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Metal-Ion-Exchanged Zeolites For Applications In Endothermic Reforming

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Metal-Ion-Exchanged Zeolites For Applications In Endothermic Reforming

Abstract
A significant challenge in the design of future hypersonic aircraft is engine cooling and one solution that has been proposed is to use the fuel as a coolant. The amount of energy that can be taken up by the thermal heat capacity of the fuel is limited but additional heat can be removed if the fuel is reformed via endothermic reactions prior to entering the combustion chamber. Two possible reactions that have been investigated in this thesis are the acid-catalyzed cracking reactions that occur in acidic zeolites and the aromatization reactions that occur over Ga- and Zn-exchanged zeolites.

The first part of this dissertation was aimed at understanding the adsorption properties of alkanes on acidic zeolites in order to understand the reactions on these materials. Calorimetric measurements with CH4 on three zeolites with widely differently pore dimensions demonstrated heats decreased strongly with increasing pore size. Calorimetric measurements for a series of alkanes on H-ZSM-5 demonstrated that hydrogen bonding increased in a regular manner with the size of the alkane.

In the second part of this dissertation, supercritical, high-pressure reactions of n-hexane over H-ZSM-5, with and without the addition of Pt, Ga, or Zn, were studied and reaction endothermicities were determined from the product distributions and from actual heat-flow measurements. The nature of the catalytic sites in these materials was also investigated using simultaneous Temperature-Programmed-Desorption (TPD) and Thermogravimetric analysis (TGA) of propyl amines. Adsorption studies showed that, at low ion-exchange levels, less than 0.5 Zn/Al, each added Zn cation in H(Zn)ZSM-5 displaced one Brønsted-acid site. FTIR of adsorbed acetonitrile-d3 and calorimetric measurements of adsorbed CO at 195 K indicated that the exchanged Zn cations form Lewis-acid centers.

The heat flows measured directly for reaction at 60 bar and both 673 and 773 K indicated the acid-catalyzed cracking of n-hexane over H-ZSM-5 zeolite catalysts was ineffective for endothermic reforming applications. Aromatization reactions over H(Zn)-ZSM-5 exhibit much better endothermicities under these conditions. Measurements of the product distributions showed that the reaction endothermicity for H(Zn)-ZSM-5 at lower conversions was likely due to formation of significant amounts of benzene, toluene, and xylene but that these were converted to higher molecular weight products at high conversions. In the development of new catalysts, careful attention must be paid to the product selectivities.

The present thesis, with systematic studies of metal-exchanged zeolites, should greatly increase our understanding of how metal cation at ion-exchange sites affect the reactions. The advances will help in predicting reactions and broadening the application, not only to use zeolites for endothermic reforming but in other important reforming reactions in the future.

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METAL-ION-EXCHANGED ZEOLITES
FOR APPLICATIONS IN ENDOOTHERMIC REFORMING

Yu-Hao Yeh
A DISSERTATION
in
Chemical and Biomolecular Engineering
Presented to the Faculties of the University of Pennsylvania
in
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METAL-ION-EXCHANGED ZEOLITES

FOR APPLICATIONS IN ENDOOTHERMIC REFORMING

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DEDICATION

To my beloved family and friends

To my adviser, Ray, for guiding and supporting me over the years
ACKNOWLEDGMENT

It has been an amazing experience pursuing my Ph.D. at the University of Pennsylvania. This journey has been challenging, colorful, and life-changing. I want to thank each and every one of you whom I met along the way, without your support and love, I would not have made it here.

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Last but not least, my deepest gratitude to my parents Chi-Min and Li-Chin as well as my siblings Pei-Yun and Chia-Yun. I could not have done it without their unconditional love and support.

~I say to each and every one of you, a heartfelt thank you~
A significant challenge in the design of future hypersonic aircraft is engine cooling and one solution that has been proposed is to use the fuel as a coolant. The amount of energy that can be taken up by the thermal heat capacity of the fuel is limited but additional heat can be removed if the fuel is reformed via endothermic reactions prior to entering the combustion chamber. Two possible reactions that have been investigated in this thesis are the acid-catalyzed cracking reactions that occur in acidic zeolites and the aromatization reactions that occur over Ga- and Zn-exchanged zeolites.

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Figure 8.1 TPD-TGA of 2-propanamine over H-ZSM-5. The peaks correspond to ammonia (m/e =17), propene (m/e = 41), and 2-propanamine (m/e =17, 41, and 44).

Figure 8.2 TPD-TGA of 2-propanamine over H(Zn)-ZSM-5. Below 550 K, the peaks correspond to 2-propanamine (m/e =17, 41, 42, and 44). Between 575 and 650 K, the peaks are due to ammonia (m/e =17) and propene (m/e = 41 and 42). Above 650 K, the peaks at m/e =17 and 41 correspond to a range of dehydrogenation products.

Figure 8.3 Schematic diagram of the apparatus used in the heat-flow measurements.

Figure 8.4 Normalized conversion of n-hexane reaction over (a) H-ZSM-5, and (b) H(Zn)-ZSM-5 at 60 bar as a function of time at 673 K (■), and 773 K (▲).

Figure 8.5 Power required to maintain a constant temperature, as a function of flow rate for heating n-hexane at 60 bar from (a) 573 K to 673 K, (b) 673 K to 723 K, and (c) 673 K to 773 K.

Figure 8.6 Power required to maintain constant temperature, as a function of flow rate for n-hexane reacting over H-ZSM-5 at 60 bar and 673 K with (a) 0.3 g and (b) 0.9 g of catalyst. The n-hexane entered the reactor at 573 K.

Figure 8.7 Power required to maintain constant temperature as a function of flow rate for n-hexane reaction over H-ZSM-5 at 60 bar and 773 K with (a) 0.02 g and (b) 0.15 g of catalyst. The n-hexane entered the reactor at 673 K.

Figure 8.8 Power required to maintain constant temperature as a function of flow rate for n-hexane reaction over H(Zn)-ZSM-5 at 60 bar and 673 K with (a) 0.3 g and (b) 0.9 g of catalyst. The n-hexane entered the reactor at 573 K.
Figure 8.9 Power required to maintain constant temperature as a function of flow rate for n-hexane reaction over H(Zn)-ZSM-5 at 60 bar and 773 K with (a) 0.02 g and (b) 0.15 g of catalyst. The n-hexane entered the reactor at 673 K................................................................. 129

Figure 8.10 Heats of reaction for n-hexane conversion at 60 bar over HZSM-5 and H(Zn)-ZSM-5: (a) 673 K and (b) 773 K........................................................................................................ 130
Chapter 1. Introduction

1.1 Background

A major challenge associated with hypersonic aircraft, defined here as vehicles that reach speeds above Mach 5, is thermal protection of the engine, since air cooling is not possible at these high velocities.\textsuperscript{1} One method for controlling the temperatures of critical engine components involves using the fuel itself as a coolant before it enters the combustion chamber.\textsuperscript{2} This approach has been used in the US Air Force X-51A program, an unmanned research aircraft with a scramjet engine that successfully reached a top speed of Mach 5.1 in 2013. However, the amount of heat that can be taken up by the fuel is limited by the maximum temperature to which the fuel can be heated before it undergoes pyrolysis. Hydrocarbon pyrolysis, which can form tars that plug the fuel lines, becomes increasingly important at temperatures above 823 K.\textsuperscript{3,4}

It is possible to increase the cooling capacity of the fuel by performing endothermic reactions on the fuel and significant effort has gone into investigating catalysts that could carry out this function. For example, dehydrogenation of alkanes to alkenes and H\textsubscript{2} is strongly endothermic\textsuperscript{5} but equilibrium conversions are low at the high pressures experienced in the fuel lines (typically greater than 50 bar) and the transition-metal catalysts commonly used for dehydrogenation have a tendency to deactivate by coking unless there is a high H\textsubscript{2} pressure. Alkane cracking by acidic zeolites has received the most attention for this application because medium pore zeolites are highly active and reasonably stable.\textsuperscript{6-11} In principle, cracking of a large alkane to a smaller alkane and an alkene is also highly endothermic;\textsuperscript{6} however, olefin production is significantly reduced by bimolecular, hydride-transfer reactions, so that the effectiveness of this approach remains unproven. An alternative to acid-catalyzed cracking and metal-catalyzed dehydrogenation is the aromatization of alkanes over Ga- and Zn-exchanged zeolites.\textsuperscript{12-17} The formation of small aromatics and H\textsubscript{2} from alkanes is highly endothermic, and the rates for n-hexane conversion are comparable to those reported for the acidic zeolites.
In the work carried out in this thesis, I considered the latter two approaches: hydrocarbon cracking using an acidic zeolite and aromatization using metal-exchanged zeolites. In addition to performing actual measurements of heat flows in the presence of these reactions, I also examined the nature of the catalytic sites in these materials.

1.2 Approaches to Endothermic Reforming

1.2.1 Homogeneous Pyrolysis

As discussed above, one proposed method for engine cooling in hypersonic aircraft involves using jet fuel as a coolant before it is burned in the combustor of the aircraft. In addition to using the heat capacity of the fuel, chemical reaction on the fuels can contribute an additional amount of heat. For example, early reports by Huang et al. suggested that much additional heat can be removed by the homogeneous reaction, with a maximum additional cooling of $\sim 950 \text{ kJ/kg}$ achieved with n-octane.\(^1\) Therefore, the total heat sink of a hydrocarbon fuel in this case comes from the thermal heat capacity of the fuels and the pyrolysis of the hydrocarbons at higher temperature.

The thermal decomposition of hydrocarbons requires energy for its accomplishment; and, therefore, this reaction supplies substantial amounts of heat sink. The fuel undergoes pyrolysis that reforms it into a mixture of lighter hydrocarbons, mainly olefins and hydrogen. The homogeneous reaction would be highly endothermic if the reaction follows this path. For example, the decomposition of n-octane into octene and hydrogen would provide a heat sink of about 1150 kJ/kg. Although pyrolysis of alkanes can produce significant quantities of olefins, which would be highly desirable for increasing reaction endothermicity, the homogeneous reactions will only be important at higher temperatures. Also, at elevated temperatures, the largest issues that affect olefin production come from alkane’s propensity to lead to higher molecular weight products when thermally decomposed. Coking is a serious problem under this circumstance. The olefins produced
by the homogeneous reaction can lead to tar formation that can “plug” fuel lines. Therefore, the idea to use homogeneous pyrolysis to enhance reaction endothermicity is inadequate, even though it is still being pursued.

1.2.2 Catalytic Reactions

Another attractive method for increasing the heat sink of the fuels is to endothermically reform the hydrocarbons by catalytic reactions. The most significant advantage of using a catalyst is to have the reaction go selectively to the desired products. For reactions to be highly endothermic, it is necessary to form unsaturated compounds, such as olefins and aromatics, together with \( \text{H}_2 \). Based on previous work in the literature, the catalytic reactions of primary interest include dehydrogenation, dehydrocyclization, and depolymerization type reactions. The most promising class of reaction that has been studied is the catalytic dehydrogenation of naphthenes. For example, very early reports by Lander and Nixon suggested that dehydrogenation of naphthenes (cyclic paraffins) to form \( \text{H}_2 \) and aromatic compounds over Pt/Al\(_2\)O\(_3\) catalyst can double the amount of heat removed by the thermal heat capacity of the fuel.\(^2\) Since that time, interest in using a catalyst for endothermic reforming for cooling purposes has increased, leading to a large number of publications\(^{18-25,7}\) and patents,\(^{26,27}\) especially for applications to scramjet engines.

Although using catalysts for endothermic reforming is potentially effective, the conditions under which the reaction has to be performed are extremely challenging. Whereas normal naphtha reforming is carried out in the presence of \( \text{H}_2 \) to prevent coking,\(^5\) endothermic reforming for engine cooling will need to take place at high hydrocarbon pressures (typically greater than 50 bar) and negligible \( \text{H}_2 \) pressures. Standard Pt/Al\(_2\)O\(_3\) naphtha-reforming catalysts deactivate very quickly under these conditions. It is unrealistic to use metal catalyst in scramjet application. Therefore, the majority of the studies in endothermic reforming have focused on reactions over acidic zeolites because these catalysts can be catalytically active and stable under harsh conditions.
1.2.3 Acid-Catalyzed Cracking

Acid-catalyzed cracking, particularly the reaction of alkanes to lighter olefins, is perhaps the simplest of the reforming reactions that could be used to remove heat from the fuel. For example, the standard heats of reaction for cracking one mole of n-hexane to one mole each of propane and propene is about 970 kJ/kg, which is equivalent to the amount of energy that would be taken up by heating liquid n-hexane several hundred degrees. Although hydrocarbon cracking on zeolite catalysts has been studied extensively for refinery operations, endothermic reforming must be carried out under very different conditions where the reactions have not been extensively studied and for which reaction mechanisms are not well understood. Therefore, a significant fraction of the literature on endothermic reforming is devoted to this approach.\textsuperscript{28–37,8,38}

Previously, our lab has shown the medium-pore zeolite, H-ZSM-5, to be catalytically active and stable for a wide range of conditions.\textsuperscript{6,39} We have found that the rates for catalytic cracking of n-hexane in H-ZSM-5 could be described by a single rate expression that accounts for the concentration of n-hexane within the pores. Based on the kinetic rate expression, there was no evidence for bimolecular reactions affecting the rates under the conditions of these experiments. In addition, a much higher activation energy, and less susceptibility to deactivation by coking, was observed at high pressures. Product distributions on H-ZSM-5 were also discussed, with less isomerization and more endothermic products being formed.

Unfortunately, acid-catalyzed, alkane cracking may not be that effective for engine cooling. Monomolecular cracking of an alkane will produce one olefin for each molecule that reacts; however, at high pressures, hydride-transfer reactions, which tend to saturate the olefin products and decrease reaction endothermicity, are important.\textsuperscript{40} Although hydride transfer can produce aromatics, the primary products in the previous study were saturated alkanes, which would not contribute significantly to heat uptakes.\textsuperscript{39} Therefore, the endothermicities of the reactions are relatively small. In our previous study of n-hexane cracking over H-ZSM-5 at high pressures,\textsuperscript{15} the reaction was determined to be endothermic by only 3.6 kJ/mol of n-hexane that reacts at 633 K.
For comparison, the heat of reaction at standard conditions for the gas-phase reaction of n-hexane to form n-hexene and H$_2$ is 125 kJ/mol. What all of this suggests is that there is still a great need for developing an effective catalyst for endothermic reforming purposes.

1.2.4 Aromatization

The most promising approach so far is aromatization using metal-exchanged zeolites to increase the heat sink of the fuels. From the literature, there have been reports that zeolites, ion-exchanged with transition metals, exhibit interesting dehydrogenation activity at lower pressures. For example, Ga- and Zn-exchanged H-ZSM-5 have been shown to be active for dehydrocyclodimerization of propane to aromatics at 500°C, a reaction typically catalyzed by metals such as Pt. More recently, Biscardi et al.\textsuperscript{12} reported that exchange of either Zn or Ga into H-ZSM-5 increases turnover frequencies and selectivities for propane reactions to form aromatics. Similarly, Ono and Kanae\textsuperscript{41} found that Ga and Zn cations in ZSM-5 were equally effective for the transformation of lower olefins into aromatics. In addition, Viswanadham et al. indicated that Zn provides an alternative pathway for aromatization in H-ZSM-5 and suppresses the formation of C9+ aromatics.\textsuperscript{42}

Zn has been reported to exhibit superior properties among a number of promoters that have been added to H-ZSM-5 for enhancing aromatization.\textsuperscript{14,43} Similar performance has been observed for Zn- and Ga-exchanged materials, according to Biscardi & Iglesia.\textsuperscript{12} Based on the above information, aromatization with metal-exchanged H-ZSM-5 appears to be ideal for application to endothermic reforming of alkanes. Therefore, the later part of my thesis has focused on aromatization over metal-exchanged zeolites.
1.3 Alkane Cracking

The endothermic reforming reactions receiving the most attention for this application are those involved in acid-catalyzed cracking.\textsuperscript{28-33,35-37} Although acidic zeolites are widely applied for catalytic cracking in petroleum refining, the conditions required for endothermic reforming are very different from that used for traditional catalytic cracking because the fuel is maintained at very high pressures before entering the combustion chamber. While the temperature of the fuel in the fuel lines may be above the critical temperature, the hydrocarbon densities will be similar to that of liquids. These high densities can have a significant impact on the reaction because catalytic cracking in zeolites involves a complex set of processes, including bimolecular hydride shift reactions. Therefore, it should be expected that rates for product formation and deactivation will be very different under these high-pressure conditions.

In general, alkane cracking over Brønsted-acidic zeolites can occur through either monomolecular or bimolecular cracking mechanisms, the characteristics of which have been reviewed by Kotrel et al.\textsuperscript{40}. They reported the following: (1) The monomolecular mechanism likely involves protonation of the alkane (formation of a carbonium ion) as a transition state, which then reacts to form products. A characteristic of monomolecular cracking of n-hexane is that propene and propane should form in equal amounts, as should methane and C-5 products. (2) The bimolecular reaction involves intermediate carbenium ions (essentially protonated olefins) and has some similarities to chain reactions. The intermediate carbenium ions are formed from the reactant alkanes by hydride transfer to a carbenium ion at the acid sites. This newly formed carbenium ion then undergoes cracking and isomerization, forming products and a carbenium ion that can accept a hydride ion, thus continuing the chain. Historically, the bimolecular mechanism was proposed earlier and is therefore considered to be the “classical” mechanism for acid-catalyzed, alkane cracking.

Evidence for the bimolecular, hydride-transfer mechanism is seen most clearly by the large rate increases that have been observed for reactions of butane upon the addition of small
concentrations of olefins to the feed. The small concentration of olefins is sufficient to form carbenium ions and initiate the reaction. Importantly, the biomolecular mechanism leads to product distributions with high P/O ratios due to the fact that the product of hydride transfer to a carbenium ion is a paraffin. Simple isomerization products are formed if hydride transfer occurs before initially formed carbenium ions accept a hydride ion before undergoing cracking. Hydride transfer is a primary cause for catalyst coking by forming large aromatic deposits. Formation of aromatic deposits may also cause an induction period, since aromatic coke precursors can act as effective hydrogen sources during the initial stages of the reaction. The activation energies for hydride-transfer reactions tend to be low.

Previously, a previous student and I examined acid-catalyzed cracking on a series of zeolite catalysts of various structures. Reaction rates for n-hexane cracking were studied under differential and integral conditions over H-ZSM-5, H-BEA, H-MOR, and USY zeolites at pressures between 0.03 and 137 bar and temperatures between 573 and 673 K. Rates on H-ZSM-5 were stable over the entire range and showed a simple, Langmuir-Hinshelwood rate expression for n-hexane in the zeolite, with the reaction being first-order at low pressures and zeroth-order at high pressures. The activation energy also changed with increasing pressure by an amount equal to the heat of adsorption of n-hexane in ZSM-5, going from 170 kJ/mol at low pressures to 90 kJ/mol at high pressures. The selectivity for C-7+ products varied only with temperature and conversion. The product distributions were also distinctly different on H-ZSM-5 compared to H-BEA, H-MOR, and USY, with H-ZSM-5 exhibiting much less isomerization and more C-4 and C-5 products.

Reaction rates on three larger-pore zeolites, H-BEA, H-MOR, and USY, were only weakly dependent on pressure and also exhibited an induction period at 137 bar before decreasing with time. It was suggested that the differences observed between n-hexane cracking over H-ZSM-5 compared to cracking over the larger pore zeolites must be due to steric limitations. Because of pore-size restrictions in H-ZSM-5, oligomerization of olefins to larger aromatic molecules is suppressed, so that coking is avoided. In the larger-pore zeolites, protonated carbenium-ion
intermediates are also more able to promote hydride transfer, as evidenced by the high concentration of isomerization products, due to the larger volume available. The low activation energy in these materials could in part be associated with the high isomerization rates, which are associated with a high termination rate of the hydride-transfer reactions.

