populations in crystal structures.

In iron-silicate zeolites, the Fe³⁺ ion is presented in three different forms: 1) in tetrahedral framework positions, 2) in extra-framework positions, and 3) iron oxides occluded within zeolite pores or precipitated outside the crystals. In a solid phase, Mössbauer spectroscopy can detect any form of iron and the observed spectrum can be deconvoluted to subspectra corresponding to iron in different environment [10]. Therefore, the ⁵⁷Fe Mössbauer spectroscopy can provide information on the environment of all of Fe³⁺ ion positions above mentioned. The ⁵⁷Fe Mössbauer spectroscopy studies exhibited that the Fe³⁺ ions were well-dispersed in the tetrahedral framework of as-made iron-silicate zeolite and some of the iron moves out of the framework sites after calcination [10, 11]. Recently, Fe particles were investigated by in-situ high temperature Mössbauer spectroscopy [12, 13]. Under the reaction conditions, the Fe³⁺ in Ir-Fe/SiO₂ catalyst is reduced to Fe⁰ and Fe²⁺, and the reduced Fe species are also oxidized upon exposure to oxygen while some amount of Fe⁰ was encapsulated by ferric oxide [12]. The oxidation of Fe particles into hermatite (α -Fe₂O₃) was observed in a CNT-Fe-Al₂O₃ nanocomposite powder [13].

The observation of H-[Fe] zeolites by in-situ ⁵⁷Fe Mössbauer spectroscopy would be helpful to reveal how the redox property of iron-silicate catalysts works under specified conditions and involves to the hydrocarbon conversion.

8.2.1.4 X-ray Absorption Spectroscopy (XAS)

X-ray absorption spectroscopy (XAS) is a powerful technique to study directly the local coordination of aluminum and silicon in zeolites. XAS can be divided into four regions based on the difference between the photon energy and the edge energy $(E-E_0)$, where E_0 is the edge energy [14]. The edge energy represents the energy required to overcome the binding energy of the core electron to be transferred to the continuum states. The first region is the pre-edge (E < E0), and the second region is the X-ray absorption near edge spectroscopy (XANES) which includes the energy is E = $E_0 \pm 10$ eV. The third region is the near edge X-ray absorption fine structure (NEXAFS) in the region between 10 eV up to 50 eV above the edge, and the forth region is the extended X-ray absorption fine structures (EXAFS) which includes all energy from 50 eV above the edge to the end of the spectrum (~1000 eV above the edge). In the pre-edge region, the electron is transferred from a core shell to empty bound states. The XANES region provides information about the local environment such as oxidation state, coordination environment, and geometric distortion. The EXAFS is related to the interference of the outgoing electron from the absorbing atom and the backscattering electron from the surrounding atoms. Since the electron has a particle and wave character, this interference could be constructive or destructive, giving rise to fine structure (oscillation) in the X-ray absorption spectrum. The photoelectron scattering amplitude in the low energy range $(5 \sim 200 \text{ eV})$ become much larger so that multiple scattering events become dominant in the NEXAFS spectra. The EXAFS data can be used to find information about distance between central and neighboring atoms, the number of neighboring atoms, the nature of neighboring atoms such as approximate atom number, and changes in central-atom coordination with changes in experimental conditions.

In our group's previous work [15], a number of thermally dehydroxylated samples were investigated by XAS using Ga-substituted zeolites because gallium has a larger absorption coefficient at an experimentally convenient energy range for X-ray absorption spectroscopy. 80% of the gallium was still in tetrahedral coordination while the rest was in octahedral coordination. The coordination environment of the assynthesized and calcined form of Ga-substituted zeolites (Ga-Beta, Ga-ZSM-5, and Ga-mordenite) has also been investigated in other earlier reports [16-19].

In earlier reports [20-22], XANES was used to investigate the local structure of iron in zeolites. The template removal by calcination and of steaming lead to minor changes, such as partial Fe migration from framework to extra-framework, but the majority of the iron stays in a 4-fold oxygen coordination. In addition to those observations, in-situ X-ray absorption technique can provide much detail information about the change in local structure of Fe under the reaction condition.