The differences in cracking activity between the various zeolites have important consequences for applications to endothermic reforming in aircraft engines. Olefins are desirable products for endothermic reforming and coking in the fuel lines is obviously not acceptable. The high selectivity to isomerization products by the larger-pore zeolites is also not desirable since it does not take up heat. All of this suggests that one should use catalysts that optimize the rates and product distributions, and our results would imply that smaller-pore materials are likely to be best for this application. Therefore, all the work carried out in the present thesis focused on H-ZSM-5 as the most promising material.

1.4 Scope of the Thesis

My thesis work fell into two parts. The first part of this dissertation was aimed at understanding the adsorption properties of alkanes on acidic zeolites in order to understand the reactions on these materials. The second part of my thesis involved the investigation of catalytic properties of high-pressure reactions of n-hexane over metal-exchanged H-ZSM-5 for application to reforming reactions.

This thesis is divided into 9 chapters. Chapter 2 provides the descriptions of the zeolite catalyst preparation, characterization techniques and the design of the apparatus used for the heat-flow measurements in this work.

In Chapter 3, CH₄ adsorption was studied experimentally and theoretically on ZSM-5, MOR, and ZSM-12 zeolites using calorimetric measurements at 195 K and plane wave DFT calculations to understand the effect of zeolite structure on the adsorption properties of alkanes,
and to determine whether differential calorimetry can be used to distinguish structural differences in similar zeolites.

As discussed in Chapter 3, I showed that Brønsted sites do not affect the heats of adsorption for methane. However, there have been reports in the literature that larger alkanes can form hydrogen bonds with the acid sites. Therefore, Chapter 4 aimed to examine the interaction between simple alkanes and the Brønsted sites in H-ZSM-5 calorimetrically and theoretically, as a function of alkane size.

In Chapter 5, the supercritical, high-pressure reaction of n-hexane over H-ZSM-5, with and without the addition of Pt and Ga, has been studied for application to endothermic reforming in scramjet engines. I began by investigating the effect of reaction conditions (pressure and temperature) on the product distributions and reaction endothermicities for n-hexane reactions over H-ZSM-5 to determine the importance of the reaction conditions. The use of n-hexane and differential reaction conditions made it possible to obtain mechanistic information on the reaction from the product distribution and to calculate reaction endothermicities.

Since Zn has been reported to exhibit superior properties among a number of promoters that have been added to H-ZSM-5 for enhancing aromatization and showed similar performance to the Ga-exchanged materials, Chapter 6 focused on the investigation of the H(Zn)-ZSM-5 samples. The nature of Zn promotion in H-ZSM-5 and its applicability for endothermic reforming were determined. A model in which the Zn cations, acting as Lewis-acid centers, polarize intermediates formed at Brønsted sites is also presented as a way of understanding the observations.

In Chapter 7, the catalytic properties of H-[Fe]ZSM-5 and H-[B]ZSM-5 were explored after addition of Zn or Ga and compared with the results from H-[Al]ZSM-5. This chapter provides several important insights into the nature of the sites responsible for aromatics formation in Zn- and Ga-exchanged ZSM-5 materials.

In chapter 5 and 6, conclusions concerning the endothermicity of reactions over H-ZSM-5 and H(Zn)-ZSM-5 were based on product selectivities. Furthermore, the product selectivities could
only be accurately determined at low conversions. This raises many questions, especially concerning the effect of higher fuel conversion. In Chapter 8, I developed a system to measure the heats of reaction at high temperature and pressures and then used this to characterize the thermal effects of n-hexane cracking on the acidic zeolite H-ZSM-5 and of aromatization on the Zn-exchanged H(Zn)-ZSM-5.

Finally, overall results and conclusions are summarized in Chapter 9.
Chapter 2. Experimental Techniques

This chapter will describe the preparation of the catalysts used in this thesis, as well as the experimental principles and applications of the various techniques used to characterize the catalysts.

2.1 Catalyst Preparation

2.1.1 ZSM-5 Zeolite

The commercial ZSM-5 zeolites (CBV 5524G, Si/Al ratio of 50; CBV 28014, Si/Al ratio of 280) were obtained in their ammonium-ion form from Zeolyst. To produce the H\(^+\) form of the zeolite, H-ZSM-5, the sample was simply heated in dry, flowing air at 773 K for 4 h.

2.1.2 Defect-Free ZSM-5 Zeolite

Two low-defect ZSM-5 samples with different Si/Al ratios were prepared by using fluoride containing media to achieve low silanol defect concentrations at the University of Delaware. A typical synthesis was as follows: distilled water was mixed with Ludox AS-40 silica sol, tetrapropylammonium bromide (TPABr), NH\(_4\)F, and Al(NO\(_3\))\(_3\)-9H\(_2\)O. (A purely siliceous ZSM-5 was prepared using the same procedure, but without the addition of Al(NO\(_3\))\(_3\)-9H\(_2\)O.) The mixture was heated at 450 K for 7 days in a Teflon-lined autoclave. After filtering, the solid was calcined at 823 K in flowing dry air for 6 h.

These samples were noticeably more hydrophobic, and 2-propanamine molecules in excess of twice the Brønsted-site densities could be easily evacuated at room temperature, whereas the excess amine molecules in the commercial samples could only be removed by heating.
2.1.3 Metal-Ion-Exchanged Zeolite

Metals were added to the H$^+$ forms of the molecular sieves by incipient wetness with aqueous solutions of the metals. The resulting materials were dried at 350 K overnight and then calcined in flowing air at 773 K for 4 h to transform them into the H(M)-ZSM-5 forms.

H(Li)-ZSM-5 and Li-ZSM-5 were prepared by ion exchange method. This was accomplished by mixing 1 g of H-ZSM-5 with a 300 mL solution that was 0.1 M LiCl and 0.001 M LiOH to obtain H(Li)-ZSM-5 or 0.1 M LiCl and 0.006 M LiOH to produce Li-ZSM-5. After filtering, the solids were calcined at 773 K in flowing air for 4 h.

2.1.4 Framework Substitution of Silicates with ZSM-5 Zeolite

The [Fe]ZSM-5 sample (Si/Fe$_2$ ratio of 60) was synthesized as follows. Fumed silica (Cab-O-Sil from Cabot) was used as the silica source to minimize any Al contamination. To prepare the silica, 29.6 g of Cab-O-Sil (97% SiO$_2$ with the remainder water) was slurried in a solution of 11.6 g of NaOH (98.9% NaOH) in 58.5 g of deionized water, using a polypropylene container. The resulting paste was transferred to a freshly cleaned, Teflon-lined autoclave and heated to 400 K for 2 days to get a clear, viscous solution. The ferrosilicate was then prepared as follows: 5.0 g Fe(NO$_3$)$_3$·9H$_2$O was dissolved in 33.33 g of deionized water. After adding 5.33 g of concentrated H$_2$SO$_4$ to this solution, 8 g of tetrapropylammonium bromide in 13.33 g of deionized water was added, which turned the mixture brown. Next, 66.66 g of the sodium silicate prepared in the first step was diluted with 66.6 g of deionized water, under stirring, and added to the brown mixture, changing the solution to a light yellow color. Finally, the mixture was sealed and heated in a stirred autoclave to 450 K for 3 days. The resulting solid was calcined at 773 K in dry flowing air for 4 h and then ammonium-ion exchanged. The final H$^+$ forms of the zeolites were formed by heating the NH$_4^+$ forms in dry flowing air at 773 K for 4 h.

The [B]ZSM-5 sample was synthesized as follows. Solutions of tetrapropylammonium bromide (TPABr, 98%, Sigma-Aldrich) and NaOH (Fisher Chemical) were added to a mixture of
Ludox AS-40 silica sol (Sigma-Aldrich), distilled water, and H₃BO₃ (>99%, Alfa Aesar). After this solution had been heated to 450 K for 7 days in a Teflon-lined autoclave, the resulting solid was calcined at 773 K in dry flowing air for 4 h and then ammonium-ion exchanged. The final H⁺ forms of the zeolites were formed by heating the NH₄⁺ forms in dry flowing air at 773 K for 4 h.

2.2 Characterization Techniques

2.2.1 TPD-TGA measurement

Simultaneous temperature programmed desorption and thermogravimetric analysis (TPD-TGA) measurements was found to be one of the most useful methods available for the initial characterization of the catalysts. The system consisted of a CAHN 2000 microbalance mounted within a vacuum chamber that could be evacuated with a diffusion pump to a base pressure of 1 × 10⁻⁵ Pa. When evacuated, the partial pressures above the sample could be monitored using an SRI quadrupole mass spectrometer (RGA100). A schematic diagram of the TPD-TGA instrument is shown in Figure 2.1.

![Figure 2.1 Schematic diagram of the TPD-TGA instrument.](image)

In a typical TPD-TGA measurement, the samples were heated in a vacuum to 823 K and cooled in a vacuum to remove any adsorbed water prior to exposing them to a few hundred Pascal
of adsorbate of interest at room temperature. After the sample had been exposed to the adsorbate of interest at room temperature, the sample can be evacuated by a diffusion pump, which ensures that the partial pressure above the sample is low enough to minimize secondary reactions. The sample was evacuated for 1 h before the TPD-TGA experiment was started. During TPD-TGA measurements, the sample weights were recorded continuously using the microbalance, which has an accuracy of 0.01 mg and allows the measurement of weight changes as small as 0.01%. The TPD spectra were obtained by ramping the sample temperature and monitoring the partial pressures in the system using the high sensitivity mass spectrometer. The heating rate during desorption was maintained at 10 K/min by a temperature controller. From the TPD-TGA results, one can quantify the desorption amount and determine whether there is a reaction on the sample during desorption.

2.2.2 Calorimetric measurements

Calorimetry is a direct method for measuring heats of adsorption for gaseous adsorbates on acid sites. Our home-built, Tian-Calvet calorimeter was constructed from five, 2.54 cm square, thermalflux meters (International Thermal Instrument Company, Del Mar, CA) placed between a cubic, Pyrex sample cell and a large Al block. The thermopiles had previously been calibrated by passing current through a Pt wire placed between the sample cell and the thermopiles. During the measurement, 1 g zeolite samples, pressed into wafers and placed at the bottom of the Pyrex cube, were covered with quartz chips in order to prevent heat loss due to radiation out the top. The samples were evacuated using a mechanical pump and heated to 573 K overnight in a vacuum to remove water. After cooling, the adsorption experiments were performed at 195 K, a temperature that was maintained by placing the Al-block heat sink in a Styrofoam container with dry ice. The zeolites were then exposed to the gaseous adsorbate of interest from a calibrated GC sample loop. The uncertainty in our measurement of each point was ∼2%, corresponding to ∼0.5 kJ/mol; however, the uncertainty in our calibration factor is larger, so that the uncertainty in the absolute
values of the differential heats is $\sim 1$ kJ/mol. The adsorption isotherm was obtained simultaneously with the adsorption heats by measuring the amount of gas remaining at equilibrium with the partial pressure above the sample. A schematic diagram of the calorimeter instrument is shown in **Figure 2.2**.

![Schematic diagram of the calorimeter instrument](image)

**Figure 2.2** Schematic diagram of the calorimeter instrument.

The data from calorimetric measurements are most reliable when the measurements are performed at the lowest temperatures for which adsorption is reversible. When there is a distribution of site strengths, low temperatures favor having molecules adsorb preferentially in the strongest sites. This is important when the difference between strong and weak sites approaches $k_B T$. However, adsorption reversibility is critical in order to avoid chromatographic adsorption in the sample and to ensure that adsorption comes to equilibrium. If the measurement temperature is too low so that adsorption is not reversible, the adsorbate will not be able to sample all possible sites. Each gas dose will saturate different parts of the sample, leading to differential heats of adsorption that are constant with coverage, even if the sites are not identical. Therefore, different temperatures were used for different adsorbates. The reversibility of the measurements was
verified by comparing isotherms obtained by adsorption and desorption of the sample at a certain temperature.

2.2.3 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is another useful technique to analyze the adsorption properties on the catalyst surface. In this thesis, the FTIR spectra were collected on a Mattson Galaxy 2020 FTIR with a diffuse-reflectance attachment (Collector II) purchased from Spectra-Tech Inc. Our spectrometer allows measurements on powdered samples with control over temperature and atmosphere pressure.

In a typical measurement, the samples were initially heated to 573 K in He that was flowing at 0.5 cm$^3$/s to remove any water. After cooling the samples to room temperature, spectra were collected at 4 cm$^{-1}$ resolution. Comparing FTIR spectra before and after adsorption of certain probe molecules provides a convenient way to characterize solid acid catalysts.

2.2.4 XRD

Powder X-ray Diffraction (XRD) was used to determine the structures and the chemical phase composition of the synthesized zeolites. The XRD patterns were recorded on a Rigaku Smartlab diffractometer equipped with a Cu Kα source ($\lambda=1.5405$ Å). The sample powders were finely dispersed in 2-propanol by sonication and then drop-cast onto glass slides. The intensities of the diffracted beam were measured while sampling different diffraction angles. The crystallite particle size ($d$) could be estimated using the Scherrer equation:

$$
\frac{k\lambda}{B(2\theta)\cos\theta}
$$

(Eqs. 2.1)

where $k$ is a shape factor usually equal to 1, $\lambda$ is the X-ray wavelength, $B$ is the peak width at half the maximum intensity, and $\theta$ is the diffraction angle.
2.3 Catalytic Studies

2.3.1 Steady State Rates Measurements

The reaction measurements were performed in the high pressure flow reactor, which was a 1/4 in. OD, 2.1 mm ID, stainless-steel tube, passed through a short tube furnace. In this thesis, most of the reactant feed was liquid n-hexane (>99% purity, Acros Organics). A high-performance liquid chromatography (HPLC) pump (Series III, Scientific Systems Inc.) introduced the liquid feed to the reactor, and the pressure was controlled using a back-pressure regulator (KPB series, Swagelok). The catalyst was first pressed into 0.5 mm thick wafers, which were then broken into pieces, before loading into the reactor. The wafers were then loaded into the middle of the reactor tube using glass wool to hold its position.

The products were analyzed with an online Gas Chromatograph (310, Buck Scientific) equipped with a TCD detector and a capillary column (ZB-1, Zebron), with helium as carrier gas. Pure methane, ethylene, propane, n-butane, n-pentane, n-hexane, benzene, toluene, and xylenes were used to calibrate the chromatographic intensities for these products, but we assumed that the calibration factors for compounds with the same number of carbons (i.e., ethylene and ethane) were the same. Products heavier than C-7, other than benzene, toluene, and xylenes (BTX), were assumed to have the same calibration factor as n-heptane. Hydrogen production rates were measured in separate experiments in which the carrier gas in the GC was switched from He to nitrogen.

Most rates were determined from measurements in which the conversion was less than 10% to ensure differential conditions. Although homogeneous reactions could be observed at the higher temperatures, the rates were significantly lower than rates observed in the presence of a catalyst.
Chapter 3. An Adsorption Study of CH$_4$ on ZSM-5, MOR, and ZSM-12

Zeolites

3.1 Introduction

As discussed in Chapter 1, to help understand the effect of zeolite structure on the adsorption properties of alkanes, I examined the adsorption of methane on three zeolites with widely differently pore dimensions in this Chapter. Because adsorption of methane is physical in nature, adsorption isotherms and energetics depend in a rather simple manner on the composition of the solid adsorbent and on the size and shape of the pores that make up the solid. Furthermore, since the theory for adsorption of methane is reasonably well developed, it is possible to predict what the adsorption properties of a crystalline material will be and what the best porous solid structures will be.

For similar reasons, it should be possible to use experimental data to characterize the nanopores in unknown or poorly crystalline materials. For example, the zero-coverage heats of adsorption for methane in siliceous zeolites with one-dimensional pores made up of 10-, 12-, and 14-membered rings (MR) (TON, MTW (also known as ZSM-12), and UTD-1) were reported to be 27.2, 20.9, and 14.2 kJ/mol, respectively. If one knew that a particular siliceous material had cylindrical pores, the heats of adsorption could be used to estimate the pore size. Real zeolite structures have more complex pore structures and the concept of using the distribution of adsorption energies could allow one to map the structure. A particularly interesting material for understanding the effect of structure on adsorption is the zeolite with the MOR structure. MOR has one dimensional, 12-MR channels with 8-MR side pockets. MOR exhibits unique catalytic properties for the carbonylation of dimethyl ether, most likely because the 8-ring pockets are able to stabilize the intermediate structures.
One complication for determining pore structure from a distribution of adsorption energies is that most zeolites are not defect free or purely siliceous. Many zeolite structures, including MOR, are synthesized with framework Al and must have non-framework cations to balance the charge. The simplest charge-balancing cation is the proton, which leads to Brønsted acidity. Even simple, polar molecules (e.g., CO) will adsorb preferentially on these sites and give an added contribution to the heats.\(^5\) With nonpolar molecules, the situation is less clear. Interactions between molecular \(O_2\) and Brønsted sites are reported to be negligible,\(^5\) but there is both experimental \(^52,53\) and theoretical \(^54,55\) evidence that adsorption on the Brønsted sites contributes to the heats of adsorption for small alkanes. Because adsorption energies have been shown to scale with proton affinities for both protonated and hydrogen-bonded adsorption complexes \(^56,57\) and because methane has a much lower proton affinity compared to even ethane (543.5 versus 596.3 kJ/mol),\(^58\) the influence of acid sites on methane adsorption is not well-known. There are a few reported studies of methane adsorption on H-ZSM-5,\(^59-61\) but the role of Brønsted sites in adsorption of methane has not been clearly demonstrated.

In order to measure the spectrum of adsorption energies in a material that has more than one type of site, it is essential that calorimetric measurements be performed at an appropriate temperature, for reasons discussed in Chapter 2. This issue is important, especially for weakly bound molecules like methane in this study. Adsorption should be performed at temperatures that are low enough for adsorption to occur preferentially at the strongest sites. Otherwise, if the weaker sites are present in higher concentrations and if adsorption on those sites is entropically preferred, it would be difficult to distinguish sites. Indeed, sample calculations have suggested that it is likely impossible to observe minority sites having a heat of adsorption that is 5 kJ/mol higher than that of the majority sites using differential calorimetry at room temperature.\(^45\)

Previously, our lab has shown that the differential heats of adsorption for CO were found to be 16 ± 1 kJ/mol, independent of coverage, in siliceous, defect-free ZSM-5.\(^5\) On the analogous acidic H-ZSM-5, the differential heats for CO adsorption were 10 kJ/mol higher at low coverages,
falling to the same value as on the siliceous ZSM-5 at coverages above one CO per Brønsted site. Molecules such as O$_2$, which do not interact with Brønsted sites, showed the same heats of adsorption on both samples. Therefore, the coverage-dependent differential heats provide a measure of the site energetics for these materials.

In the present chapter, we set out to determine whether differential calorimetry can be used to distinguish structural differences in similar zeolites, using MOR and MTW as the examples. Using both theoretical calculations, which is done by Srinivas Rangarajan and Manos Mavrikakis at University of Wisconsin, and experimental measurements, we will show that methane adsorption at 195 K appears to be an excellent probe for determining structural differences. By studying CH$_4$ adsorption in a series of H-ZSM-5 samples, we show that the presence of Brønsted sites does not affect the heats of adsorption for CH$_4$.

3.2 Experimental Section

3.2.1 Experimental

The Tian-Calvet calorimeter used in this study was home-built and has been described in detail in Chapter 2. The zeolites in this study, along with some of their properties, are listed in Table 3.1. Two of the H-ZSM-5 and the H-MOR samples are commercially available from Zeolyst. The two ZSM-5 samples, prepared at the University of Delaware, used fluoride-containing media to achieve low silanol defect concentrations. Details of the synthesis were described in Chapter 2. The H-ZSM-12 sample was used in a previous study and has been described there in more detail. Brønsted-site concentrations were determined using simultaneous temperature-programmed desorption and thermogravimetric analysis of 2-propanamine. Pore volumes were determined from gravimetric uptakes of n-hexane at room temperature and 10 Torr, assuming the pore volume becomes filled with liquid-like n-hexane.
Table 3.1 Zeolite Samples Used in This Study

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Bronsted-acid site densities (µmol/g)</th>
<th>Pore volume with n-hexane (cm&lt;sup&gt;3&lt;/sup&gt;/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolyst, H-ZSM-5(50)</td>
<td>50</td>
<td>470</td>
<td>0.1856</td>
</tr>
<tr>
<td>Zeolyst, H-ZSM-5(280)</td>
<td>280</td>
<td>80</td>
<td>0.1875</td>
</tr>
<tr>
<td>Defect free, H-ZSM-5(F,Al)</td>
<td>-</td>
<td>240</td>
<td>0.1744</td>
</tr>
<tr>
<td>Defect free, ZSM-5(F,Si)</td>
<td>-</td>
<td>10</td>
<td>0.1696</td>
</tr>
<tr>
<td>H-MOR</td>
<td>20</td>
<td>-</td>
<td>0.1026</td>
</tr>
<tr>
<td>ZSM-12</td>
<td>-</td>
<td>20</td>
<td>0.0939</td>
</tr>
</tbody>
</table>

3.2.2 Calculations

The calculations in this study were performed in collaboration with Srinivas Rangarajan and Manos Mavrikakis at University of Wisconsin. All electronic structure calculations were carried out using Vienna ab initio simulation package (VASP), a plane wave density functional theory (DFT) code. PAW potentials with generalized gradient approximation (GGA) using the PBE exchange correlation functional with Grimme-D2 semi empirical dispersion corrections were used. The Brillouin zone was sampled using only the gamma point in view of the large supercell size. A Gaussian smearing of 0.1 eV was used, and all energies were extrapolated to 0 K. A plane wave cutoff of 400 eV and density wave cutoff of 600 eV were used with a convergence criteria of all forces being smaller than 0.02 eV/Å. We refer to this level of theory as DFT-D2 in this work. The calculated (experimental in parentheses) lattice parameters for the three zeolites in their siliceous forms are (a) 20.2 × 19.9 × 13.3 Å<sup>3</sup> (20.1 × 19.7 × 13.1 Å<sup>3</sup>) for the orthorhombic phase of ZSM-5, (b) 18.4 × 20.7 × 7.6 Å<sup>3</sup> (18.3 × 20.5 × 7.5 Å<sup>3</sup>) for the orthorhombic mordenite (MOR) structure, and (c) 25.8 × 5.3 × 12.2 Å<sup>3</sup> (25.6 × 5.3 × 12.1 Å<sup>3</sup> with β = 109.3° for both) for zeolite ZSM-12 in the monoclinic form. In these calculations, the atoms of the zeolite were fixed at coordinates specified in the structural information published on the IZA Web site. All molecular adsorption calculations for ZSM-5 and MOR were performed in a supercell comprising one full periodic unit while those on
ZSM-12 were carried out in a supercell that had two unit cells (two units in the y-axis); these cells enable us to explore low adsorbate coverages. All atoms were relaxed in these calculations and spin polarization was considered for the oxygen molecule in the gas and adsorbed phase. Gas phase calculations were carried out in the same level of theory as above in a cell of size 20 × 20.5 × 21 Å³ allowing for more than 10 Å of vacuum between periodic images. Figures of zeolite structures and adsorbate configurations were generated using VESTA.71

The binding energy (BE) of an adsorbate molecule is calculated as

\[
BE = E_{\text{molecule+Zeolite}} - E_{\text{molecule,gas}} - E_{\text{Zeolite}} \quad \text{(Eqs. 3.1)}
\]

where \( E_{\text{molecule+Zeolite}} \) is the total energy of the zeolite with the adsorbed molecule, \( E_{\text{molecule,gas}} \) is the total energy of the gaseous molecule, and \( E_{\text{Zeolite}} \) is the total energy of the zeolite (catalyst).

We report results on both Brønsted and non-Brønsted forms of multiple sites on the zeolite ZSM-5; for MOR and ZSM-12, only the non-Brønsted sites are considered. The calculation of \( E_{\text{molecule+Zeolite}} \) and \( E_{\text{Zeolite}} \) on a Brønsted site involved performing electronic structure calculations on a zeolite supercell with a single Si atom being replaced by an Al atom (and adding one H atom to a neighboring oxygen atom); for the corresponding non-Brønsted site, similar calculations were performed on its topologically identical site in a siliceous supercell.

Zero point energy (ZPE) corrections were included (unless otherwise stated) in all binding energy values reported here. The vibrational frequencies \( \nu \) of the adsorbate (and the Brønsted proton, if present) were computed using harmonic approximation and ZPE was calculated using the following formula

\[
ZPE = \frac{1}{2} \sum_{i=1}^{\text{modes}} h\nu_i \quad \text{(Eqs. 3.2)}
\]
Since there are multiple topologically identical locations in a zeolite supercell, we also performed sample calculations to test if the presence of a Brønsted site in a supercell affects adsorption on a topologically identical non-Brønsted site and compared this with the binding energy values on the siliceous supercell; we observed negligible (<1 kJ/mol) differences in all cases. Temperature corrections were added to the energy calculations to get the enthalpy values. This was done by calculating temperature-dependent entropy values for the adsorbate in the gas and adsorbed phases, fitting polynomials (Shomate equations) to this data, calculating heat capacity from the resulting expression, and calculating a temperature contribution to the total energy. The details of this procedure are given in the models below.

3.2.2.1 Calculating temperature-dependent thermochemistry of adsorption in zeolites

Shomate equations were derived for the thermochemistry of adsorbed and gas phase species. These equations are defined as:

\[ t = \frac{T[K]}{1000} \]

\[ C_p \left[ \frac{J}{mol \cdot K} \right] = A + Bt + Ct^2 + Dt^3 + \frac{E}{t} \]

\[ H \left[ \frac{kJ}{mol} \right] = At + Bt^2/2 + Ct^3/3 + Dt^4/4 - \frac{E}{t} + F \]

\[ S \left[ \frac{J}{mol \cdot K} \right] = A \ln(t) + Bt + Ct^2/2 + Dt^3/3 - \frac{E}{2t^2} + G \]

The procedure for the calculation of these parameters is as follows:

I. Calculate entropy of species at different temperatures.

II. Fit the Shomate expression for entropy to this data set.

III. Extract parameters A, B, C, D, and E from the fit, and fix F to H at a reference temperature. Here, we choose the reference temperature to be 10 K and \( H = E + ZPE \) where \( E \) is the total energy of the species calculated using DFT and \( ZPE \) is the zero point energy.
The entropy of the species is calculated by summing together translational, rotational, and vibrational components.

\[ S = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}} \quad \text{(Eqs. 3.3)} \]

For gas phase, the translational entropy is calculated assuming 3D translational freedom while rotational entropy is calculated based on the moments of inertia and symmetry. The vibrational term is calculated using the harmonic approximation.\(^{72}\) For the adsorbed species, a 2D translational freedom is assumed Eqs 3.3. The Hessian matrix is transformed to remove the modes corresponding to translation before diagonalization. All rotations are assumed to be frustrated vibrations. The translational surface area was assumed based on the estimates given by De Moor et al.;\(^{55}\) values for MTW were taken to be the same as FAU.

For the calculation of vibrational entropy values, we assumed a minimum cutoff of 100 cm\(^{-1}\). All values lower than this were re-set to this cutoff value and all spurious imaginary frequencies were set to 100. A careful analysis of the sensitivity of this minimum value on the thermochemistry revealed that the entropy values vary within 10 J/mol · K and enthalpy by 2 - 4 kJ/mol.

3.3 Results and Discussion

3.3.1 H-ZSM-5

Experimental. In order to understand the possible effects of Brønsted sites and silanol defects on CH\(_4\) adsorption, calorimetric measurements were performed at 195 K on the four H-ZSM-5 samples listed in Table 3.1. The differential heats are reported as a function of coverage in Figure 3.1, with results for the two Zeolyst samples in Figure 3.1a and for the two defect-free samples in Figure 3.1b.
Figure 3.1 Differential heats for CH₄ adsorption on the different H-ZSM-5 samples at 195 K. (a) (●) H-ZSM-5(50) and (○) H-ZSM-5(280). (b) (◆) ZSM-5(F, Si) and (◇) H-ZSM-5(F, Al).

Within experimental uncertainty, the heats of adsorption at coverages below 0.6 mmol/g were independent of coverage on all of the samples. The differential heats were 22.5 ± 1 kJ/mol on the two Zeolyst samples and 22 ± 1 on the two defect-free samples. The Brønsted-site densities on these samples ranged from 0.010 mmol/g to 0.47 mmol/g, implying that interactions with the Brønsted sites were too small to observe in calorimetry. The very small difference between the results on the defect-free samples and the Zeolyst samples were less than the experimental uncertainty. Interestingly, the equilibrium constants, determined from the slope of the isotherm near zero coverage and reported in Table 3.2, were not identical on the four samples.
Table 3.2 Equilibrium Constants for Adsorption of CH₄ on the Four H-ZSM-5 Samples at 195 K, Determined from the Slope of the Isotherms near Zero Coverage

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>slope at zero coverage (X10⁻⁷ (mol/(g·Pa))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5(50)</td>
<td>6.47</td>
</tr>
<tr>
<td>H-ZSM-5(280)</td>
<td>4.15</td>
</tr>
<tr>
<td>H-ZSM-5(F,Al)</td>
<td>4.80</td>
</tr>
<tr>
<td>ZSM-5(F,Si)</td>
<td>1.54</td>
</tr>
</tbody>
</table>

The values for the four samples differed by a factor of about 4, with H-ZSM-5(50) showing the highest value and ZSM-5(F,Si) the lowest. There is a strong correlation between the equilibrium constant and the Brønsted-site density but there does not appear to be any dependence on whether or not the samples are defect-free. If the change in equilibrium constant were simply due to enthalpic interactions with the Brønsted sites, the factor of 4 at 195 K would imply that the heats of adsorption should be 2.2 kJ/mol higher on H-ZSM-5(50) compared to ZSM-5(F,Si). This is significantly higher than the uncertainty in the calorimetric measurements, implying that there may be some entropic effects associated with adsorption near the Brønsted sites. For example, since adsorbed CH₄ is likely very mobile, we suggest that the effect of the Brønsted sites might be to reduce this mobility. The change in adsorption entropy associated with a factor of 4 change in equilibrium constant is 11.5 J/mol·K at 195 K. If Brønsted sites were to reduce the mobility from something like a two-dimensional to a one-dimensional gas, the partition functions could be calculated using Eqs 3.3 and 3.4:

\[
S_{\text{trans,2D}} = R \left[ \ln \left( \frac{2\pi m k T}{h^2} \right) + \ln \left( \frac{SA}{N} \right) + 2 \right] \tag{Eqs. 3.3}
\]

\[
S_{\text{trans,1D}} = R \left[ \log \left( \frac{\sqrt{2\pi m k T}}{h} \right) + \log(L_0) + 1.5 \right] \tag{Eqs. 3.4}
\]

where \(m\) is the mass of the molecule, \(k\) is the Boltzmann constant, and \(h\) is Planck’s constant. \((SA/N)\) is the average surface area available for a molecule at the reference state of a
monolayer coverage, equal to 200 pm \times 600 pm for ZSM-5, and \textit{L}_0 can be taken to be a lattice parameter, on the order of 600 pm in this case. For CH\textsubscript{4} at 195 K, the difference between these values is nearly 20 J/mol·K.

**Calculations.** Since previous theoretical studies have indicated hydrocarbons should interact with Brønsted sites\textsuperscript{60,73}, we performed theoretical studies on H-ZSM-5 to understand what effect Brønsted sites might have on the adsorption of simple molecules. In addition to examining the adsorption of CH\textsubscript{4}, we also examined adsorption of CO on H-ZSM-5, since previous measurements indicated that CO adsorbs on Brønsted sites with an additional 10 kJ/mol (this result was repeated here for the H-ZSM-5(F,Al) sample, with data shown in Figure 3.2).\textsuperscript{51} Two locations for the acid sites were considered. The most stable acid site (Al\textsubscript{7}-O\textsubscript{17}–Si\textsubscript{8} defined per the scheme adopted by IZA) is shown in Figure 3.3, where the Brønsted proton (bonded to O\textsubscript{17}) is hydrogen bonded to another oxygen atom (O-H distance of 1.85 Å). A less stable site (Si\textsubscript{12}-O\textsubscript{26}-Al\textsubscript{12}) (by 0.23 eV or \sim 22 kJ/mol) was also considered at the entrance of the sinusoidal channel and pointing into the straight channel is shown in Figure 3.4.

![Figure 3.2 CO adsorption on the defect free H-ZSM-5(F,Al) at 195 K. The dashed line is shown at the Brønsted-site concentration.](image)

\textsuperscript{51}
Figure 3.3 Zeolite ZSM-5 with the most stable location of Brønsted site (Al7-O17-Si8). The left hand side shows the view perpendicular to the axis of the straight channel. The right hand side explicitly shows the structure along the axis of the straight channel. The dashed line indicates a hydrogen bond between the Brønsted proton and a nearby oxygen atom. Key: Oxygen (●), silicon (○), aluminum (●), and hydrogen (○).

Figure 3.4 Zeolite ZSM-5 with a Brønsted site (Al12-O26-Si12) at the intersection of straight and sinusoidal channels. The left hand side shows the view perpendicular to the axis of the straight channel. The right hand side explicitly shows the structure along the axis of the straight channel. Key: Oxygen (●), silicon (○), aluminum (●), and hydrogen (○).

These two sites have been considered in the literature as the likely positions for the Brønsted sites in H-ZSM-5.\textsuperscript{74–77} The enthalpy of adsorption at the DFT-D2 level of theory for CO and CH\textsubscript{4} on these two locations, with and without the Brønsted site, are reported in Table 3.3 and discussed below. The corresponding binding energy values (ZPE-corrected) are in Table 3.4.
Table 3.3 Calculated Enthalpy of Adsorption for CO and CH₄ (in kJ/mol) on Brønsted and Non-Brønsted Forms of Two Sites in ZSM-5 at 195 K

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>T7-O17-T8&lt;sup&gt;a&lt;/sup&gt;</th>
<th>T12-O26-T12&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Brønsted&lt;sup&gt;b&lt;/sup&gt;</td>
<td>non-Brønsted&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>CO</td>
<td>-26.7</td>
<td>-19.1</td>
</tr>
<tr>
<td>Methane</td>
<td>-23.2</td>
<td>-21.2</td>
</tr>
</tbody>
</table>

<sup>a</sup> “T” refers to the tetrahedral atom that is either Si or Al atom.

<sup>b</sup> “Brønsted” refers to adsorption on a Brønsted site formed by replacing a Si atom of Tx-Oy-Tz site by Al atoms and adding a hydrogen to the oxygen atom “y”. For T7-O17-T8, Al replaces a Si atom in the tetrahedral position 7 and for T12-O26-T12 Al replaces Si atom in the tetrahedral position 12.

Table 3.4 Calculated binding energy (ZPE corrected) values for CO and CH₄ (in eV) on Brønsted and non-Brønsted forms of two sites in ZSM-5 (1eV ~ 96.5 kJ/mol).

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>T7-O17-T8&lt;sup&gt;a&lt;/sup&gt;</th>
<th>T12-O26-T12&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Brønsted&lt;sup&gt;b&lt;/sup&gt;</td>
<td>non-Brønsted&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>CO</td>
<td>-0.27</td>
<td>-0.17</td>
</tr>
<tr>
<td>Methane</td>
<td>-0.27</td>
<td>-0.24</td>
</tr>
</tbody>
</table>

<sup>a</sup> “T” refers to the tetrahedral atom that is either Si or Al atom.

<sup>b</sup> “Brønsted” refers to adsorption on a Brønsted site formed by replacing a Si atom of Tx-Oy-Tz site by Al atoms and adding a hydrogen to the oxygen atom “y”. For T7-O17-T8, Al replaces a Si atom in the tetrahedral position 7 and for T12-O26-T12 Al replaces Si atom in the tetrahedral position 12.

Figure 3.5 - Figure 3.8 show the adsorption structures for CH₄ and CO on the Brønsted and non-Brønsted forms of the two sites considered. CO binds via the carbon atom on both Brønsted and non-Brønsted sites of ZSM-5 similar to the observations made in computational studies of other proton-form zeolites;<sup>78,79</sup> in the presence of a Brønsted site, the molecule points toward the Brønsted proton, leading to an additional stabilization of about 7 kJ/mol for T7-O17-T8 and 22 kJ/mol for the T12-O26-T12 site. The adsorption enthalpy values (~26.7 kJ/mol) on the most stable Brønsted acid site (T7-O17-T18) match remarkably well with the microcalorimetric data.
kJ/mol) for carbon monoxide on ZSM-5. On the other hand, the binding energy on the Brønsted site of T12-O26-T12 is about 14 kJ/mol higher than that of T7-O17-T8. The calculated adsorption enthalpies of CH₄ on the Brønsted (~23.2 kJ/mol) and siliceous forms (~21.2 kJ/mol) of the T7-O17-T8 site are close to experimental values (~22 kJ/mol); however, DFT-D2 calculations show an effect of the Brønsted site of about 2 kJ/mol. The binding energy on the Brønsted site of T12-O26-T12 is about 12 kJ/mol larger than that on T7-O17-T8, leading again to a more pronounced effect of the Brønsted site at the T12-O26-T12 location. It should be noted that the lower effect of hydrogen bonding for the T7-O17-T8 site is potentially due to stabilization of the Brønsted hydrogen atom through hydrogen bonding (Figure 3.3).

![Figure 3.5 Preferred CH₄ adsorbed state on T7-O17-T8 location with a Brønsted site (left) and in purely siliceous form (right) in zeolite ZSM-5. Two views (top and bottom) are shown for comparison on the CH₄ location in the presence and absence of Brønsted proton. Key: Oxygen (●), silicon (○), aluminum (●), carbon (●), and hydrogen (○).]
Figure 3.6 Preferred CH₄ adsorbed state on T12-O26-T12 location with a Brønsted site (left) and in purely siliceous form (right) in zeolite ZSM-5. Key: Oxygen (●), silicon ( ○), aluminum (●), carbon (●), and hydrogen (○).

Figure 3.7 Preferred CO adsorbed state on T7-O17-T8 location with a Brønsted site (left) and in purely siliceous form (right) in zeolite ZSM-5. Key: Oxygen (●), silicon ( ○), aluminum (●), carbon (●), and hydrogen (○).

Figure 3.8 Preferred CO adsorbed state on T12-O26-T12 location a with Brønsted site (left) and in purely siliceous (right) form of zeolite ZSM-5. Key: Oxygen (●), silicon ( ○), aluminum (●), carbon (●), and hydrogen (○).
Recently, Tuma and Sauer adopted a hybrid MP2:DFT method to calculate the binding energy and proton transfer barriers of methane on a number of proton-form zeolites. This higher level of theory can be used to benchmark our results. The authors report a ZPE-corrected binding energy value of −28.5 kJ/mol on the T7-O17 site (although named T7-O7 according to their naming convention) compared to our −26 kJ/mol (see Table 3.4). In addition, we performed additional calculations on the T12 site studied by Tuma and Sauer (T12-O20 in their naming convention and T12-O8 in ours); the ZPE-corrected binding energy values of methane adsorption on this site was found to be −29.9 kJ/mol, in close agreement with the published value of −30.1 kJ/mol (see Table 3.5). The effect of Brønsted site for methane adsorption on the T12-O8 site is about 3.5 kJ/mol.