8.2.1.5 Theoretical Verification of Redox Mechanism

The reaction mechanism for the monomolecular hydrocarbon conversion has been thoroughly investigated theoretically [23-30]. With the experimental studies [31-35], it is now well-known that the reaction proceeds through the protolytic mechanism over BAS in zeolite catalysts. The first step is the protonation of the alkane at an acid site, followed by formation of alkanium cation, and the second step is the breakage of alkanium ion leading to alkane and alkene production. Various simulation techniques such as density functional theory (DFT), configurational-bias Monte Carlo (CBMC) simulation, ab initio DFT calculation in combination with harmonic transition state theory (hTST) have been used for the reaction mechanism study and provided relevant kinetic parameters such as the intrinsic activation energies and information about the reaction active centers and the elementary steps of the reaction mechanisms [23-30].

In this dissertation, the observation of the real structure of the postdehydroxylation SSZ-13 samples and H-[Fe] zeolite catalyst is insufficient especially under reaction conditions. It would accompany laborious tasks which is technically and practically difficult to carry out. The theoretical investigation can provide complementary information about the suggested redox reaction mechanism. Especially, the reaction intermediates and the structural change of the zeolites during reactions can be supposed in combination with the observed results in this work.

8.2.2 Other Zeolites

8.2.2.1 H-[Fe]CHA

CHA type zeolite, H-SSZ-13 was used for the propane conversion in the Chapter 3, and MFI type zeolite, H-[Fe]ZSM-5 was investigated for the propane dehydrogenation and propene hydrogenation in Chapters 4 and 5. As discussed in Chapter 3, the complexity of ZSM-5 zeolite makes one difficult to complete understand the structure of active sites. On the contrary, SSZ-13 (CHA) has only one topologically distinct tetrahedral site. H-[Fe]CHA can be used to investigate the reaction mechanism for the propane dehydrogenation and propene hydrogenation. Since the pore size of CHA is smaller than that of MFI (ZSM-5), the incorporation of Fe into the framework of CHA can lead to the higher selectivity toward dehydrogenation of alkanes. In addition, the small pore size does not allow large iron oxide clusters within the intra-crystalline structures, which can be formed at high temperatures [36]. Securing the stability of [Fe]CHA sample under high temperature conditions could be a key matter for usage of catalyst because [A1]CHA sample with low Si/Al ratio has low thermal stability. The migration of Fe species prevents obtaining the exact information about the real active sites in H-[Fe] zeolites. The synthesis of H-[Fe] CHA with higher thermal stability can be much helpful for the reactions at the high temperatures.

8.2.2.2 Zeolite Synthesized with Other Heteroatoms

Isomorphous substitution of Fe^{3+} for Al^{3+} was used to prepare Fe-silicate zeolites in Chapter 4 and 5. As well, isomorphous substitution of metal elements with valence of 4+, such as Ti^{4+} , Zr^{4+} , and Sn^{4+} , has been investigated by many researchers. (References) The quadrivalent cations containing zeolites exhibit redox properties even though the preparation is not as smooth as for preparing trivalent cations containing zeolites. Titanium silicalite-1 (TS-1, MFI) is the most well-known material of this type. After the invention of TS-1, great success in the area of redox catalysis has been achieved [37, 38]. In addition to MFI structure, Ti-beta zeolite and Ti-MWW were synthesized to obtain larger pore size than MFI structure. Ti-beta zeolite shows advantages in the epoxidation of cyclic alkenes with H2O2, but shows worse catalytic activity than TS-1 in the reactions involving the small-size substrates [39]. MWW structure is stable and unique because it has 12MR supercages and two independent 10MRs. [AI]MWW type zeolite, well known as MCM-22, has shown great performance for benzene alkylation [40]. Ti-containing MWW is expected to show unusual activity as a redox catalyst [41, 42]. Synthesis methods to prepare Sn and Zr containing zeolites have been developed, too. Sn-beta zeolite has received high

attention for its Lewis acid properties. For example, Sn-beta is used for the direct formation of methyl lactate from common sugars and glucose isomerization [43, 44], and is an excellent catalysts for the reduction of aldehydes and ketones to alcohols and the oxidations of alcohols to the corresponding carbonyl group [45, 46].

The different heteroatom (especially quadrivalent cations) other than Fe^{3+} and Al^{3+} can be prepared and examined for the hydrocarbon conversion. The isomorphous substitution can change the acid properties, as well as the topological properties, such as distortion of framework structure and different bond strength. The incorporation of such quadrivalent cations into zeolite framework can also change the catalytic properties and the selectivity, and can provide the important information about the reaction mechanism and the local structure of active sites in zeolites.