Table 3.5 Calculated enthalpy of adsorption for CH₄ (in kJ/mol) on the T12-O8-T3 Brønsted and non-Brønsted forms of ZSM-5

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>T12-O8-T3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Brønsted</td>
</tr>
<tr>
<td>Methane</td>
<td>-24.8</td>
</tr>
</tbody>
</table>

Note: T12-O8-T3 site is topologically equivalent to T12-O20 site of Tuma and Sauer (Journal of Chemical Physics (2010), 143, 102810). “Brønsted” refers to adsorption on a Brønsted site formed by replacing a Si atom of Tx-Oy-Tz site by Al atoms and adding a hydrogen to the oxygen atom “y”. For T12-O8-T3, Al replaces Si atom in the position 12.

Because experimental data suggests acid sites have a negligible effect on CH₄ adsorption enthalpies, we investigated the origin of this DFT-predicted effect by considering other exchange correlation functionals, as well as alternative treatments of dispersion effects. Table 3.6 lists the different levels of theory considered in this study, and the corresponding calculated difference in the binding energy values (not ZPE corrected) of CH₄ on the Brønsted and non-Brønsted forms of the T7-O17-T8 site. The difference values are between 0.01 and 0.07 eV (∼1 to 7 kJ/mol) in all cases and arise primarily due to the choice of the exchange correlation functional used in the calculations. Similar observations can be made for the T12-O26-T12 site as well (see Table 3.7).
Table 3.6 Difference in CH$_4$ Binding Energies between Brønsted and Non-Brønsted T7-O17-T8 Site of ZSM-5 Using Different Functionals and Dispersion Treatments

<table>
<thead>
<tr>
<th>Method</th>
<th>Dispersion-corrected</th>
<th>Difference [eV (kJ/mol)]$^{ab}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference (PBE+D2)$^{68,69}$</td>
<td>Yes</td>
<td>0.05 (4.7)</td>
</tr>
<tr>
<td>PBE$^{68}$</td>
<td>No</td>
<td>0.05 (4.7)</td>
</tr>
<tr>
<td>PW91$^{81,82}$</td>
<td>No</td>
<td>0.05 (4.9)</td>
</tr>
<tr>
<td>RPBE$^{83}$</td>
<td>No</td>
<td>0.01 (1.3)</td>
</tr>
<tr>
<td>PBE$^{68}$ + D3$^{84}$</td>
<td>Yes</td>
<td>0.07 (6.6)</td>
</tr>
<tr>
<td>PBEsol$^{85}$</td>
<td>No</td>
<td>0.07 (6.5)</td>
</tr>
<tr>
<td>BEEF-vdW$^{86}$</td>
<td>Yes</td>
<td>0.06 ± 0.03 (6.0 ± 2.9)</td>
</tr>
</tbody>
</table>

$^a$ Positive value of the difference indicates CH$_4$ binds more strongly on the Brønsted site.

$^b$ Energy values are non-ZPE-corrected.

$^c$ Estimated Bayesian statistical error calculated from a distribution of total energies estimated using an ensemble of parameter values representing the functional.

Table 3.7 Difference in CH$_4$ Binding Energies between Brønsted and Non-Brønsted T12-O26-T12 Site of ZSM-5 Using Different Functionals and Dispersion Treatments

<table>
<thead>
<tr>
<th>Method</th>
<th>Dispersion-corrected</th>
<th>Difference [eV (kJ/mol)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference (PBE+D2)</td>
<td>Yes</td>
<td>0.17 (16.3)</td>
</tr>
<tr>
<td>PBE</td>
<td>No</td>
<td>0.16 (15.1)</td>
</tr>
<tr>
<td>PW91</td>
<td>No</td>
<td>0.16 (15.3)</td>
</tr>
<tr>
<td>RPBE</td>
<td>No</td>
<td>0.13 (11.8)</td>
</tr>
<tr>
<td>PBE + D3</td>
<td>Yes</td>
<td>0.16 (15.1)</td>
</tr>
<tr>
<td>PBEsol</td>
<td>No</td>
<td>0.20 (19.2)</td>
</tr>
</tbody>
</table>

These results are consistent with other theoretical studies$^{60,73}$ but do not agree with the experimental observations. We suggest the discrepancy between theory and experiment in this case is due to the inability of standard DFT methods to capture hydrogen bonding effects accurately. Various benchmarking studies on the accuracy of DFT functionals to treat hydrogen
bonding have been reported.\textsuperscript{67-90} While the specific conclusions of these studies vary (some report under-prediction while others observed overprediction with respect to a higher level of theory such as coupled cluster calculations) and the reference set of molecules considered are different, they all point to intrinsic errors in standard generalized gradient-corrected exchange correlation functionals in treating hydrogen bonding, in line with our observations. In view of our experimental data, the Brønsted sites will not be considered further in our calculations.

3.3.2 MOR and MTW

\textbf{Experimental.} In order to determine the effect of zeolite structure on adsorption properties, we performed calorimetric measurements of \(\text{CH}_4\), \(\text{O}_2\), and \(\text{Ar}\) on MOR and ZSM-12. As discussed in the Introduction, the main channels in both MOR and ZSM-12 are 12-MR. However, MOR also has 8-MR pockets on the sides. Although the volume of these pockets is small compared to that of the main channels, the corrugation that results from the openings to the side pockets causes the pore surfaces to be rougher on the molecular scale. As with \(\text{CH}_4\), \(\text{O}_2\) and \(\text{Ar}\) are not expected to interact with Brønsted sites, so that most of the interactions should be due to dispersion forces with the siliceous walls.\textsuperscript{62} \textbf{Figure 3.9} shows the differential heats for \(\text{CH}_4\) on ZSM-12 and MOR. On ZSM-12, the differential heats are reasonably constant, starting at 23.0 kJ/mol at zero coverage and decreasing slightly to 21.5 kJ/mol at 0.4 mmol/g. In a previous calorimetric study carried out at room temperature, the differential heats also decreased slightly with coverage but the reported heats were about 2 kJ/mol lower.\textsuperscript{49} About 1.2 kJ/mol of this difference can be explained by the heat of adsorption changing with temperature. This value was determined by assuming \(\text{CH}_4\) loses its translational degrees of freedom in going to the adsorbed phase, so that the heat capacities of gas phase and adsorbed-phase \(\text{CH}_4\) change by \((3/2)R\).
In any case, the numbers here are probably more accurate than those reported previously due to the fact that lower gas pressures were required to obtain a given coverage at 195 K. Although ZSM-12 consists of 12-MR channels, the differential heats are very close to that found on the 10-MR zeolite, ZSM-5. This is due to the fact that the intersecting channels in ZSM-5 make the channels effectively larger. The heats of adsorption for CH₄ on MOR were significantly higher than those on MTW. At low coverages, the differential heats in MOR were almost 30 kJ/mol. For coverages between 0.25 and 0.45 mmol/g, the differential heats fell to 25 kJ/mol, then remained constant at that value. The higher heats are almost certainly associated with the 8-MR side pockets. While there are no simple, one-dimensional zeolites with 8-MR channels, it is noteworthy that the zero-coverage differential heats were only about 27 kJ/mol on the 10-MR, one dimensional zeolite, TON. Furthermore, the coverage at which the differential heats fall on MOR is close to the side pocket concentration of 0.35 mmol/g. The fact that there is no sharp demarcation at 0.35 mmol/g is due to the adsorption energies for molecules in the side pockets and in the corrugated main channels differing by a relatively small amount, so that both sites are being occupied simultaneously at 195 K, as discussed in the Introduction. Figure 3.10 shows the corresponding...
differential heats for O$_2$ in the ZSM-12 and MOR samples. Heats of adsorption for O$_2$ in ZSM-12 were 16 kJ/mol, independent of coverage. As with CH$_4$, this value is again similar to the heat of adsorption reported for O$_2$ in siliceous ZSM-5.$^{62}$ The differential heats for O$_2$ on MOR, 20 kJ/mol, were higher than those found on ZSM-12; however, unlike the case for CH$_4$, the differential heats for O$_2$ were independent of coverage. Because O$_2$ should be able to fit in the 8-ring side pockets, we suggest that difference in adsorption enthalpies between the side pockets and the main channels is similar or less than $kT$, so that both sites fill simultaneously. The results for Ar in MOR and ZSM-12, shown in Figure 3.11, are nearly the same as those for O$_2$.

Figure 3.10 Differential heats of adsorption for O$_2$ at 195 K on (■) HMOR and (▲) H-ZSM-12.
Figure 3.11 Differential heats of adsorption for Ar at 195 K on (■) HMOR and (▲) H-ZSM-12.

Figure 3.12 Siliceous mordenite (MOR) showing the channels along z axis. Two channels with eight (8 MR) and twelve (12 MR) membered-ring openings and a side pocket with eight membered ring opening (8 MR side pocket). Two regions of adsorption have been marked - 12 MR channel near the walls (I) and 8 MR side pocket (II). Key: Oxygen (●) and silicon (○).
**Calculations.** The adsorption of CH$_4$, O$_2$, and Ar in siliceous MOR and ZSM-12 was studied using DFT-D2. Figure 3.12 shows a schematic of MOR. Molecules can adsorb in the 12-MR channel and the 8-MR side pocket. While MOR also has an 8-MR channel as marked in Figure 3.12, the dimension of its minor axis (4.3 Å) prevents adsorption in this region; we did not observe strong adsorption in the 8-MR channels except for a few less stable structures at the intersection of 8-MR channels and 8-MR side pockets. The 12-MR channel close to the walls (marked region I) and the region of 8-MR side pockets (marked region II) are potential locations for adsorption. The calculated adsorption enthalpy of CH$_4$, O$_2$, and Ar in the two regions of MOR are given in Table 3.8 (ZPE-corrected binding energies are in Table 3.9), and their adsorption structures are shown in Figure 3.13.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>12-MR channel</th>
<th>8-MR side pocket</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>-17.0</td>
<td>-27.5</td>
</tr>
<tr>
<td>O$_2$</td>
<td>-14.7</td>
<td>-19.9</td>
</tr>
<tr>
<td>Ar</td>
<td>-14.0</td>
<td>-20.6</td>
</tr>
</tbody>
</table>

*All values are in kJ/mol.

Table 3.9 ZPE corrected binding energy of CH$_4$, O$_2$, and Ar in the two adsorption regions of MOR. All binding energy values are in eV (1eV ~ 96.5 kJ/mol)

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>12-MR channel</th>
<th>8-MR side pocket</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>-0.20</td>
<td>-0.31</td>
</tr>
<tr>
<td>O$_2$</td>
<td>-0.13</td>
<td>-0.19</td>
</tr>
<tr>
<td>Ar</td>
<td>-0.14</td>
<td>-0.21</td>
</tr>
</tbody>
</table>
Figure 3.13 Most stable adsorption structure of (a) methane in 12-MR channel, (b) methane in 8-MR side pockets, (c) oxygen in 12-MR channel, (d) oxygen in 8-MR side pockets, (e) argon in 12-MR channel, and (f) argon in 8-MR side pockets of MOR. Key: oxygen (red), silicon (yellow), carbon (gray), hydrogen (white), and argon (blue).

CH$_4$ binding energies vary from $\sim$28 to $-17$ kJ/mol, while O$_2$ and Ar binding energy variations are smaller. In all cases, DFT-D2 predicts a higher binding energy for the side pockets than the straight channels. Further, the DFT-D2 binding energy in the 8-MR side pockets match experimental heats at low coverage, corroborating our argument that the side pockets get filled first. DFT-D2 under predicts the binding energy of CH$_4$ in the 12-MR channel by 5 kJ/mol (compared to experimental heats at high coverage). This underprediction appears to be uniform for all three adsorbates because accounting for this brings DFT-D2 predictions to within 2 kJ/mol of experimental heats at high coverages for O$_2$ and Ar. This uniform deviation probably arises from intrinsic error in the variation of the dispersion potential as a function of distance of the adsorbate from the wall. The trends from DFT-D2, however, suggest that the heats of adsorption of O$_2$ and Ar are independent of the coverage because the difference between the adsorption enthalpies of the side pockets and the main channel is small compared to kT.
Figure 3.14 Siliceous ZSM-12 showing the channel along z axis. Adsorption is in the channel with 12 membered ring opening (12 MR channel). Key: Oxygen (●) and silicon (○).

Table 3.10 Enthalpy of Adsorption of CH₄, O₂, and Ar in ZSM-12 at 195 K.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Binding Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>-20.3</td>
</tr>
<tr>
<td>O₂</td>
<td>-13.8</td>
</tr>
<tr>
<td>Ar</td>
<td>-16.6</td>
</tr>
</tbody>
</table>

Table 3.11 ZPE corrected binding energy of CH₄, O₂, and Ar in ZSM-12. All binding energy values are in eV (1eV ~ 96.5 kJ/mol).

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>-0.23</td>
</tr>
<tr>
<td>O₂</td>
<td>-0.13</td>
</tr>
<tr>
<td>Ar</td>
<td>-0.17</td>
</tr>
</tbody>
</table>
A schematic of ZSM-12 showing the 12-MR channels is given in Figure 3.14. The DFT-D2 adsorption enthalpies of CH₄, O₂, and Ar in ZSM-12 are given in Table 3.10 (ZPE-corrected binding energy values are in Table 3.11) and the adsorption structures are shown in Figure 3.15. CH₄ (−20.3 kJ/mol) binds more strongly than O₂ (−13.8 kJ/mol) and Ar (−16.6 kJ/mol), similar to what was found in MOR; these are within 4 kJ/mol of the experimental differential heats. The binding energy of CH₄ in ZSM-12 is within 1 kJ/mol of that on ZSM-5 in agreement with the experiments. Clearly, comparing the three zeolites, the binding energy of adsorbates is higher in confined spaces of the zeolite (such as the side pockets of MOR) due to increased dispersion interactions. Overall, the calculations confirm our initial proposition and experimental results that a probe molecule that interacts with the zeolite purely through dispersion interactions (such as methane) can be used to characterize the pore geometry of zeolites.

Figure 3.15 Most stable adsorption structure of (a) methane, (b) oxygen, and (c) argon in the 12-MR channels of ZSM-12. Key: oxygen (red), silicon(yellow), carbon (gray), argon (blue), and hydrogen (○).
3.4 Summary

In this chapter, we have shown that experimental differential heats of adsorption for CH₄ depend strongly on the solid nanostructure but not on the presence of Brønsted sites, implying that calorimetric measurements at 195 K could be used to probe the nanostructure of unknown materials. The comparison of the experimental results with DFT demonstrated that the theory accurately describes the effect of zeolite structure on CH₄ adsorption but tends to overpredict the effect of Brønsted sites.
Chapter 4. Adsorption of Small Alkanes on ZSM-5 Zeolites: Influence of Brønsted Sites

4.1 Introduction

In Chapter 3, I showed that Brønsted sites do not affect the heats of adsorption for methane. However, there have been reports in the literature that larger alkanes can form hydrogen bonds with the acid sites. In order to determine the effect of Brønsted sites on alkane adsorption, it was necessary to measure differential heats on a series of materials with varying site densities in order to extrapolate the effect of the acid sites.

The hydrogen forms of zeolites are of great commercial importance as solid, Brønsted-acid catalysts. Although acidic zeolites catalyze many of the same reactions as homogeneous acids, there are important differences, in large part due to different solvation effects, so that there is a continuing need to characterize and model how molecules interact with the acid sites. The high-silica zeolite, H-ZSM-5 is one of the most widely studied materials, both because of its commercial importance and because of its relative simplicity. Rates for a number of important reactions increase linearly with the Al content of this zeolite. Furthermore, adsorption studies have demonstrated the formation of stoichiometric adsorption complexes, one molecule per Al site, for alcohols, amines, nitriles, thiols, and other classes of molecules. The reactivities of these adsorption complexes in Temperature-Programmed Desorption (TPD) do not depend on the Si/Al ratio of the sample. This, together with the fact that differential heats of adsorption for simple bases like NH₃ and pyridine are constant with coverage up to one molecule per site, suggests that the Brønsted sites in H-ZSM-5 are essentially equivalent.

For bases with proton affinities higher than that of ammonia, heats of formation of the stoichiometric adsorption complexes have been shown to scale with the gas-phase proton affinities; however, for weaker bases, the situation is less clear. An important example is that of...
simple alkanes wherein the adsorption thermochemistry depends on the dispersive interactions with the zeolite wall and the non-covalent interactions with the acid site. In Chapter 3, I showed that interactions of CH$_4$ with the Brønsted sites in H-ZSM-5 do not contribute significantly to the heats of adsorption. However, in the literature, there are both experimental$^{53,99}$ and theoretical$^{80,100}$ reports that the contributions to the heats of adsorption from interactions with Brønsted sites are significant for larger alkanes. For example, Eder and Lercher$^{53}$ reported that differential heats for n-hexane to n-octane are 10 kJ/mol higher on H-ZSM-5 than on a siliceous ZSM-5. Arik et al. measured the temperature dependences for Henry’s Law constants and also reported that heats of adsorption for normal alkanes increased with Al site density.$^{99}$

There are several factors which make it difficult to determine how strongly alkanes interact with the Brønsted sites in H-ZSM-5. First, at realistic measurement temperatures, the alkane/Brønsted-site interaction is relatively small compared to $k_BT$. This issue is very important, for reasons discussed in Chapter 2. On the basis of thermodynamic arguments, this implies that a significant fraction of adsorbed molecules will not be present at the Brønsted sites at any given coverage.$^{45}$ Measured differential heats will be an averaged value between that of molecules adsorbed at the acid sites and molecules not at acid sites. Second, theoretical determination of the interactions between alkanes and Brønsted sites is difficult because the standard DFT methods may not accurately capture hydrogen-bonding effects with alkanes. For example, in Chapter 3, calculations performed using various functionals indicated that CH$_4$ should bind to the Brønsted sites with an additional 1 to 7 kJ/mol,$^{101}$ but this was not observed experimentally. Finally, most real zeolites have significant concentrations of vacancy defects, observable as nested silanols; and these have a profound effect on the adsorption of polar molecules, like water.$^{57}$ Although vacancy sites do not appear to affect CH$_4$ adsorption, as demonstrated in Chapter 3, CH$_4$ adsorption was also not affected by the presence of Brønsted sites.

In the present Chapter, I set out to examine the interaction between simple alkanes and the Brønsted sites in H-ZSM-5 calorimetrically and theoretically, as a function of alkane size. The
theoretical calculations were done by Srinivas Rangarajan and Manos Mavrikakis at University of Wisconsin. In the calorimetric measurements, the additional interactions with the Brønsted sites were extracted by measuring the differential heats on materials with varying Si/Al ratio; and the possible effects of defect sites were determined by comparison with results on a defect-free ZSM-5 synthesized in a fluoride medium. To understand the effect of alkane size on the additional interactions with the Brønsted sites from a theoretical side, gas-phase acid-affinities were calculated for the strong acid, fluorosulfonic acid (FSO₃H), as a possible descriptor. Both experimental and theoretical considerations indicate that the size of the alkane can significantly affect interactions with the Brønsted sites.

4.2 Experimental Section
4.2.1 Materials

Four different H-ZSM-5 samples with widely varying Brønsted-site concentrations were used in this Chapter and have been described in detail in Chapter 2. The commercial samples are referred to here as H-ZSM-5(50) and H-ZSM-5(280) based on the Si/Al ratios. Two low-defect samples are referred to here as ZSM-5(F,Si) and H-ZSM-5(F,Al). The Si/Al ratio for these two samples were determined by ICP-OES and listed in Table 4.1. Brønsted-site concentrations were determined using TPD/TGA measurements of 2-propanamine. Pore volumes were determined from gravimetric uptakes of n-hexane at room temperature and 10 Torr, assuming the pore volume becomes filled with liquid-like n-hexane. Key properties of these four samples are given in Table 4.1.
Table 4.1 Zeolite Samples Used in This Study

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al₂</th>
<th>Brønsted-acid site densities (µmol/g) (^b)</th>
<th>Pore volume with n-hexane (cm(^3)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5(F,Si)</td>
<td>&gt; 1100(^a)</td>
<td>10</td>
<td>0.17</td>
</tr>
<tr>
<td>H-ZSM-5(F,Al)</td>
<td>75(^a)</td>
<td>260</td>
<td>0.17</td>
</tr>
<tr>
<td>H-ZSM-5(50)</td>
<td>50</td>
<td>470</td>
<td>0.19</td>
</tr>
<tr>
<td>H-ZSM-5(280)</td>
<td>280</td>
<td>90</td>
<td>0.19</td>
</tr>
</tbody>
</table>

\(^a\) Determined by ICP-OES analysis.
\(^b\) Measured by TPD-TGA of 2-propanamine.

4.2.2 Calorimetry

The Tian-Calvet calorimeter was home-built and has been described in detail in Chapter 2. A series of small alkanes were used as adsorbates in this study, includes CH\(_4\), C\(_2\)H\(_6\), C\(_3\)H\(_8\), n-C\(_5\)H\(_{12}\), iso-C\(_5\)H\(_{12}\), and n-C\(_6\)H\(_{14}\). It is extremely important that the measurements are performed at the lowest temperatures for which adsorption is reversible, for reasons discussed in Chapter 2 already. In this study, experiments with CH\(_4\) were performed at 195 K. Adsorption of C\(_2\)H\(_6\) and C\(_3\)H\(_8\) were performed at room temperature; for n-C\(_5\)H\(_{12}\), iso-C\(_5\)H\(_{12}\), and n-C\(_6\)H\(_{14}\), adsorption measurements were performed between 353 and 373 K.

4.2.3 Calculations

The calculations in this study were performed in collaboration with Srinivas Rangarajan and Manos Mavrikakis at University of Wisconsin. The binding of alkanes to a gas phase Brønsted acid (and other cationic proton donors) can be viewed as a hydrogen-bonded interaction;\(^{103-105}\) analogously, the additional heats of adsorption of alkanes on H-ZSM-5 can be related to the strength of hydrogen bonding between the alkane and the Brønsted proton of the zeolite. In the complete absence of a solvent, the strength of the hydrogen bond is the proton affinity, but this interaction is moderated in the condensed phase by solvent interactions. Further, while proton
affinity intrinsically captures the stability of a three-center-two-electron complex that a proton can form with two neighboring carbon atoms of the alkane and the included bond\textsuperscript{106,107} the interactions of an alkane with a Brønsted proton does not lead to such a strong covalently bonded complex\textsuperscript{55,60,80,100,108} Therefore, we explored an alternative descriptor of alkane-Brønsted site interaction by calculating acid affinities for the various alkanes, $E_{\text{acid-affinity}}$, using a gas-phase superacid, fluorosulfonic acid (FSO$_3$H). The acid affinity is the energy of complexation for an acid-alkane complex, as given in Eqs. 4.1.

$$E_{\text{acid-affinity}} = E_{\text{alkane-acid}} - E_{\text{acid}} - E_{\text{alkane}}$$

(Eqs. 4.1)

Here, $E_{\text{alkane-acid}}$ is the energy of the hydrogen-bonded, alkane acid complex, $E_{\text{acid}}$ is the energy of the acid in the gas phase, and $E_{\text{alkane}}$ is the energy of the alkane in the gas phase. Because the acid affinity of an alkane is expected to depend on the strength of the acid, the optimal choice of acid to explore hydrogen bonding would be one with a deprotonation energy (DPE) equal to that of H-ZSM-5 (1200 kJ/mol as computed by Sauer et al.\textsuperscript{75} It should be noted that the particular choice of acid is, in principle, not critical as any acid could be used as reference if (i) it is not so weak that the corresponding acid affinity of most alkanes is negligibly small (<0.5 kJ/mol), (ii) it is not so strong to completely protonate the alkane, and (iii) it is not bulky enough to lead to steric effects with larger or branched alkanes. Although the deprotonation energy of fluorosulfonic acid (DPE ≈ 1280-1300 kJ/mol)\textsuperscript{109,110} is slightly higher than that of H-ZSM-5, it is one of the smallest superacids and is, therefore, a simple choice for mimicking a Brønsted-site in zeolites. It is further noted that, since we experimentally extract the interaction of the alkanes with the Brønsted sites and thereby remove the strength of interaction with the zeolite wall, the inclusion of the 3D structure and confinement effects of the zeolite is not necessary in the calculations, and the strong acid is a sufficiently accurate model of the Brønsted sites of the zeolite for the purposes of this study.
4.3 Results and Discussion

4.3.1 Calorimetric Results

With stronger bases, such as ammonia or pyridine, the interaction between the base and the Brønsted sites can be measured directly using micro calorimetry. For coverages below one molecule per site, the molecules bind preferentially to the acid sites and the differential heats measure that interaction, together with the other interactions the molecule may have with the zeolite cavity. For coverages above one per site, the differential heats are significantly lower, reflecting the fact that the sites are fully occupied, so that the primary interactions are between the base and the zeolite cavity. With weak bases, like alkanes that do not interact strongly with the acid sites, the differential heats are an averaged value. Therefore, in order to determine the effect of Brønsted sites, it was necessary to measure differential heats on a series of materials with varying site densities in order to extrapolate the effect of the acid sites. In the present study, we measured adsorption on the four H-ZSM-5 samples shown in Table 4.1. In addition to the fact that these materials had very different Si/Al ratios, two of the zeolites were low-defect materials prepared in a fluoride media in order to determine whether the presence of defects could affect the results.

The experimentally measured, differential heats of adsorption for CH$_4$ and n-C$_6$H$_{14}$ are shown as a function of coverage in Figure 4.1 for all four samples. For reasons given in the Experimental Section, the adsorption measurements were performed at 195 K with CH$_4$ and 373 K with n-C$_6$H$_{14}$. As discussed in detail elsewhere, the differential heats of adsorption for CH$_4$ were constant with coverage and equal to 22.5 ± 1 kJ/mol on all four samples, independent of Brønsted-site density or the presence of defects in the zeolite. However, for n-C$_6$H$_{14}$, the effect of acid-site density was significant. The differential heats on all four samples were approximately independent of coverage, perhaps increasing slightly due to attractive interactions; however, the heats were clearly higher for the H-ZSM-5(50) and H-ZSM-5(F,Al) samples than for the H-ZSM-5(280) or ZSM-5(F,Si) samples. The average values for the differential heats were 77 ± 2 kJ/mol on ZSM-5(F,Si), 80 ± 2 kJ/mol on H-ZSM-5(280), 88 ± 2 kJ/mol on H-ZSM-5(F,Al), and 90 ± 2 kJ/mol on H-ZSM-
Although the average differential heats were higher on samples with higher Brønsted-site concentrations, they appear to be unaffected by whether or not the samples were prepared in a fluoride medium.

**Figure 4.1** Differential heats for CH$_4$ and n-C$_6$H$_{14}$ adsorption on four ZSM-5 samples. (▲/■) ZSM-5(F,Si), (△/□) H-ZSM-5(F,Al), (★/●) H-ZSM-5(50), and (☆/○) H-ZSM-5(280)

Because the differential heats do not decrease at coverages above one molecule per site, there must be some averaging for molecules adsorbed at acid sites and molecules not at acid sites. There is the further complication that differential heats could increase with coverage due to attractive interactions between molecules.$^{61,111}$ Therefore, there remains some uncertainty as to how large the effect of the Brønsted sites on n-C$_6$H$_{14}$ adsorption actually is. However, the fact that the differences between ZSM-5(F,Si) and H-ZSM-5(280) and between H-ZSM-5(F,Al) and H-ZSM-5(50) were relatively small suggests that our results are representative of values for siliceous and acid sites, respectively.
Similar trends were obtained with other small alkanes, as shown in Table 4.2 and Figure 4.2. For simplicity, we show the differential heats for $\text{C}_3\text{H}_8$, n-$\text{C}_5\text{H}_{12}$, and iso-$\text{C}_5\text{H}_{12}$ as a function of coverage for only the H-ZSM-5(F,Al) and ZSM-5(F,Si) samples in Figure 4.2. The differential heats were again approximately constant, higher on the samples with high Brønsted-site concentrations, and independent of defect concentrations. In agreement with the literature, the adsorption enthalpy for the various alkanes increased by $\sim 10 \text{ kJ/mol}$ per added -CH$_2$- group. More important for the present study, the differences observed in the average differential heats increased with the size of the alkane. The extra heats, determined as difference between the heats of adsorption in H-ZSM-5 and its siliceous counterpart, were negligible for CH$_4$, 2 ± 1 for C$_2$H$_6$, 5 ± 1 for C$_3$H$_8$, 8 ± 2 for n-C$_5$H$_{12}$, 9 ± 2 for iso-C$_5$H$_{12}$, and 11 ± 2 for n-C$_6$H$_{14}$.

Table 4.2 Differential Heats for Alkane Adsorption on the Different ZSM-5 Samples

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>543.5$^a$</td>
<td>195</td>
<td>22 ± 1</td>
<td>22 ± 1</td>
<td>22 ± 1</td>
<td>23 ± 1</td>
<td>0 ± 1</td>
</tr>
<tr>
<td>Ethane</td>
<td>596.3$^a$</td>
<td>298</td>
<td>31 ± 1</td>
<td>33 ± 1</td>
<td>32 ± 1</td>
<td>33 ± 1</td>
<td>2 ± 1</td>
</tr>
<tr>
<td>Propane</td>
<td>625.7$^a$</td>
<td>298</td>
<td>41 ± 1</td>
<td>46 ± 1</td>
<td>40 ± 2</td>
<td>46 ± 1</td>
<td>5 ± 1</td>
</tr>
<tr>
<td>n-pentane</td>
<td>666.7$^b$</td>
<td>353</td>
<td>72 ± 2</td>
<td>80 ± 1</td>
<td>-</td>
<td>81 ± 2</td>
<td>8 ± 2</td>
</tr>
<tr>
<td>Iso-pentane</td>
<td>-</td>
<td>353</td>
<td>74 ± 2</td>
<td>83 ± 2</td>
<td>-</td>
<td>85 ± 2</td>
<td>9 ± 2</td>
</tr>
<tr>
<td>n-hexane</td>
<td>672.5$^b$</td>
<td>373</td>
<td>77 ± 2</td>
<td>88 ± 2</td>
<td>80 ± 2</td>
<td>90 ± 2</td>
<td>11± 2</td>
</tr>
</tbody>
</table>

$^a$NIST.

Figure 4.2 Differential heats for (a) Propane, (b) n-Pentane, and (c) Iso-Pentane adsorption on two ZSM-5 samples. (■/▲/●) ZSM-5(F, Si) and (□/△/○) H-ZSM-5(F, Al).

4.3.2 Computational Results

We propose that the interactions of the acid site with the alkanes is described by hydrogen bonding; the relevant arguments are discussed in this section. A hydrogen bond is characterized by electron transfer from the hydrogen acceptor (the alkane in this case) to the hydrogen donor...
(the acid).\textsuperscript{112} The extent of this transfer, as can be quantified by an natural bonding orbital (NBO) analysis\textsuperscript{113,114} for instance, determines the strength of the hydrogen bond; an negligible or small transfer is indicative of a weak hydrogen bond, a moderate transfer implies a strong hydrogen bond, and a complete transfer indicates full protonation. In principle, this electron transfer depends on intrinsic properties of the donor and acceptor. For instance, the strength of hydrogen bonds has shown to be correlated to the differences in proton affinity, $\Delta PA$, of the acceptor and the deprotonated conjugate of the donor.\textsuperscript{115–118} For a given acid, therefore, the hydrogen bond strength should correlate with the proton affinity of the alkane. Further, our previous work involving the adsorption of stronger bases on zeolites has also shown a correlation with proton affinities. To explore such a correlation for alkanes, we have plotted the difference in the differential heats observed for ZSM-5(F, Si) and H-ZSM-5(F, Al) as a function of reported gas phase proton affinity in Figure 4.3.

![Figure 4.3](image-url)

Figure 4.3 The extra differential heats of adsorption between ZSM-5(F, Si) and H-ZSM-5(F, Al), from Table 4.2, plotted as a function of the proton affinity of the various alkanes examined.
While there is clearly a correlation with proton affinity, indicating the hydrogen bonded nature of interactions, the variation in proton affinities is clearly much larger (>200 kJ/mol). This is because, while proton affinity captures strong covalent interactions (as discussed in Calculations), the extent of interactions (and electron transfer) for alkanes with Brønsted sites are significantly weaker. The extent of the electron transfer (or the extent of overlap of the occupied orbitals of the alkane and the unoccupied orbitals of the acid, from classical molecular orbital theory) can also depend on the intrinsic electronic properties of the alkane and the acid, such as the energy of the lowest unoccupied molecular orbital of the acid or the highest occupied molecular orbital of the alkane. To explore this further, we tried comparing the energy of the highest occupied molecular orbital ($E_{\text{HOMO}}$) of the alkane with the experimentally measured additional heats of adsorption. Figure 4.4 clearly shows a monotonic variation across alkanes; $E_{\text{HOMO}}$ of methane is significantly lower than that of other alkanes (1-2 eV) and this can explain the negligible additional heat observed experimentally.

Figure 4.4 A comparison of the extra differential heat of alkanes in proton-form ZSM-5 over the siliceous form and the energy of the highest occupied molecular orbital (calculated at the CBS-QB3 level of theory).
As in the case of proton affinity (Figure 4.3), however, the variation in $E_{HOMO}$ is much larger than that of the extra heats. To overcome the limitations of these two descriptors, we considered acid affinity, as described in Eqs 4.1, as an alternative descriptor. The individual acid-alkane complexes are shown in Figure 4.5. All energies and structures were calculated using the ωB97X-D density functional with the 6-311++/G(d) basis set implemented in Gaussian 09. Clearly, the OH bond of the fluorosulfonic acid points toward the alkane indicating the formation of a hydrogen bond.

Figure 4.5 Hydrogen bonded alkane-acid complexes. The acid is fluorosulfonic acid (i), and the alkanes are: (ii) methane, (iii) ethane, (iv) propane, (v) pentane, (vi) iso-pentane, and (vii) hexane. The energy of the complex without hydrogen bonded interactions is obtained by rotating OH bond so that the hydrogen points away from the alkane; the structure of the acid in the resulting complex relaxes to a structure that is the mirror image of (i) owing to the symmetry. Carbon, hydrogen, oxygen, sulfur, and fluorine atoms are colored gray, white, red, yellow, and aqua respectively.
We believe that extra acid affinity ($\Delta E_{\text{acid-affinity}}$) is a more relevant descriptor than proton affinities for understanding hydrogen-bonding of weak bases in zeolites. This can be estimated by calculating the energy of the hydrogen-bonded complex and that with the OH bond of the fluorosulfonic acid rotated so that the hydrogen atom points away from the alkane, thereby breaking the hydrogen bond. The coordinates of the alkane and the rest of the atoms of the acid are fixed (at the positions of the hydrogen-bonded complex) while calculating the latter energy so that the dispersion contributions can be subtracted from the energy of the hydrogen-bonded complex. It should be noted that the final structure of the acid is the mirror image of Figure 4.5(i).

Mathematically,

$$\Delta E_{\text{acid-affinity}} \equiv E_{\text{alkane-acid-with-HB}} - E_{\text{alkane-acid-without-HB}} \quad \text{(Eqs. 4.2)}$$

where $E_{\text{alkane-acid-with-HB}}$ is the energy of the hydrogen bonded complex and $E_{\text{alkane-acid-without-HB}}$ is the energy of the complex where the hydrogen bond was broken. Figure 4.6 shows a clear correlation between the extra heat and extra acid affinity ($-\Delta E_{\text{acid-affinity}}$). The variation of the calculated difference in acid affinity across alkanes is a factor of 2 smaller than that of the experimentally measured additional heats. This can be attributed to the higher deprotonation energy of fluorosulfonic acid. The $\Delta E_{\text{acid-affinity}}$ value for methane is about 12 kJ/mol while our experimental data shows negligible effect of the Brønsted site. This difference can arise from (1) not including temperature corrections which was calculated to be about 3.5 kJ/mol for methane, (2) $E_{\text{alkane-acid-without-HB}}$ slightly over estimating the energy of non-hydrogen bonded complex because the alkane and acid molecules are fixed, although correctly canceling dispersion effects from the first term of Eqs. 4.2, and (3) intrinsic errors in the functional which only included relatively more strong hydrogen-bonded complexes in parametrization and testing. The calculated affinity differences values are, however, consistent with similar values reported for weaker acids (HCl and HF) with higher levels of theory, including MP2 and CCSD(T) with aug-cc-pVTZ basis sets. Specifically,
the difference in acid affinity for methane with HF and HCl was about 6 kJ/mol at MP2/aug-cc-pVTZ level of theory; super acids like FSO\(_3\)H is expected to show a larger difference in acid affinity at this level of theory. Nevertheless, the high degree of correlation between \(\Delta E_{\text{acid-affinity}}\) and experimental heats reinforces our proposition of the hydrogen-bonded nature of the alkane-H-ZSM-5 interaction.

Figure 4.6 A comparison of experimental extra differential heat between H-form and siliceous ZSM-5 and computed extra acid affinity (\(-\Delta E_{\text{acid-affinity}}\)). Experimental and computational errors are included for each data point; the latter errors are based on reported mean absolute error in the prediction of non-covalent interactions (~1.8 kJ/mol\(^1\))\(^9\) using \(\omega\)B97X-D functional with the 6-311++G(3df,3dp) basis set and are shown only to provide a qualitative guidance on the magnitude of the error. The trend line (dashed red line) fit is given by: \(y=2.1217x-25.01\) kJ/mol with an \(R^2>0.97\).
4.4 Summary

In this chapter, I have successfully demonstrated that the differential heats of adsorption of simple alkanes on H-ZSM-5 zeolite strongly depends on the presence of Brønsted-acid sites. The extra heats of adsorption in H-form zeolites over its siliceous counterparts can be associated with the strength of hydrogen bonding between the adsorbed alkane and the Brønsted sites, as can be inferred from the correlation between experimental extra heats and computed extra acid affinity which captures non-covalent interactions between a weak base and strong acid. The comparison of the experimental and computational results demonstrated that the hydrogen bonded interaction theory accurately describes the effect of Brønsted sites for alkane adsorption on zeolites.
Chapter 5. Endothermic Reforming of n-Hexane on Metal (Pt, Ga)

Containing H-ZSM-5 at High Pressures

5.1 Introduction

As pointed out in Chapter 1, much of the previous work on endothermic reforming has focused on acid-catalyzed cracking in zeolites. The medium-pore zeolite, H-ZSM-5, has been shown to be catalytically active and stable for a wide range of conditions. Unfortunately, for cracking of simple alkanes, the reactions may not be that endothermic. Reaction endothermicity depends on producing olefins; and, at high pressures, hydrocarbon cracking occurs primarily through a bimolecular mechanism in which hydride transfer is an important step. Although hydride transfer can produce aromatics, the primary products in the previous study were saturated alkanes, which would not contribute significantly to heat uptakes. Therefore, as part of the present Chapter, I began by investigating the effect of reaction conditions (pressure and temperature) on the product distributions and reaction endothermicities for n-hexane reactions over H-ZSM-5 to determine the importance of the reaction conditions. The use of n-hexane and differential reaction conditions made it possible to obtain mechanistic information on the reaction from the product distribution and to calculate reaction endothermicities.

The results show acid-catalyzed reactions can be reasonably endothermic at high temperatures and low pressures, but the heats of reaction calculated from the product distributions at the higher pressures required for this application were found to be negligible. To change the product distribution, I also investigated the effect of adding a dehydrogenation component to the H-ZSM-5. Because Pt is used commercially in naphtha reforming, Pt-modified H-ZSM-5 was used as the benchmark material in the present study. Because Ga-promoted H-ZSM-5 has been reported to catalyze the formation of aromatics from small alkanes, we examined this catalyst system as well. The results demonstrate that Pt promotion did not significantly affect the
product distributions or the reaction endothermicities, but Ga promotion could be reasonably effective for this application.