8.2.3 Methane Conversions on Zeolite-based Heterogeneous Catalysts

C1 chemistry based on single carbon-bearing molecules, such as synthesis gas, methane, methanol and carbon dioxide, provides many routes to industrial chemicals [47]. With recent rise of shale gas, technologies to provide petrochemical feedstock using methane have received much attention. However, it is very challenging process because methane is very stable hydrocarbon and the breakage of C-H bond in methane requires a substantial amount of energy. As well, selectivity and activities in most reactions were poor. Therefore, many efforts have focused on feasible processes, such as methanol-to-olefins and syngas-to-olefins. The direct conversion of methane to fuels and petrochemicals has remained unattractive [47].

Recently, Guo et al. [48] reported direct and nonoxidative conversion of methane using iron-containing silica as a catalyst. The lattice-confined single iron site

initiates dehydrogenation of methane by forming methyl radical. The radicals combine to generate ethane, and the ethane is further dehydrogenated, giving vinyl radical ready to react with other ethane molecules. In this way, further dehydrogenation and cyclization leads to benzene and naphthalene. In addition, direct conversions of methane to methanol and acetic acid are also very challenging research issues because methanol and acetic acid can be readily used by various techniques already developed. Zeolite-based heterogeneous catalysts, such as Mo/zeolites, have been examined to study the direct conversions of methane [49, 50].

The Fe-containing zeolites studied in Chapter 4 and 5 also have very strong dehydrogenation ability and are considered to lead to formation of propane radical intermediates. These abilities of Fe-silicate zeolites evoke the expectation that they can be used as catalysts or as precursors to catalysts. The improvement of thermal stability of Fe-silicate zeolites is required because of very high temperature about 1300 K for direct conversion of methane.

8.3 Final Remarks

The work presented in this thesis has shown the redox catalytic cycle for hydrocarbon conversion over thermally treated zeolites and iron-silicate zeolites. The propane reaction experiments were mainly used to identify the important kinetic parameters and selectivity toward cracking and dehydrogenation. Dehydrogenation selectivity was enhanced for the SSZ-13 catalysts treated at high temperatures, while cracking is favored than dehydrogenation for the pristine acid zeolites. High dehydrogenation selectivity was observed for iron-silicate ZSM-5 catalysts (~22 times higher than cracking). The dehydrogenation of propane over iron-silicate zeolites was

examined with higher reaction conversion to consider a possibility for industrial use. With increase of dehydrogenation selectivity, lower activation energy was observed for both thermally treated SSZ-13 and iron-silicate ZSM-5, compared to that for the pristine acid zeolite such as H-[A1]ZSM-5. The observed results cannot be explained by the typical protolytic mechanism for hydrocarbon activation. The proposed redox mechanism was verified using the reverse reaction, propene hydrogenation reaction. Both propane dehydrogenation and propene hydrogenation reactions proceed through common elementary steps. The thermodynamic analysis including electron transfer (Marcus theory) shows that the cracking requires more energy (~ 30 kJ/mol) than dehydrogenation is kinetically favored over the cracking. The zeolites have played important roles in petrochemical industry and the endeavor for development of zeolite catalysis has continued. This new reaction chemistry in thermally treated zeolites and iron-silicate zeolites and its further development can contribute to both existing applications and emerging challenges in petrochemical industry.

8.4 References

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Appendix A

SUMMARY OF UNITS USED IN KINETIC ANALYSIS OF PROPANE CONVERSION OVER H-[AL]ZSM-5 AND H-[FE]ZSM-5

<Propane dehydrogenation over H-[A1]ZSM-5>

Start from the equations
$$r_D = k_D^{app} P_{C_3 H_8}$$
 and $k_D^{app} = \frac{k_B T}{h} K_D^*$
TOF $r_D = \left[mol (mol Al)^{-1} s^{-1} \right], P_{C_3 H_8} = \left[bar \right]$
 $\Rightarrow k_D^{app} = \left[mol (mol Al)^{-1} s^{-1} bar^{-1} \right]$
 $k_B T / h = \left[s^{-1} \right] \Rightarrow K_D^? = \left[mol (mol Al)^{-1} bar^{-1} \right]$