5.2 Experimental Section

The reaction measurements were performed in the high pressure flow reactor described in detail in Section 2.3.1. The reactant feed was liquid n-hexane (>99% purity, Acros Organics) in this study. The catalyst was first pressed into thin pellets before loading between 3 and 150 mg into the reactor. For most of the measurements, the n-hexane feed rate was fixed at 0.3 mL/min. Reaction measurements were performed at pressures between 1 to 137 bar and temperatures between 633 and 823 K. The products were analyzed with an online Gas Chromatograph.

The endothermicities of the reactions were calculated from the product distributions. The standard heats of formation for each species were obtained from the NIST Chemistry WebBook and translated to 633, 723, or 823 K using heat capacity data, also from NIST. For each calculation, we assumed the carbon balance was 100%. Because the carbon and hydrogen balances were greater than 98% in most of the runs, this does not introduce a significant error.

The ZSM-5 sample (CBV 5524G; Si/Al ratio of 50) was obtained from Zeolyst and has been described in detail in Chapter 2. H(Ga)-ZSM-5 samples were prepared by the wet impregnation of the parent NH⁴-ZSM-5 using aqueous solutions of Ga(NO₃)₃ (Aldrich Chemical, 99.999% purity). The resulting materials were dried at 350 K overnight and then calcined in flowing air at 773 K for 4 h. Samples were prepared with three different Ga loadings and are designated by the weight percent Ga in parentheses (e.g., H(Ga)-ZSM-5(1.1) has 1.1 wt % Ga). To form a sample with Ga sites but no Brønsted sites, Ga(NO₃)₃ was impregnated into Li-ZSM-5, which was itself produced by mixing 1 g of H-ZSM-5 with a 300 mL solution containing 0.1 M LiCl and 0.005 M LiOH. An H(Pt)-ZSM-5 sample with 1.1 wt % Pt was prepared by impregnating a solution of
Pt(NH$_3$)$_4$(NO$_3$)$_2$ (Alfa Aesar) into H-ZSM-5 using a procedure similar to that used in preparing H(Ga)-ZSM-5.

The types of sites present in the catalysts of this study were identified using simultaneous TPD-TGA measurements with 2-propanamine. These experiments were performed using a system described in Chapter 2.$^{137}$

The Pt dispersions were quantified by volumetric CO adsorption measurements at room temperature. The calcined samples were placed in the adsorption apparatus, heated in 200 Torr of O$_2$ at 400 °C, and then reduced at 150 °C in 200 Torr of H$_2$. Next, the samples were evacuated, cooled to room temperature, and then exposed to CO.

5.3 Results

5.3.1 Characterization of Sites by 2-Propanamine TPD-TGA

TPD-TGA results for 2-propanamine on H-ZSM-5, H(Pt)-ZSM5-(1.1), H(Ga)-ZSM-5(26), Li-ZSM-5, and Li-(Ga)ZSM-5(26) are shown in Figure 5.1, and the site densities obtained from the TPD-TGA results are reported in Table 5.1.

Results for H-ZSM-5 in Figure 5.1(a) are similar to what has been published elsewhere.$^{64,97}$ Below 550 K, only unreacted 2-propanamine (m/e = 44, 17, 41, and 42) is observed leaving the sample. The remaining 2-propanamine desorbs in a sharp feature between 575 and 650 K, reacting to form propene (m/e = 41, 42) and ammonia (m/e = 17). Above 650 K, the sample weight returns to its initial value prior to being exposed to 2-propanamine vapor. On the basis of the TGA data, the quantity of adsorbed amine that reacts above 550 K corresponds to 470 μmol/g, a value that is reasonably close to the Al content of this sample, 625 μmol/g. This desorption feature is due to decomposition of the alkyl-ammonium ions via the Hoffman elimination reaction and is clearly associated with Brønsted sites. The discrepancy between the Al concentration and the
Brønsted site density recorded by the TPD-TGA measurements is likely due to Al sites that are inaccessible to amine molecules, possibly because of crowding at the relatively high site densities.

Figure 5.1 TPD-TGA of 2-propanamine over (a) H-ZSM-5, (b) H(Pt)-ZSM-5, (c) H(Ga)-ZSM-5(26), (d) Li-ZSM-5, (e) Li(Ga)-ZSM-5(26). The peaks correspond to ammonia (m/e = 17), propene (m/e = 41, 42), acetonitrile (m/e=17, 41), and 2-propanamine (m/e = 17, 41, 42, and 44).
TPD-TGA data for the H(Pt)-ZSM-5 sample are shown in Figure 5.1(b). On the basis of the appearance of a peak at m/e = 17 between 450 and 500 K, there is some reaction of the amine at lower temperatures. Because this is not observed on H-ZSM-5, the reaction must be due to amine molecules adsorbed on Pt, but it was not possible to determine the products or quantify the amounts based on this data. The reaction to propene and ammonia between 575 and 650 K is again consistent with the presence of Brønsted sites. Surprisingly, the concentration of Brønsted sites based on this TPD feature was significantly lower than we obtained on the parent H-ZSM-5, only ~310 μmol/g, and the difference between the two values was greater than the Pt content of the sample, 60 μmol/g. Finally, two additional desorption features were observed at higher temperatures. Between 650 and 700 K, additional reaction features at m/e = 41 and 42 are observed; between 700 and 800 K, broad peaks at m/e = 17 and 41 appeared. On the basis of a comparison with results for H-ZSM-5, it is clear that these high temperature desorption features are associated with dehydrogenation on Pt. The amount of 2-propanamine that reacts at higher temperatures, ~100 μmol/g, is likely greater than the Pt content of the sample due to readsorption effects in TPD.\textsuperscript{102} TPD-TGA results for H(Ga)-ZSM-5(26) are shown in Figure 5.1(c). As with H-ZSM-5, unreacted amine molecules desorb below 550 K, and the reaction to propene and ammonia between 575 and 650 K is again consistent with the presence of Brønsted sites, which in this sample is ~240 μmol/g. With the addition of Ga, additional reaction features at m/e = 17 and 41 are observed between 650 and 850 K. Because there is no peak at m/e = 42 above 650 K, the high-temperature products cannot be simply additional propene and ammonia. On the basis of a complete analysis of the mass spectrum of the products at higher temperature, we tentatively assign the main product above 650 K to be acetonitrile in agreement with previous reports from Kanazirev et al.\textsuperscript{138} Again, all of the 2-propanamine is removed from the sample by 850 K, and the sample weight returns to its initial value. The change in the sample weight above 650 K indicated that the Ga site density in the H(Ga)-ZSM-5(26) sample was 180 μmol/g.
TPD-TGA results for H-ZSM-5 samples with lower Ga concentrations were qualitatively similar. H(Ga)-ZSM-5(1.1) and H(Ga)-ZSM-5(9.8) also showed features associated with Brønsted sites (reaction to propene and ammonia between 575 and 650 K) and Ga sites (reaction above 650 K). The only difference between the three H(Ga)-ZSM-5 samples was in the amounts of 2-propanamine that reacted in the two high temperature features. These concentrations are listed in Table 5.1.

**Table 5.1 Zeolite Samples Used in This Study**

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Metal content (µmol/g)</th>
<th>Metal content (wt %)</th>
<th>Brønsted-acid site densities (µmol/g)</th>
<th>Metal site densities (µmol/g)</th>
<th>Brønsted + Metal site densities (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5</td>
<td>0</td>
<td>0</td>
<td>470</td>
<td>0</td>
<td>470</td>
</tr>
<tr>
<td>H(Pt)-ZSM-5(1.1)*</td>
<td>60</td>
<td>1.1</td>
<td>310</td>
<td>120</td>
<td>430</td>
</tr>
<tr>
<td>H(Ga)-ZSM-5(1.1)</td>
<td>150</td>
<td>1.1</td>
<td>390</td>
<td>70</td>
<td>460</td>
</tr>
<tr>
<td>H(Ga)-ZSM-5(9.8)</td>
<td>1560</td>
<td>9.8</td>
<td>320</td>
<td>90</td>
<td>410</td>
</tr>
<tr>
<td>H(Ga)-ZSM-5(26)</td>
<td>5060</td>
<td>26</td>
<td>240</td>
<td>180</td>
<td>420</td>
</tr>
</tbody>
</table>

*The Pt dispersion (18%) was quantified by volumetric CO adsorption measurements at room temperature.

It is important to note that the total concentration of Brønsted sites and metal sites summed to a value that was approximately a constant. For example, the total concentration of Brønsted and Ga sites in H(Ga)-ZSM-5(26) was 420 µmol/g, a value that is very close to the Brønsted site density of the initial H-ZSM-5, especially given that the change in the sample weight due to the addition of Ga will change the concentration of exchange sites. Therefore, it appears that formation of Ga sites occurs at the expense of Brønsted sites. However, the Ga site concentration from amine desorption was much lower than the Ga concentration, suggesting that most of the Ga ions are simply spectators. Complete exchange of Brønsted sites with Ga was not possible, even with a large excess of Ga (26 wt % Ga is equal to 3700 µmol/g.).
To further explore the nature of the Ga sites, we examined a sample in which Ga(NO₃)₃ was added to Li-ZSM-5. TPD-TGA results for 2-propanamine are shown first for the Li-ZSM-5 in Figure 5.1(d). The TPD-TGA shows two desorption features centered at approximately 450 and 600 K; however, unlike the case with H-ZSM-5, there is no reaction of the amine, consistent with the fact that there are no Brønsted sites in the Li-exchanged sample. The amount of amine desorbing in the high-temperature peak is roughly 450 μmol/g, similar to the Brønsted site density of H-ZSM-5, implying that a second desorption feature must be due to adsorption on the Li sites. Results for the Li(Ga)-ZSM-5(26) are shown in Figure 5.1(e). Most of the 2-propanamine desorbs unreacted, and there is again no evidence for Brønsted sites. However, there is a relative change in the intensity of the m/e = 17 peak between 550 and 650 K, indicating that additional products are being formed. Above 650 K, there is again a reaction of 2-propanamine. In this case, there is a peak in the mass spectrum at m/e = 42, suggesting that the products may be different from that which formed at high temperatures on H(Ga)-ZSM-5(26).

5.3.2 n-Hexane Reaction Over H-ZSM-5.

Reaction rates for n-hexane conversion over H-ZSM-5 were examined as a function of temperature and pressure in previous studies. Here, we focused more carefully on the product distributions to determine the reaction endothermicities. Table 5.2 summarizes the product distributions at three different temperatures and pressures for n-hexane conversions between 6.1 and 9.6%. Both the carbon and hydrogen balances were greater than 98% in all cases, often greater than 99%, so that essentially all products from the reaction of n-hexane were accounted for.
It is instructive to first consider how the product distribution changes with temperature at a pressure of 1 bar. At 633 K, there is a significant amount of simple isomerization to iso-C₆H₁₄, a reaction that is not helpful for this application, but iso-C₆H₁₄ production decreases with temperature. With the exception of n-C₆H₁₂, larger olefins were not produced in measurable quantities, and only small amounts of light aromatics (benzene, toluene, and xylenes; BTX) were observed. What is most significant is that the concentrations of small olefins C₃H₆ and C₂H₄ increased steadily with temperature. Because we observed only trace amounts of H₂ in our products, the formation of products with a lower H:C ratio was balanced by products with a higher H:C ratio, such as CH₄, C₂H₆, and C₃H₈, so that both the carbon and hydrogen balances were maintained. However, it is

| Table 5.2 Molar Selectivities (%) and Heat of Reaction for n-Hexane Cracking over H-ZSM-5 at 0.067, 1, and 137 bar at 633, 723, and 823 K |
|------------------------------|---------|---------|---------|---------|---------|---------|---------|
| Pressure (bar)               | 0.067   | 1       | 137     |         |         |         |         |
| Temperature (K)              | 633     | 723     | 633     | 723     | 823     | 633     | 723     |
| Catalyst amount (mg)         | 150     | 40      | 100     | 20      | 10      | 20      | 6       |
| CH₄                          | 4.9     | 12.2    | 2.9     | 3.3     | 3.3     | 0.1     | 0.5     |
| C₂H₄                         | 7.1     | 7.8     | 2.3     | 6.7     | 7.8     | 0.1     | 1.0     |
| C₂H₆                         | 1.7     | 9.0     | 1.7     | 7.4     | 6.3     | 0.1     | 1.1     |
| C₃H₆                         | 7.9     | 21.8    | 5.8     | 17.4    | 21.3    | 0.2     | 2.5     |
| C₃H₈                         | 17.2    | 21.0    | 7.2     | 14.6    | 20.4    | 4.3     | 8.2     |
| Iso-C₄H₁₀                     | 8.4     | 2.8     | 7.6     | 4.5     | 3.2     | 5.8     | 6.8     |
| n-C₆H₁₀                       | 20.6    | 11.3    | 13.9    | 15.6    | 15.4    | 9.5     | 13.5    |
| Iso-C₅H₁₂                     | 11.2    | 9.7     | 12.6    | 4.9     | 3.2     | 15.2    | 13.2    |
| n-C₅H₁₂                       | 13.6    | 1.4     | 26.2    | 15.0    | 10.6    | 28.4    | 28.0    |
| n-C₆H₁₂                       | 3.6     | 1.5     | 6.1     | 5.6     | 5.0     | 3.1     | 2.8     |
| Iso-C₆H₁₄                     | 3.8     | 1.4     | 9.0     | 3.3     | 2.5     | 15.6    | 12.3    |
| BTX                          |         | -       | -       | 1.6     | 0.9     | 0.7     | 7.0     |
| Total C-6+                    |         | -       | -       | 4.8     | 1.8     | 0.9     | 17.6    |
| Conversion (%)                | 9.2     | 8.6     | 7.7     | 6.1     | 9.2     | 6.3     | 6.4     |
| Carbon Balance (%)            | 99.2    | 99.5    | 99.0    | 98.8    | 98.1    | 99.2    | 99.3    |
| Hydrogen Balance (%)          | 98.6    | 98.8    | 98.4    | 98.2    | 98.0    | 98.6    | 98.4    |
| Heat of Reaction (kJ/mol)      | 1.1     | 11.1    | 3.6     | 17.5    | 20.1    | 7.7     | 1.1     |

It is instructive to first consider how the product distribution changes with temperature at a pressure of 1 bar. At 633 K, there is a significant amount of simple isomerization to iso-C₆H₁₄, a reaction that is not helpful for this application, but iso-C₆H₁₄ production decreases with temperature. With the exception of n-C₆H₁₂, larger olefins were not produced in measurable quantities, and only small amounts of light aromatics (benzene, toluene, and xylenes; BTX) were observed. What is most significant is that the concentrations of small olefins C₃H₆ and C₂H₄ increased steadily with temperature. Because we observed only trace amounts of H₂ in our products, the formation of products with a lower H:C ratio was balanced by products with a higher H:C ratio, such as CH₄, C₂H₆, and C₃H₈, so that both the carbon and hydrogen balances were maintained. However, it is
the olefin products that most influence the calculated heats of reaction. At 633 K, the reaction was
determined to be endothermic by only 3.6 kJ/mol of n-hexane that reacts. This increased to 20.1
kJ/mol at 823 K. For comparison, the heat of reaction at standard conditions for the gas-phase
reaction of n-hexane to form n-hexene and H₂ is 125 kJ/mol.

Increasing the pressure to 137 bar changed the product distribution considerably. In
general, the product distribution shifted to larger alkanes with negligible amounts of CH₄ and C-2
products forming. For reaction endothermicity, what is most significant is that the production of
C₂H₄ and C₃H₆ decreased dramatically at the higher pressures. The production of light olefins was
negligible at 633 K. Some C₃H₆ was formed at 823 K, but the amount was less than half of what
had been produced at 1 bar. Primarily because of aromatics production, the overall reaction was
endothermic by 7.7 kJ/mol at 633 K. However, aromatics production decreased with increasing
temperature, so that the reaction endothermicity was lower at 823 K, even with the increased
formation of C₃H₆.

Obviously, these results are discouraging in that they indicate the cracking reactions at
high pressures are not effective for endothermic reforming. Dehydrogenation activity is required to
achieve the goals of endothermic reforming.

5.3.3 n-Hexane Reactions Over Metal-Containing ZSM-5.

To determine the effect of adding Pt or Ga to ZSM-5 on reactions of n-hexane, we first
examined the conversions under differential conditions on samples with different metal contents.
Figure 5.2 shows the differential rates for H-ZSM-5, H(Pt)ZSM-5, Li(Pt)-ZSM-5, H(Ga)ZSM-5(1.1),
and Li(Ga)-ZSM-5(26) as a function of temperature at 1 and 137 bar. The rates for n-hexane
conversion reported here for the H-ZSM-5 sample are quantitatively and qualitatively the same as
what has been reported in previous publications,⁶,³⁹ but the rates on the metal-containing zeolites
appear to follow the Brønsted site density. For example, both the Li(Pt)-ZSM-5 and Li(Ga)-ZSM-
5(26) samples had negligible concentrations of Brønsted sites, and both exhibited rates that were
approximately 100 times lower than what was observed on H-ZSM-5. This low activity could well be associated with residual Brønsted sites that were not removed by ion exchange. Rates on the H(Pt)-ZSM-5 and H(Ga)-ZSM-5 samples were slightly lower than those on H-ZSM-5, but the Bronsted site densities, reported in Table 5.1, were also slightly lower. It appears that the rates for n-hexane conversion are simply proportional to the Brønsted site concentrations.

![Graphs showing rates of n-hexane conversion over different catalysts at 1 bar and 137 bar](image)

Figure 5.2 Rates for n-hexane conversion over H-ZSM-5 (▲), H(Ga)-ZSM-5(1.1) (○), H(Pt)-ZSM-5 (●), Li(Pt)-ZSM-5 (□), and Li(Ga)-ZSM-5(26) (★) as a function of temperature, under (a) 1 bar, and (b) 137 bar.

The effect of adding metals to the product distributions at 137 bar are shown in Table 5.3. The product distributions on H(Pt)-ZSM-5 at 633 and 723 K are nearly identical to what was observed on H-ZSM-5 without Pt. There may be small increases in the aromatics (BTX) production, also reflected in the C-6+ concentrations, but the changes are of questionable significance and do not dramatically increase the endothermic heats of reaction. However, the product distributions on the H(Ga)-ZSM-5(1.1) were much more promising. The H(Ga)-ZSM-5(1.1) sample produced significantly more product in the C-6+ range with much of that being BTX aromatics. This was especially true at 633 K, at which temperature more than 22% of the n-hexane was converted to
BTX; however, the increased BTX production was also present in the product distribution at 823 K. BTX was formed primarily at the expense of smaller molecules in the C-2 to C-4 range, and it was the formation of BTX that led to the increased heats of reaction, almost 50 kJ/mol at 633 K and still greater than 20 kJ/mol at 823 K.