In different way, $r_D = k_{TS}\Theta^{\dagger}$, $\tilde{K}_D = \frac{\Theta^{\dagger}}{\Theta^{\ast}}$, $\Theta^{\ast} = \frac{K_1 P_{C_3 H_8}}{1 + K_1 P_{C_3 H_8}} \sim K_1 P_{C_3 H_8}$ $r_D = k_{TS}\Theta^{\dagger} = k_{TS}\tilde{K}_D\Theta^{\ast} = k_{TS}\tilde{K}_D K_1 P_{C_3 H_8}$ $k_{TS} = [s^{-1}]$, $K_1 = \frac{\Theta^{\ast}}{P_{C_3 H_8}} = [mol(mol \ Al)^{-1} bar^{-1}] \Rightarrow \tilde{K}_D = [-]$ $K_D^{?} = \tilde{K}_D K_1 = \frac{\Theta^{\dagger}}{P_{C_3 H_8}} = [mol(mol \ Al)^{-1} bar^{-1}]$ Again, $k_D^{app} = k_2 K_1 \Rightarrow k_2 = [s^{-1}]$

<Propene hydrogenation over H-[A1]ZSM-5>

Start from the equations $r_H = k_H^{app} P_{C_3H_6} P_{H_2}$ and $k_H^{app} = \frac{k_B T}{h} K_H^{\dagger}$ TOF $r_H = \left[mol \left(mol \ Al \right)^{-1} s^{-1} \right], P_{C_3H_6} = \left[bar \right], P_{H_2} = \left[bar \right]$ $k_H^{app} = \left[mol \left(mol \ Al \right)^{-1} s^{-1} bar^{-2} \right] \Rightarrow K_H^{?} = \left[mol \left(mol \ Al \right)^{-1} bar^{-1} \right]$

In different way, $r_{H} = k_{TS}\Theta^{\dagger}$, $\tilde{K}_{H} = \frac{\Theta^{\dagger}}{\Theta^{\bullet}P_{H_{2}}^{*}}$ $\Theta^{*} = \frac{K_{3}^{-1}P_{C_{3}H_{6}}^{*}}{1+K_{3}^{-1}P_{C_{3}H_{6}}^{*}} \sim K_{3}^{-1}P_{C_{3}H_{6}}^{*}$, $P_{C_{3}H_{6}}^{*} \sim K_{4}^{-1}P_{C_{3}H_{6}}$, $P_{H_{2}}^{*} \sim K_{5}^{-1}P_{H_{2}}$ $r_{H} = k_{TS}\Theta^{\dagger} = k_{TS}\tilde{K}_{H}\Theta^{*}P_{H_{2}}^{*} = k_{TS}\tilde{K}_{H}K_{3}^{-1}K_{4}^{-1}K_{5}^{-1}P_{C_{3}H_{6}}P_{H_{2}}$ $K_{4}^{-1} = \frac{P_{C_{3}H_{6}}^{*}}{P_{C_{3}H_{6}}} = \left[mol (mol \ Al)^{-1} \ bar^{-1} \right]$ $K_{5}^{-1} = \frac{P_{H_{2}}^{*}}{P_{H_{2}}} = \left[mol (mol \ Al)^{-1} \ bar^{-1} \right]$ $K_{3}^{-1} = \frac{\Theta^{\dagger}}{P_{C_{3}H_{6}}^{*}} = \left[-\right]$ $\tilde{K}_{H} = \frac{\Theta^{\dagger}}{\Theta^{*}P_{H_{2}}^{*}} = \left[(mol \ Al) \ mol^{-1} \right]$ $K_{H}^{?} = \tilde{K}_{H}K_{3}^{-}K_{4}^{-1}K_{5}^{-1} = \frac{\Theta^{\ddagger}}{P_{C_{3}H_{6}}P_{H_{2}}} = \left[\frac{mol \ Al}{mol} \ \frac{mol}{(mol \ Al)} \ bar \ (mol \ Al)^{bar} \right]$ $= \left[mol (mol \ Al)^{-1} \ bar^{-2} \right]$ Again, $k_{H}^{app} = k_{-2}K_{3}^{-1}K_{4}^{-1}K_{5}^{-1} \Rightarrow k_{-2} = \left[(mol \ Al) \ mol^{-1}s^{-1} \right]$

<H-[Fe]ZSM-5, step 1a in Scheme 3>

Start from the equations $r'_D = k'^{app}_D P_{C_3H_8}$ and $k'^{app}_D = \frac{k_B T}{h} K'_D$ TOF $r'_D = \left[mol \left(mol \ Fe \right)^{-1} s^{-1} \right], P_{C_3H_8} = \left[bar \right]$

$$\Rightarrow k_D^{\prime app} = \left[mol \left(mol \ Fe \right)^{-1} s^{-1} bar^{-1} \right]$$

$$k_B T / h = \left[s^{-1} \right] \Rightarrow K_D^{\prime ?} = \left[mol \left(mol \ Fe \right)^{-1} bar^{-1} \right]$$

In different way, $r'_D = k'_{TS} \Theta'^*$, $\tilde{K}'_D = \frac{\Theta'^*}{P_{C_3H_8^{\bullet+}}^{*(II-)}}$, $P_{C_3H_8^{\bullet+}}^{*(II-)} \sim K_7 P_{C_3H_8}^{*(III)}$, $P_{C_3H_8}^{*(III)} \sim K_6 P_{C_3H_8}$

here,
$$P_{C_{3}H_{8}^{*+}}^{*(II-)}$$
 is equivalent to Θ^{*} for H-[A1]ZSM-5.
 $r'_{D} = k'_{TS}\Theta'^{*} = k'_{TS}\tilde{K}'_{D}\Theta'^{*} = k'_{TS}\tilde{K}'K_{6}K_{7}P_{C_{3}H_{8}}$
 $k'_{TS} = [s^{-1}], K_{6} = \frac{P_{C_{3}H_{8}}^{*(III)}}{P_{C_{3}H_{8}}} = [mol(mol Fe)^{-1} bar^{-1}],$
 $K_{7} = \frac{P_{C_{3}H_{8}^{*+}}^{*(II-)}}{P_{C_{3}H_{8}}^{*(III)}} = [-] \Rightarrow \tilde{K}' = [-]$
 $K'_{D}{}^{?} = \tilde{K}'_{D}K_{6}K_{7} = \frac{\Theta'^{*}}{P_{C_{3}H_{8}}} = [mol(mol Fe)^{-1} bar^{-1}]$
Again, $k'_{D}^{app} = k_{8}K_{6}K_{7} \Rightarrow k_{8} = [s^{-1}]$

<Propene hydrogenation over H-[Fe]ZSM-5>

Start from the equations
$$r'_{H} = k'^{app}_{H} P_{C_{3}H_{6}} P_{H_{2}}$$
 and $k^{app}_{H} = \frac{k_{B}T}{h} K^{\dagger}_{H}$
TOF $r'_{H} = \left[mol (mol \ Fe)^{-1} s^{-1} \right], P_{C_{3}H_{6}} = \left[bar \right], P_{H_{2}} = \left[bar \right]$
 $k'^{app}_{H} = \left[mol (mol \ Fe)^{-1} s^{-1} bar^{-2} \right] \Rightarrow K'_{H}^{?} = \left[mol (mol \ Fe)^{-1} bar^{-1} \right]$

In different way, $r'_{H} = k'_{TS} \Theta'^{*}$, $\tilde{K}'_{H} = \frac{\Theta'^{*}}{P_{C_{3}H_{6}\bullet+}^{*(II-)}P_{H_{2}}^{*}}$ here, $P_{C_{3}H_{6}\bullet+}^{*(II-)}$ is equivalent to Θ^{*} for H-[A1]ZSM-5. $P_{C_{3}H_{6}\bullet+}^{*(II-)} \sim K_{9}^{-1}P_{C_{3}H_{6}}^{*(III)}$, $P_{C_{3}H_{6}}^{*(III)} \sim K_{10}^{-1}P_{C_{3}H_{6}}$, $P_{H_{2}}^{*} \sim K_{11}^{-1}P_{H_{2}}$