Table 5.3 Molar Selectivities (%) and Heat of Reaction for n-Hexane Reactions over H(Pt)-ZSM-5(1.1), and H(Ga)-ZSM-5(1.1) at 137 bar, under Temperature of 633, 723, and 823 K

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>H(Pt)-ZSM-5(1.1)</th>
<th>H(Ga)-ZSM-5(1.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>633</td>
<td>723</td>
<td>633</td>
</tr>
<tr>
<td>723</td>
<td>723</td>
<td>823</td>
</tr>
<tr>
<td>Catalyst amount (mg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>&lt; C2</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>0.6</td>
<td>2.6</td>
</tr>
<tr>
<td>C₄H₈</td>
<td>4.7</td>
<td>5.6</td>
</tr>
<tr>
<td>Iso-C₅H₁₀</td>
<td>3.5</td>
<td>4.5</td>
</tr>
<tr>
<td>n-C₅H₁₀</td>
<td>6.0</td>
<td>8.3</td>
</tr>
<tr>
<td>Iso-C₆H₁₂</td>
<td>17.8</td>
<td>18.4</td>
</tr>
<tr>
<td>n-C₆H₁₂</td>
<td>31.3</td>
<td>33.2</td>
</tr>
<tr>
<td>Iso-C₇H₁₄</td>
<td>12.5</td>
<td>8.9</td>
</tr>
<tr>
<td>BTX</td>
<td>9.9</td>
<td>7.4</td>
</tr>
<tr>
<td>Total C-6+</td>
<td>22.2</td>
<td>15.6</td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>9.8</td>
<td>9.2</td>
</tr>
<tr>
<td>Carbon Balance (%)</td>
<td>98.9</td>
<td>98.6</td>
</tr>
<tr>
<td>Hydrogen Balance (%)</td>
<td>98.5</td>
<td>98.5</td>
</tr>
<tr>
<td>Heat of Reaction (kJ/mol)</td>
<td>13.7</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Although the carbon and hydrogen balances were better than 96% on the Ga-containing sample, they were clearly lower than we achieved on H-ZSM-5 and on H(Pt)-ZSM-5. This is due primarily to the fact that this sample gave much more C6+ product. We were not able to separate all of the C-7 products, and our GC calibration factors for these were less accurate. The increased
aromatics production also raised the question as to whether we produce H\textsubscript{2} in significant amounts, but attempts to measure H\textsubscript{2} by changing the carrier gas in the chromatograph to N\textsubscript{2} detected only trace amounts. Furthermore, the hydrogen balances in Table 5.3 were nearly as good as the carbon balances, implying that most of the hydrogen ends up in the hydrocarbon products.

Table 5.4 Molar Selectivities (%) for n-Hexane Reactions over H-ZSM-5, H(Ga)-ZSM-5(1.1) and H(Ga)-ZSM-5(9.8) at 1 and 137 bar and a Temperature of 633 K

<table>
<thead>
<tr>
<th>Pressure</th>
<th>H-ZSM-5</th>
<th>H(Ga)-ZSM-5(1.1)</th>
<th>H(Ga)-ZSM-5(9.8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst amount (mg)</td>
<td>100</td>
<td>250</td>
<td>350</td>
</tr>
<tr>
<td>&lt; C2</td>
<td>6.8</td>
<td>2.7</td>
<td>1.7</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{8}</td>
<td>5.8</td>
<td>4.2</td>
<td>4.2</td>
</tr>
<tr>
<td>C\textsubscript{5}H\textsubscript{8}</td>
<td>7.2</td>
<td>6.3</td>
<td>6.6</td>
</tr>
<tr>
<td>Iso-C\textsubscript{4}H\textsubscript{10}</td>
<td>7.6</td>
<td>7.6</td>
<td>4.0</td>
</tr>
<tr>
<td>n-C\textsubscript{4}H\textsubscript{10}</td>
<td>13.9</td>
<td>11.1</td>
<td>12.8</td>
</tr>
<tr>
<td>Iso-C\textsubscript{5}H\textsubscript{12}</td>
<td>12.6</td>
<td>15.6</td>
<td>15.5</td>
</tr>
<tr>
<td>n-C\textsubscript{5}H\textsubscript{12}</td>
<td>26.2</td>
<td>25.3</td>
<td>25.1</td>
</tr>
<tr>
<td>n-C\textsubscript{6}H\textsubscript{12}</td>
<td>6.1</td>
<td>5.1</td>
<td>7.4</td>
</tr>
<tr>
<td>Iso-C\textsubscript{6}H\textsubscript{14}</td>
<td>9.0</td>
<td>7.7</td>
<td>6.3</td>
</tr>
<tr>
<td>BTX</td>
<td>1.6</td>
<td>7.6</td>
<td>5.5</td>
</tr>
<tr>
<td>Total C-6+</td>
<td>4.8</td>
<td>14.3</td>
<td>16.5</td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>7.7</td>
<td>5.1</td>
<td>7.2</td>
</tr>
<tr>
<td>Carbon Balance (%)</td>
<td>99.0</td>
<td>98.8</td>
<td>96.0</td>
</tr>
<tr>
<td>Hydrogen Balance (%)</td>
<td>98.4</td>
<td>98.7</td>
<td>95.2</td>
</tr>
<tr>
<td>Heat of Reaction (kJ/mol)</td>
<td>3.6</td>
<td>15.9</td>
<td>14.7</td>
</tr>
</tbody>
</table>

To further understand the effect of Ga on n-hexane reactions, we determined product selectivities at 633 K with varying Ga contents at 1 and 137 bar. The data are reported in Table 5.4. First, there is no significant difference between the results for the H(Ga)-ZSM-5(1.1) and H(Ga)-ZSM-5(9.8) samples. Second, we observed that BTX production increases with pressure on
both Ga-containing samples, such that the heats of reaction were significantly more endothermic at the higher pressures on the H(Ga)-ZSM-5 samples.

![Normalized conversion plots](image)

Figure 5.3 Normalized conversion of n-hexane over (a) H-ZSM-5, (b) H(Pt)-ZSM-5, and (c) H(Ga)-ZSM-5(1.1) at 137 bar as a function of time. 633 K (+), 723 K (○), 823 K (□)

Although formation of aromatic products is desirable from the standpoint of endothermicity, aromatics formation does raise coking concerns. Figure 5.3 shows plots of the normalized
conversions of n-hexane as a function of time over H-ZSM-5, H(Pt)-ZSM-5, and H(Ga)ZSM-5(1.1) at 137 bar and 633, 723, and 823 K. In all cases, the initial conversions were approximately 10-15%, achieved by using less catalyst at the higher temperatures. Differences in the coking rates were not significant for the three samples. At 633 K, the deactivation rates were negligible and physical examination of the catalysts after 5 h reactions showed that the samples remained off-white in color. Deactivation was more important at the higher temperatures, but all of the catalysts remained reasonably active over the entire run. Finally, there was no change in the product selectivities for the H-ZSM-5 and H(Ga)-ZSM-5(1.1) after 0.5 and 5 h. These product selectivities are reported in Table 5.5.

Table 5.5 Molar Selectivities (%) for n-Hexane Reactions over H-ZSM-5, and H(Ga)-ZSM-5(1.1) at 137 bar, and 823 K as a function of time

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>H-ZSM-5</th>
<th>H(Ga)-ZSM-5(1.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst amount (mg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time (h)</td>
<td>0.5</td>
<td>5.0</td>
</tr>
<tr>
<td>&lt; C2</td>
<td>4.0</td>
<td>3.2</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>8.5</td>
<td>9.0</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>12.3</td>
<td>11.5</td>
</tr>
<tr>
<td>Iso-C₄H₁₀</td>
<td>5.3</td>
<td>4.8</td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td>14.2</td>
<td>14.2</td>
</tr>
<tr>
<td>Iso-C₅H₁₂</td>
<td>12.5</td>
<td>13.6</td>
</tr>
<tr>
<td>n-C₅H₁₂</td>
<td>25.9</td>
<td>26.9</td>
</tr>
<tr>
<td>n-C₆H₁₂</td>
<td>5.5</td>
<td>5.2</td>
</tr>
<tr>
<td>Iso-C₆H₁₄</td>
<td>4.5</td>
<td>3.1</td>
</tr>
<tr>
<td>BTX</td>
<td>3.0</td>
<td>3.6</td>
</tr>
<tr>
<td>Total C-6+</td>
<td>7.3</td>
<td>8.6</td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>9.6</td>
<td>6.0</td>
</tr>
<tr>
<td>Carbon Balance (%)</td>
<td>98.3</td>
<td>98.4</td>
</tr>
<tr>
<td>Hydrogen Balance (%)</td>
<td>98.2</td>
<td>98.6</td>
</tr>
</tbody>
</table>
5.4 Discussion

The present results demonstrate that a detailed examination of product distributions is critical for determining the effectiveness of different catalysts for endothermic reforming applications. In principle, simple acid-catalyzed cracking can be endothermic. However, the hydride-transfer reactions, which dominate for high-pressure operation, tend to eliminate the olefin products that make cracking endothermic. As a result, acid-catalyzed cracking can be thermally neutral and ineffective for this application. Although Pt is likely the best hydrogenation/dehydrogenation catalyst, it is also not effective for endothermic reforming. When Pt is used to catalyze these reactions industrially in naphtha reforming, there is always a high overpressure of H₂ present to prevent coking. The fact that Pt does not significantly affect the product distribution in our experiments suggests that the Pt is deactivated by coking almost immediately.

The most promising materials in our studies were the Ga-containing samples. In agreement with previous publications, the addition of Ga to H-ZSM-5 significantly increases the yields for alkanes reacting to aromatics. In effect, the addition of Ga provides dehydrogenation activity, although the hydrogen from n-hexane is consumed in the formation of smaller alkanes that have a higher H:C ratio. Unlike metallic reforming catalysts, the Ga-containing H-ZSM-5 is stable against coking under conditions that would be very harsh for most metal catalysts. All metal, hydrocarbon-reforming catalysts would likely deactivate rapidly in the absence of H₂ or O₂ to prevent carbon formation.

It is significant that the rates of n-hexane conversion on the H(Ga)-ZSM-5 samples closely followed the Brønsted site concentration and that Li(Ga)-ZSM-5, which had no Brønsted sites, was not catalytically active. This implies that the Ga sites do not function in the absence of a Brønsted site. Because aromatics are formed in hydride-transfer reactions when carbenium ions extract hydride ions from neighboring molecules, it would appear that Ga primarily assists and modifies this hydride transfer but does not otherwise catalyze the activation of the alkane. This would
suggest that the Ga must be in close proximity to the Brønsted sites to participate in the reaction. Also, viewed in this way, the Ga is not acting as a hydrogenation/dehydrogenation catalyst in this system but could be considered to be part of the Brønsted acid site, perhaps by providing Lewis acid character.

It is interesting to ask what is the active form of Ga. On the basis of earlier TEM studies, Lopez-Sanchez et al.\textsuperscript{139} indicated that Ga$_2$O$_3$ clusters were responsible for aromatics formation from methanol reactions in Ga-substituted ZSM-5 because they observed carbon at the cluster-zeolite interface. In contrast to this, Krishnamurthy, et al. reported that Ga substitutes for Brønsted sites with Ga possibly present as GaH$_2^+$.\textsuperscript{140} As discussed in the Introduction, there have also been suggestions based on XAS that the Ga exists in a +1 oxidation state, possibly stabilized by the ion-exchange sites.\textsuperscript{120} It should be noted that those authors also reported that the change in Brønsted acidity upon addition of Ga was small, implying that the majority of the Ga cannot be present at ion-exchange sites. Interestingly, because XAS is a bulk technique that probes all of the Ga in the sample and only one type of Ga was observed, it appears unlikely that the majority of the Ga is located at ion-exchange sites.

The observation of a dehydrogenation product in the TPD-TGA results for 2-propanamine adsorbed on Ga sites in H(Ga)-ZSM-5 is intriguing; however, the sites that are probed in this reaction may or may not be responsible for the formation of aromatics in reaction. First, they do not appear to be catalytically active toward alkanes on their own based on the reaction results for Li(Ga)-ZSM-5. Second, the Ga in those sites appears to displace Brønsted sites, making it difficult to understand how they would work in combination with Brønsted sites. One possibility is that the Ga sites can only catalyze reactions of species that are produced on Brønsted sites, such as olefins. This possibility needs to be explored.

Endothermic fuel reforming is obviously a very challenging problem because of the very harsh conditions experienced by the catalyst. On the basis of the present results, we believe that Ga-exchanged H-ZSM-5 shows great promise for this application, both because of its excellent
selectivity to aromatic products and its high stability in a very harsh environment. Obviously, significantly more work needs to be done to understand why the material gives the product distribution that it does and to determine how best to use it.

5.5 Summary

In this chapter, I have shown that because of hydride-transfer reactions that occur at high pressures, acid-catalyzed cracking of alkanes is not effective for endothermic reforming applications. The addition of Pt to a zeolite is also not effective. However, the addition of Ga to an H-ZSM-5 zeolite significantly affects the product distribution, significantly increasing the endothermicity of the reactions. The Ga atoms appear to work in combination with Brønsted sites in the zeolite to produce small aromatic compounds. The Ga-containing zeolites were shown to a similar stability as normal acidic zeolites under supercritical conditions.
Chapter 6. Zn-Promoted H-ZSM-5 for Endothermic Reforming of n-Hexane at High Pressures

6.1 Introduction

My work in Chapter 5 showed that olefin production is minimal in acid-catalyzed cracking at high pressures, so that these reaction are nearly thermoneutral and therefore not helpful. However, promising results were obtained with Ga-modified H-ZSM-5. Ga-promoted H-ZSM-5 is well-known to catalyze formation of aromatics from small alkanes, and aromatics production significantly improves the endothermicity of the reactions. Exactly how Ga promotes aromatization reactions is not entirely understood. There is a loss of Brønsted sites upon addition of Ga to H-ZSM-5. However, the change in the concentration of Brønsted sites is much less than the amount of Ga that is added, implying that most of the added Ga was not present at ion-exchange sites. Rates of n-hexane conversion on the H(Ga)-ZSM-5 samples closely followed the Brønsted-site concentration suggesting that the Ga sites do not function in the absence of a Brønsted site. It was hypothesized that Ga atoms located near Brønsted sites assist hydride transfer reactions that promote aromatics formation, possibly by providing Lewis-acid character.

Zn has been reported to exhibit superior properties among a number of promoters that have been added to H-ZSM-5 for enhancing aromatization. For example, Biscardi et al. reported that exchange of either Zn or Ga into H-ZSM-5 increases turnover frequencies and selectivities for propane reactions to form aromatics. Similarly, Ono and Kanae found that Ga and Zn cations in ZSM-5 were equally effective for the transformation of lower olefins into aromatics. In addition, Viswanadham et al. indicated that Zn provides an alternative pathway for aromatization in H-ZSM-5 and suppresses the formation of C9+ aromatics.

In this Chapter, I set out to examine the nature of Zn promotion in H-ZSM-5 and determine its applicability for endothermic reforming. For low concentrations of Zn, I will show that there is a
loss of one Brønsted site per Zn ion, implying that most Zn atoms are present at ion-exchange sites. Adsorption studies of CD$_3$CN and CO on the exchanged Zn cations indicate that the Zn cations are Lewis-acid sites. Although rates for the n-hexane reaction decreased linearly with the loss of Brønsted sites, the presence of Zn changed the product distribution, generating significant amounts of H$_2$ and small aromatic products.

6.2 Experimental Section

6.2.1 Materials

Zn-containing, H-ZSM-5 samples were prepared from the ZSM-5(50) and ZSM-5(F) samples by incipient wetness of either the NH$_4^+$ or H$^+$ forms of the zeolites using aqueous solutions of Zn(NO$_3$)$_2$ (98%, extra pure, ACROS Organics). The resulting materials were dried at 350 K overnight and then calcined in flowing air at 773 K for 4 h to transform them into the H(Zn)-ZSM-5 forms. Samples were prepared with various Zn loadings and are designated by the weight percent Zn in parentheses (e.g., ZSM-5(50) with 1.3 wt % Zn is referred to as H(Zn)-ZSM-5(50,1.3) and the ZSM-5(F) samples with 0.5 wt % Zn is referred to as H(Zn)-ZSM-5(F,0.5).). H(Sr)-ZSM-5(50,2.0), H(Li)-ZSM-5(50), and Li-ZSM-5(50) samples were also prepared. The H(Sr)-ZSM-5(50,2.0) was again made using incipient wetness with aqueous Sr(NO$_3$)$_2$ (ACS, 99.0% min, Alfa Aesar). H(Li)-ZSM-5(50) and Li-ZSM-5(50) were prepared by ion exchange and described in detail in Chapter 2. The samples used in this study are summarized in Table 6.1.

6.2.2 Characterization Techniques

Simultaneous TPD/TGA measurements were used for the initial characterization of the catalysts. Fourier Transform Infrared Spectroscopy was used to analyze the adsorption properties on the catalyst surface. The Tian-Calvet calorimeter was used for measuring heats of adsorption
for gaseous adsorbates on catalytic sites. The details of each technique has been described in Chapter 2.

Table 6.1 Zeolite Samples Used in This Study

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al₂</th>
<th>Brønsted-acid site densities (µmol/g)</th>
<th>Pore volume with n-hexane (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5(50)</td>
<td>50</td>
<td>470</td>
<td>0.19</td>
</tr>
<tr>
<td>H-ZSM-5(280)</td>
<td>280</td>
<td>90</td>
<td>0.19</td>
</tr>
<tr>
<td>H-ZSM-5(F)</td>
<td>-</td>
<td>280</td>
<td>0.17</td>
</tr>
<tr>
<td>H(Sr)-ZSM-5(50,2.0)</td>
<td>50</td>
<td>430</td>
<td>0.19</td>
</tr>
<tr>
<td>H(Li)-ZSM-5(50)</td>
<td>50</td>
<td>280</td>
<td>0.19</td>
</tr>
<tr>
<td>Li-ZSM-5(50)</td>
<td>50</td>
<td>0</td>
<td>0.19</td>
</tr>
</tbody>
</table>

6.2.3 Reaction Measurements.

The reaction measurements were performed in the same high-pressure, flow reactor used in Chapter 5. Measurements were performed at pressures between 1 to 137 bar and temperatures between 633 and 823 K. The products were analyzed with an online Gas Chromatograph. All catalysts were completely stable for a period of at least 4 h, the time typically required to perform rate measurements on a sample, and the catalysts always remained off-white in color when removed from the reactor, suggesting that coking was minimal. Hydrogen production rates were measured in separate experiments in which the carrier gas in the GC was switched from He to nitrogen. The endothermicities of the reactions were calculated from the product distributions and based on the same method described in Chapter 5. For each calculation, we assumed the carbon balance was 100%.

In this study, the carbon balances were always greater than 98%. However, the calculation of reaction endothermicity depends most strongly on the H₂ production rate and H:C ratio in the products. Therefore, in the present study, hydrogen balances are reported as total H in the products to total H in the n-hexane converted.
6.3 Results

6.3.1 Characterization of Zn Exchange with Brønsted Sites.

We examined a series of H(Zn)-ZSM-5 samples to determine whether Zn could replace Brønsted-acid sites. The concentration of Brønsted sites in solid acids can be determined with high accuracy from TPD-TGA measurements of 2-propanamine because, upon adsorption, 2-propanamine forms 2-propylammonium ions, which then react via the Hofmann elimination reaction in a narrow temperature range between 575 and 650 K. The concentration of Brønsted sites was determined as a function of Zn loading on both the H-ZSM-5(50) and H-ZSM-5(F) samples. For increased accuracy, the Brønsted-site densities were calculated by integrating the area under the TPD peak for propene (m/e = 41 in the mass spectrum) between 575 and 650 K.

Figure 6.1 TPD-TGA of 2-propanamine over (a) H-ZSM-5(50), (b) H(Zn)-ZSM-5(50,1.3), and (c) H(Zn)-ZSM-5(50,9.9). The peaks correspond to ammonia (m/e =16, 17), propene (m/e = 41, 42), acetonitrile (m/e = 17, 41), and 2-propanamine (m/e =16, 17, 41, and 44).
Figure 6.1 shows TPD-TGA results for 2-propanamine on HZSM-5(50), H(Zn)-ZSM5(50,1.3), and H(Zn)-ZSM-5-(50,9.9). Results for H-ZSM-5(50) in Figure 6.1a are similar to what has been published elsewhere. Unreacted 2-propanamine (m/e = 16, 17, 41, and 44) is observed leaving the sample below 550 K. The remaining 2-propanamine desorbs in a sharp feature between 575 and 650 K, reacting to form propene (m/e = 41, 42) and ammonia (m/e = 16, 17). The quantity that reacts between 575 and 650 K corresponds to 470 μmol/g, a value that is somewhat less than the bulk Al content, 625 μmol/g. The discrepancy between the Al concentration and the Brønsted-site density is likely due in part to the presence of non-framework Al, but probably also due to steric crowding of amine molecules at adjacent sites for zeolites with relatively low Si/Al ratios.