$$\begin{aligned} r'_{H} &= k'_{TS} \Theta'^{\dagger} = k'_{TS} \tilde{K}'_{H} P_{C_{3}H_{6}\bullet+}^{*} P_{H_{2}}^{*} = k'_{TS} \tilde{K}'_{H} K_{9}^{-1} K_{10}^{-1} K_{11}^{-1} P_{C_{3}H_{6}} P_{H_{2}} \\ K_{10}^{-1} &= \frac{P_{C_{3}H_{6}}^{*(II)}}{P_{C_{3}H_{6}}} = \left[mol (mol \ Fe)^{-1} bar^{-1} \right] \\ K_{11}^{-1} &= \frac{P_{H_{2}}^{*}}{P_{H_{2}}} = \left[mol (mol \ Fe)^{-1} bar^{-1} \right] \\ K_{9}^{-1} &= \frac{P_{C_{3}H_{6}\bullet+}^{*(II-)}}{P_{C_{3}H_{6}\bullet+}^{*}} = \left[- \right] \\ \tilde{K}'_{H} &= \frac{\Theta'^{\dagger}}{P_{C_{3}H_{6}\bullet+}^{*(II-)}} = \left[(mol \ Fe) mol^{-1} \right] \\ K_{H}'^{?} &= \tilde{K}'_{H} K_{9}^{-} K_{10}^{-1} K_{11}^{-1} = \frac{\Theta'^{\dagger}}{P_{C_{3}H_{6}} P_{H_{2}}} = \left[\frac{mol \ Fe}{mol} \frac{mol}{(mol \ Fe) bar} \frac{mol}{(mol \ Fe) bar} \right] \\ &= \left[mol (mol \ Fe)^{-1} bar^{-2} \right] \\ \text{Again, } k'_{H}^{app} &= k_{-8} K_{9}^{-1} K_{10}^{-1} K_{11}^{-1} \Rightarrow k_{-8} = \left[(mol \ Fe) mol^{-1} s^{-1} \right] \end{aligned}$$

Summary of Units

Common units						
$k_{B}T/h$	s^{-1}	$P_{C_3H_6}$	bar			
E_a^{app}	kJ mol ⁻¹	$P_{C_3H_8}$	bar			
ΔS^{app}	J mol ⁻¹ K ⁻¹	P_{H_2}	bar			

Units for H-[Al]ZSM-5

<i>k</i> ₂	s^{-1}	K_4^{-1}	mol (mol Al) ⁻¹ bar ⁻¹
<i>k</i> ₋₂	(mol Al) mol ⁻¹ s ⁻¹	K_5^{-1}	mol (mol Al) ⁻¹ bar ⁻¹
$k_{\scriptscriptstyle D}^{\scriptscriptstyle app}$	mol (mol Al) ⁻¹ s ⁻¹ bar ⁻¹	K_D^{\ddagger}	mol (mol Al) ⁻¹ bar ⁻¹
$k_{\scriptscriptstyle H}^{\scriptscriptstyle app}$	mol (mol Al) ⁻¹ s ⁻¹ bar ⁻¹ bar ⁻¹	$ ilde{K}_{_D}$	-
K_1	mol (mol Al) ⁻¹ bar ⁻¹	$K_{_H}{}^\ddagger$	$mol (mol Al)^{-1} bar^{-1} bar^{-1}$
K_{3}^{-1}	-	$ ilde{K}_{\scriptscriptstyle H}$	(mol Al) mol ⁻¹

Units for H-[Fe]ZSM-5

$$k_8$$
 s⁻¹ K_{10}^{-1} mol (mol Al)⁻¹ bar⁻¹

k_{-8}	(mol Al) mol ⁻¹ s ⁻¹	K_{11}^{-1}	mol (mol Al) ⁻¹ bar ⁻¹
$k_D^{\prime app}$	mol (mol Al) ⁻¹ s ⁻¹ bar ⁻¹	$K_D^{\prime \ \ddagger}$	mol (mol Al) ⁻¹ bar ⁻¹
$k_{H}^{\prime app}$	mol (mol Al) ⁻¹ s ⁻¹ bar ⁻¹ bar ⁻¹	$ ilde{K}_D'$	-
K_6	mol (mol Al) ⁻¹ bar ⁻¹	$K'_{\scriptscriptstyle H}{}^{\ddagger}$	mol (mol Al) ⁻¹ bar ⁻¹ bar ⁻¹
K_7	-	$ ilde{K}'_{H}$	(mol Al) mol ⁻¹
K_{9}^{-1}	-		

Appendix B

THERMODYNAMIC CALCULATIONS

<Reaction enthalpy calculation>

$$C_{3}H_{8} \rightleftharpoons C_{3}H_{6} + H_{2}$$
$$C_{3}H_{8} \rightleftharpoons C_{2}H_{4} + CH_{4}$$

The reaction enthalpy was calculated using thermodynamic data on the assumption of the ideal gas.

$$\Delta H_{R}^{\circ}(T) = \sum_{i} v_{i} \Delta H_{f,i}^{\circ}(T)$$

$$\Delta H_{R,D}^{\circ}(T) = \Delta H_{f,C_{3}H_{6}}^{\circ}(T) + \Delta H_{f,H_{2}}^{\circ}(T) - \Delta H_{f,C_{3}H_{8}}^{\circ}(T)$$

$$\Delta H_{R,H}^{\circ}(T) = \Delta H_{f,C_{2}H_{4}}^{\circ}(T) + \Delta H_{f,CH_{4}}^{\circ}(T) - \Delta H_{f,C_{3}H_{8}}^{\circ}(T)$$

$$\Delta H_{R,D}^{\circ}(298K) = 20.4 + 0 - (-103.9) = 124.3kJ / mol$$

$$\Delta H_{R,H}^{\circ}(298K) = (-74.9) + 52.5 - (-103.9) = 81.5kJ / mol$$

The enthalpies of formation at the reaction temperature of 773 K were calculated using the specific heat constants for each substance based on the enthalpies of formation at 298 K.

$$C_p / R = a + bT + cT^2 + dT^3 + eT^4$$

$$\Delta H_{f,i}^{\circ}(T) = \Delta H_{f,i}^{\circ}(298K) + \int_{298}^{T} C_p dT$$
$$\Delta S_{f,i}^{\circ}(T) = \Delta S_{f,i}^{\circ}(298K) + \int_{298}^{T} \frac{C_p}{T} dT$$

Table B1. The specific heat constants

	C_3H_8	C_3H_6	H_2	C_2H_4	CH_4	
а	1.213	1.637	3.057	1.424	1.702	
b×10 ³	28.785	22.706	2.677	14.394	9.081	
$c \times 10^{6}$	-8.824	-6.915	-5.18	-4.392	-2.164	
d×10 ⁹		5.521				
e×10 ¹²		-1.812				

 $\Delta H_{R,D}^{\circ}(773K) = 66.5 + 14.7 - (-48.8) = 130kJ / mol$ $\Delta H_{R,H}^{\circ}(773K) = 83.3 + (-51.6) - (-48.8) = 80.5kJ / mol$

<Equilibrium constant calculation>

$$\ln \frac{K_p(T_2)}{K_p(T_1)} = \int_{T_1}^{T_2} \frac{\Delta H_{rxn}(T)}{RT^2} dT$$

The equilibrium constants at different reaction temperatures are obtained based on van't Hoff equation by using ThermoSolver.

In other way, the equilibrium constants can be calculated based on the relationship between Gibbs free energy and enthalpy.

$$\Delta G = \Delta H - T \Delta S$$

$$\Delta S_{R,D}^{\circ}(773K) = -54.6 + 29.2 - (-165.2) = 139.8J / mol / K$$
$$\Delta G_{R,D}^{\circ}(773K) = \Delta H_{R,D}^{\circ}(773K) - T\Delta S_{R,D}^{\circ}(773K) = 21.93kJ / mol$$
$$K_{p}(773K) = \exp\left[-\frac{\Delta G_{R,D}^{\circ}(773K)}{RT}\right] = 0.033$$

<Entropy of the translation in classical ideal gas phase> Sackur-Tetrode equation

$$S = kN \left[\ln \left\{ \frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{\frac{3}{2}} \right\} + \frac{5}{2} \right]$$

Using the following relationship for ideal gas: $U = \frac{3}{2} kNT$, V = nRT / P,

P = 1 a t m

The entropies for propane, propene, and hydrogen are obtained at 298 K and the entropy change was calculated.

$$S_{C_{3}H_{8}}(298K) = 156J / mol / K \qquad S_{C_{3}H_{8}}(773K) = 167.9J / mol / K$$
$$S_{C_{3}H_{6}}(298K) = 155.4J / mol / K \qquad S_{C_{3}H_{6}}(773K) = 167.3J / mol / K$$
$$S_{C_{3}H_{8}}(298K) = 117.5J / mol / K \qquad S_{C_{3}H_{8}}(773K) = 129.3J / mol / K$$

Appendix C

REORGANIZATION ENERGY ESTIMATION

The Gibbs free energy of activation ΔG^* and the free energy of reaction ΔG° can be established with this equation:

$$\Delta G^* = \frac{\left(\lambda + \Delta G^\circ\right)^2}{4\lambda}$$

The Gibbs free energies are obtained from the formation of propane radical cation to the bifurcation position between dehydrogenation and the cracking channels (Figure C1). Therefore, ΔG^* can be estimated by subtracting the heat of adsorption of propane from the apparent activation energy: $\Delta G^* = 161 kJ / mol$



Figure C1. Conceptual illustration for reorganization calculation after the formation of propane radical cation.

Unfortunately, at this point, we do not know the free energy of reaction ΔG° in that state. The reorganization energy is supposed to be proportional to the free energy of reaction ΔG° and then the reorganization energy is substituted for $a \Delta G^{\circ}$. Assuming that the reaction is not in the Marcus inverted region, the reorganization energy should be larger than ΔG° .

$$\Delta G^* = \Delta G^\circ = 161 kJ / mol$$
2) $a = 2, \lambda = 2\Delta G^\circ$

$$\Delta G^* = \frac{9}{8} \Delta G^\circ$$
3) $a = 3, \lambda = 3\Delta G^\circ$

$$\Delta G^* = \frac{16}{12} \Delta G^\circ$$

$$\Delta G^* = \frac{16}{12} \Delta G^\circ$$

$$\Delta G^* = \frac{16}{12} \Delta G^\circ$$

$$\Delta G^* = \frac{25}{16} \Delta G^\circ$$

$$\Delta G^* = \frac{25}{16} \Delta G^\circ$$

$$\Delta G^* = 6, \lambda = 6\Delta G^\circ$$

$$\Delta G^* = \frac{49}{24} \Delta G^\circ$$

$$\Delta G^\circ = 78.9 kJ / mol$$

1) $a=1, \lambda = \Delta G^{\circ}$

The gas phase reaction enthalpies of cracking and dehydrogenation are 81 kJ/mol and 130 kJ/mol, respectively. When a value is 6, the Gibbs free energy of reaction is closed to the gas phase reaction enthalpy of cracking. The Gibbs free energy of reaction is closed to the gas phase reaction enthalpy of dehydrogenation when a=3. Therefore, the reorganization energy should be between 362.4 and 473.4

kJ/mol. However, these values are too large to accept reasonable. The Marcus Inverted region should be considered as follows.

The case of $\lambda < \left| \Delta G^{\circ} \right|$ (Marcus inverted region)

1) $a = 1/2, \lambda = 1/2\Delta G^{\circ}$ $\Delta G^{*} = \frac{9}{8}\Delta G^{\circ}$ $\Delta G^{\circ} = 143.1kJ / mol$ 2) $a = 1/3, \lambda = 1/3\Delta G^{\circ}$ $\Delta G^{*} = \frac{16}{12}\Delta G^{\circ}$ $\Delta G^{*} = \frac{16}{12}\Delta G^{\circ}$ $\Delta G^{*} = \frac{25}{16}\Delta G^{\circ}$ $\Delta G^{*} = \frac{25}{16}\Delta G^{\circ}$ $\Delta G^{*} = \frac{49}{24}\Delta G^{\circ}$ $\Delta G^{\circ} = 78.9kJ / mol$

The proper range of Gibbs free energy of reaction is from 78.9 to 120.8 kJ/mol
$$(a = 1/6 \sim 1/3)$$
. The corresponding reorganization energy can be $13.2 \sim 40.3$ kJ/mol. The higher reorganization energy is expected for the dehydrogenation channel than the cracking channel since the Gibbs free energy values are matched to the gas phase reaction enthalpy for cracking and dehydrogenation. In Marcus inverted region, the smaller Gibbs free energy leads to the lower reaction rate. Therefore, it is expected that the reaction rates of the cracking channel are lower than the rates of the dehydrogenation channel.