TPD-TGA results for H(Zn)-ZSM-5(50,1.3) and H(Zn)-ZSM-5(50,9.9) are shown in Figure 6.1b,c, respectively. The amounts of 2-propanamine remaining in the samples after 1 h of evacuation at room temperature were almost the same, ~1000 μmol/g; and about half of this again desorbed as unreacted amine below 550 K, leaving close to 470 μmol/g, the Brønsted-site density of the H-ZSM-5(50). However, similar to what was reported for H(Ga)-ZSM-5, the amine molecules that desorb at higher temperatures left the zeolite in two regions. The propene and ammonia features between 575 and 650 K can be assigned to molecules that were adsorbed on Brønsted sites, but there is an additional feature above 650 K that must be due to adsorption that is associated with Zn. All of the adsorbate was removed by 823 K and the samples were not changed by performing the TPD-TGA measurements. The products leaving the H(Zn)-ZSM-5 samples above 650 K were not simply additional propene and ammonia, as demonstrated by the fact that the fragmentation patterns in the mass spectra were different. Most notably, there was no peak at m/e = 42 (a peak for propene) and the ratio of peaks at m/e = 16 and 17 was different in the desorption products above 650 K. In previous work with 2-propanamine desorption from Ga-exchanged ZSM-5, products above 650 K were tentatively identified to include acetonitrile and...
other dehydrogenation products;\(^9\) and the similarities in the TPD-TGA results shown here would suggest that similar chemistry is occurring on the Zn sites.

![Figure 6.2](image)

Figure 6.2 Brønsted-site density of Zn-containing H-ZSM-5 as a function of Zn content. (■) H-ZSM-5(F) and (▲) H-ZSM-5(50).

Table 6.2 Zn-containing H-ZSM-5 samples used in this study

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Metal content (µmol/g)</th>
<th>Metal content (wt %)</th>
<th>Brønsted-acid site densities (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5(50)</td>
<td>0</td>
<td>0</td>
<td>470</td>
</tr>
<tr>
<td>H(Zn)-ZSM-5(50,0.5)</td>
<td>80</td>
<td>0.5</td>
<td>420</td>
</tr>
<tr>
<td>H(Zn)-ZSM-5(50,1.3)</td>
<td>200</td>
<td>1.3</td>
<td>300</td>
</tr>
<tr>
<td>H(Zn)-ZSM-5(50,2.0)</td>
<td>310</td>
<td>2.0</td>
<td>260</td>
</tr>
<tr>
<td>H(Zn)-ZSM-5(50,4.0)</td>
<td>610</td>
<td>4.0</td>
<td>100</td>
</tr>
<tr>
<td>H(Zn)-ZSM-5(50,9.9)</td>
<td>1510</td>
<td>9.9</td>
<td>50</td>
</tr>
<tr>
<td>H-ZSM-5(F)</td>
<td>0</td>
<td>0</td>
<td>280</td>
</tr>
<tr>
<td>H(Zn)-ZSM-5(F,0.5)</td>
<td>80</td>
<td>0.5</td>
<td>220</td>
</tr>
<tr>
<td>H(Zn)-ZSM-5(F,0.9)</td>
<td>140</td>
<td>0.9</td>
<td>180</td>
</tr>
<tr>
<td>H(Zn)-ZSM-5(F,1.3)</td>
<td>200</td>
<td>1.3</td>
<td>120</td>
</tr>
<tr>
<td>H(Zn)-ZSM-5(F,1.8)</td>
<td>280</td>
<td>1.8</td>
<td>80</td>
</tr>
<tr>
<td>H(Zn)-ZSM-5(F,9.9)</td>
<td>1510</td>
<td>9.9</td>
<td>30</td>
</tr>
</tbody>
</table>
A notable difference in the results for H(Zn)-ZSM-5 and H(Ga)-ZSM-5 is that Zn was much more effective at removing Brønsted sites. The amount of Zn added to these samples was much lower and the decrease in the desorption feature associated with Brønsted sites was much greater. The Brønsted-site density on the H(Zn)-ZSM-5(50,1.3) was only 300 μmol/g, 170 μmol/g lower than that H-ZSM-5(50), for a Zn loading of only 200 μmol/g. The H(Zn)-ZSM-5(50,9.9) sample had a Brønsted-site density of only 50 μmol/g. By comparison, the addition of even 26-wt % Ga to the same zeolite reduced the Brønsted-site density by only half. To quantify the exchange process, we measured the Brønsted-site density as a function of Zn concentration on a series of samples prepared from H-ZSM-5(50) and H-ZSM-5(F) zeolites. The data are reported in Table 6.2 and plotted in Figure 6.2. The dashed lines in the figure indicate the result that would be obtained if one Brønsted site were removed for each Zn cation. At low Zn loadings, the decrease in Brønsted-site concentration is very close to one per Zn, suggesting that Zn may be present as Zn^+1 or as Zn(OH)^+1. Exchange was incomplete, even at the highest loadings that were examined, demonstrating that Zn can also be present at nonexchange sites. Still, the fact that there is a nearly 1:1 relationship between loss of Brønsted sites and addition of Zn sites, on two samples with differing Si/Al ratios and different defect concentrations, supports the above conclusion. Although we cannot confidently identify the products that form above 650 K during TPD-TGA of 2-propanamine, the total concentration of these sites, when summed with the Brønsted sites, is approximately equal or slightly less than the Brønsted-site concentration of the parent H-ZSM-5(50). This point is important in that it shows the high-temperature feature must be associated with Zn that is present at exchange sites. For example, if there was a contribution to the high-temperature feature from Zn that was not present at exchange sites, one would expect the amount of amine desorbing above 650 K to have been much higher on the H(Zn)-ZSM-5(50,9.9) sample.
Figure 6.3 DRIFTS spectra of the following samples: (a) H-ZSM-5(50), (b) H(Zn)-ZSM-5(50,4.0), and (c) Li-ZSM-5(50).

FTIR measurements were performed on the H-ZSM-5(50), H(Zn)-ZSM-5(50,4.0), and Li-ZSM-5(50) samples to confirm the loss of Brønsted sites and to look for evidence of Zn(OH)$^{+1}$ species. The H(Zn)-ZSM-5(50,4.0) sample had a Zn loading, 610 μmol/g, close to the Al content of the parent material and a Brønsted-site density of only 100 μmol/g; the Li-ZSM-5(50) sample had a negligible Brønsted-site density. Figure 6.3 shows that the hydroxyl peak at 3605 cm$^{-1}$, associated with Brønsted sites, is effectively removed by exchange with either Li or Zn. There is also no evidence for a new hydroxyl peak that might be present on the Zn cations, a result that argues against forming a Zn(OH)$^{+1}$ species. However, we cannot rule out the possibility a υ(O−H) stretch that is too broad to observe.
Figure 6.4 TPD-TGA of 2-propanamine over (a) H(Sr)-ZSM-5(50,2.0), (b) Li-ZSM-5(50), and (c) H(Li)-ZSM-5(50). The peaks correspond to ammonia (m/e =16, 17), propene (m/e = 41, 42), acetonitrile (m/e = 17, 41), and 2-propanamine (m/e =16, 17, 41, and 44).

Finally, to confirm that TPD-TGA results on the H(Zn)-ZSM-5 samples are not simply the result of having partial exchange of any +1 or +2 ions, we also examined the adsorption of 2-propanamine on H(Sr)-ZSM-5(50,2.0) (230 μmol/g of Sr) and a partially and fully exchange H(Li)-ZSM-5(50), prepared as described in the Characterization Techniques section. The TPD-TGA for each of these samples is shown in Figure 6.4. Unlike the case for Zn, the impregnation of Sr(NO₃)₂ into H-ZSM-5 had very little effect on the Brønsted-site density and gave no additional high-temperature reaction features, as shown in Figure 6.4a. The Brønsted-site density decreased only slightly, to 430 μmol/g. This demonstrates that Sr²⁺ does not significantly exchange into the high-silica zeolite. TPD-TGA on Li-ZSM-5(50) and H(Li)-ZSM-5(50), Figure 6.4b,c, also exhibited no additional high temperature reaction peaks. However, in addition to the formation of propene and ammonia that occurs on the Brønsted sites, adsorption of 2-propanamine onto Li sites leads to a second, unreacted-amine peak, centered at 550 K.¹⁴²
6.3.2 Catalytic Properties of Zn-Promoted H-ZSM-5

To determine the effect of Zn-exchange on the catalytic properties of H-ZSM-5, rates and selectivities were measured for the reactions of n-hexane at differential conversions. In Figure 6.5, the rates for n-hexane conversion are plotted as a function of Brønsted-site density for the series of H(Zn)-ZSM-5(50) and H(Li)-ZSM-5(50) samples at 633 K and pressures of 1 and 137 bar. At 1 bar, Figure 6.5a, there is essentially a linear relationship between the n-hexane conversion rate and the Brønsted-site density. The completely exchanged Li-ZSM-5(50) exhibited no measurable activity. Rates on the samples that were partially exchanged with either Li or Zn were between that of Li-ZSM-5(50) and H-ZSM-5(50) and increased linearly with the Brønsted-site density for both the Li- and the Zn-exchanged materials. Rates also increased with Brønsted-site density at 137 bar, but the dependence on site density seemed to be stronger than linear. It is noteworthy that the correlation between activity and site density fits well for all of the materials investigated: pure H-ZSM-5 with a different Si/Al ratios, and partially exchanged samples with either Li or Zn. The stronger than linear dependence of the rates on site densities may result from the fact that n-hexane cracking reactions are dominated by bimolecular processes at these high pressures and relatively low temperatures. In any case, there is certainly no enhancement in the rate of n-hexane conversion with the incorporation of Zn. This observation also indicates that the rate-determining step for the activation of the n-hexane occurs at the Brønsted-acid sites, and not on the Zn cations.
The effects of Li and Zn exchange on the product distributions for the reaction of n-hexane at 137 bar are shown in Table 6.3. Measurements were performed on H-ZSM-5(50), H(Zn)-ZSM-5(50,1.3), and H(Zn)-ZSM-5(50,9.9) at 633 K and on H-ZSM-5(50) and H(Zn)-ZSM-5(50,1.3) at 823 K. The product selectivities for H-ZSM-5(50) are very similar to what was reported earlier at both temperatures, with the exception that some H₂ production is observed due to improvements in our detection capabilities. At 633 K, there was very little olefin production and some aromatics formation (benzene, toluene, and xylenes = BTX), indicating that bimolecular, hydride-transfer reactions must dominate. At 823 K, olefin production increased and BTX production decreased, suggesting that the monomolecular processes may be somewhat more important. Partial exchange of the Brønsted sites with Li reduced the activity at 633 K, as evidenced by the fact that more catalyst was needed for a given conversion; but the product distribution was not affected.
The addition of Zn had a much stronger effect on the product distribution, greatly increasing $\text{H}_2$ and BTX production, primarily at the expense of small alkanes. Hydrogen balances, calculated as the amount of hydrogen in the products as a percent of that in the reacting n-hexane, were reasonably good in all cases. The fact that $\text{H}_2$ is produced together with the aromatics suggests that the mechanism for aromatics formation is not due to classical hydride-transfer reactions, as is likely the case for aromatics formation on H-ZSM-5(50). Although pressure certainly influences the product selectivity, the overall conclusions concerning the effects of Li and Zn exchange are the same for measurements performed at 1 bar total pressure, as shown in Table 6.4.
Table 6.4 Molar Selectivities (%) and Heat of Reaction for n-Hexane Cracking over H-ZSM-5(50), H(Li)-ZSM-5(50), H(Zn)-ZSM-5(50,1.3), and H(Zn)-ZSM-5(50,9.9) at 1 bar, under Temperature of 633 K

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>H-ZSM-5(50)</th>
<th>H(Li)-ZSM-5(50)</th>
<th>H(Zn)-ZSM-5(50,1.3)</th>
<th>H(Zn)-ZSM-5(50,9.9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst amount (mg)</td>
<td>100</td>
<td>100</td>
<td>300</td>
<td>500</td>
</tr>
<tr>
<td>H₂</td>
<td>2.7</td>
<td>1.4</td>
<td>5.8</td>
<td>5.6</td>
</tr>
<tr>
<td>&lt; C2</td>
<td>6.8</td>
<td>6.7</td>
<td>1.3</td>
<td>1.4</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>5.3</td>
<td>4.8</td>
<td>5.9</td>
<td>5.2</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>6.9</td>
<td>7.5</td>
<td>8.9</td>
<td>9.6</td>
</tr>
<tr>
<td>Iso-C₄H₁₀</td>
<td>7.2</td>
<td>7.8</td>
<td>6.7</td>
<td>5.9</td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td>13.2</td>
<td>12.2</td>
<td>8.9</td>
<td>9.6</td>
</tr>
<tr>
<td>Iso-C₅H₁₂</td>
<td>12.4</td>
<td>11.7</td>
<td>16.6</td>
<td>15.1</td>
</tr>
<tr>
<td>n-C₅H₁₂</td>
<td>24.8</td>
<td>26.6</td>
<td>22.6</td>
<td>22.9</td>
</tr>
<tr>
<td>n-C₆H₁₂</td>
<td>6.2</td>
<td>5.5</td>
<td>6.8</td>
<td>6.9</td>
</tr>
<tr>
<td>Iso-C₆H₁₄</td>
<td>8.5</td>
<td>9.5</td>
<td>4.4</td>
<td>4.6</td>
</tr>
<tr>
<td>BTX</td>
<td>1.6</td>
<td>1.8</td>
<td>8.0</td>
<td>8.6</td>
</tr>
<tr>
<td>C-6+ (Exclude BTX)</td>
<td>4.6</td>
<td>4.6</td>
<td>4.2</td>
<td>4.6</td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>3.7</td>
<td>3.1</td>
<td>8.5</td>
<td>5.0</td>
</tr>
<tr>
<td>Hydrogen Balance (%)</td>
<td>99.5</td>
<td>99.8</td>
<td>96.1</td>
<td>94.8</td>
</tr>
<tr>
<td>H/C ratio</td>
<td>2.36</td>
<td>2.35</td>
<td>2.25</td>
<td>2.24</td>
</tr>
<tr>
<td>Heat of Reaction (kJ/mol)</td>
<td>4.1</td>
<td>3.2</td>
<td>21.0</td>
<td>22.1</td>
</tr>
</tbody>
</table>

It is noteworthy that the product distributions on the samples with 1.3 and 9.9 wt % Zn were essentially the same. The higher Zn loading decreased the rates so that more catalyst was required to achieve a similar conversion but did not affect the product distribution. This result is somewhat surprising because the proportion of Brønsted-acid sites and Zn sites is different for the two catalysts. In the case of H(Zn)-ZSM-5(50,1.3), the Zn content was 200 μmol/g and the Brønsted-site concentration was 300 μmol/g. If each type of site acted independently of the other, one would expect there to be a regular progression in the product selectivities as the Brønsted sites are replaced, in the same way that the rates increase almost linearly with Brønsted-site density. This implies that the Zn sites either catalyze reactions of molecules produced at Brønsted sites or somehow modify intermediates formed at neighboring sites.
6.3.3 Nature of the Zn Sites

We performed additional adsorption experiments in order to understand better the properties and role of Zn-exchange sites, starting with FTIR measurements of adsorbed acetonitrile, on the assumption that the Zn-exchange sites may have Lewis-acid character. Previous studies of the Lewis-acid sites formed by framework Sn in siliceous zeolites showed that CD$_3$CN adsorbed on those sites exhibit a $\nu$(CN) stretch centered near 2310 cm$^{-1}$.\textsuperscript{143} When CD$_3$CN was present at coverages above one per Lewis site, additional vibration bands were observed at 2268 and 2276 cm$^{-1}$, which were assigned to physisorbed acetonitrile and acetonitrile on silanols. CD$_3$CN adsorbed on Li-exchanged zeolites at low coverages showed a single peak at 2287 cm$^{-1}$,\textsuperscript{142} demonstrating that the $\nu$(CN) stretch observed on Lewis sites formed by framework Sn cannot be explained by interactions of acetonitrile with simple cations.

Figure 6.6 shows FTIR results for CD$_3$CN adsorbed on H-ZSM-5(50) and H(Zn)-ZSM-5(50,4.0). (Figure 6.7 provides TPD-TGA results for CH$_3$CN on both of these samples and shows that, upon evacuation, there is approximately one CH$_3$CN molecule remaining per ion-exchange site in these materials.) FTIR spectra were initially collected while exposing the samples to the vapor pressure of CD$_3$CN at room temperature in flowing He. Additional spectra were collected in pure flowing He as the temperature was ramped upward. Results on H-ZSM-5(50) are similar to what has been reported previously.\textsuperscript{144} At high coverages, there was a broad $\nu$(CN) stretching region extending from 2260 to 2300 cm$^{-1}$. After excess CD$_3$CN is removed by mild heating in flowing He, a better-defined peak at 2298 cm$^{-1}$ is observed. The results on the Zn-exchanged material more closely resemble what is observed on Sn-containing zeolites. Upon exposure to CD$_3$CN vapor, two $\nu$(CN) stretching regions were observed: one centered near 2310 cm$^{-1}$ and the other near 2275 cm$^{-1}$.\textsuperscript{143} Upon removal of excess CD$_3$CN, only the 2310 cm$^{-1}$ peak remains. The similarity in these results with those obtained previously on framework Sn strongly implies that the ion-exchanged Zn cations must have Lewis-acid character.
Figure 6.6 (i) DRIFTS spectra of H-ZSM-5(50): (a) in He flow with CD₃CN vapor at RT; (b) in pure He flow at RT immediately removing CD₃CN vapor; (c) in He flow after heating to 323 K; (d) in He flow after heating to 373 K; (e) in He flow after heating to 423 K; (f) in He flow after heating to 423 K. (ii) DRIFTS spectra of H(Zn)-ZSM-5(50,4.0): (a) in He flow with CD₃CN vapor at RT; (b) in pure He flow at RT immediately removing CD₃CN vapor; (c) in He flow after heating to 323 K; (d) in He flow after heating to 373 K; (e) in He flow after heating to 573 K; (f) in He flow after heating to 553 K.

Figure 6.7 TPD-TGA of Acetonitrile over (a) H-ZSM-5(50), (b) H(Zn)-ZSM-5(50,4.0).
We also examined CO adsorption on the H-ZSM-5(F) and H(Zn)-ZSM-5(F,9.9) by microcalorimetry at 195 K, with results shown in Figure 6.8. CO is a polar molecule that adsorbs strongly on both Brønsted sites and alkali cations. With adsorption on alkali cations, the strength of the interaction varies with cation size and polarity. Previous reports showed that the heats of adsorption for CO on Li-ZSM-5 and H-ZSM-5 are 36 and 27 kJ/mol, respectively. The data in Figure 6.8 for H-ZSM-5(F) are in good agreement with literature reports. At low coverages, when all of the CO molecules are likely present at Brønsted sites, the differential heats are 27 kJ/mol. The differential heats fall to approximately 16 kJ/mol for high coverages above that at which all the acid sites have been saturated. On H(Zn)-ZSM-5(F,9.9), the differential heats at low coverages were 34 kJ/mol, decreasing to 17.0 kJ/mol. The data suggest that the exchanged Zn cations at ion-exchange sites are polar and able to couple with polar molecules.

![Figure 6.8](image)

Figure 6.8 Differential heats of adsorption for CO at 195 K on (■) H-ZSM-5(F) and (▲) H(Zn)-ZSM-5(F,9.9)
6.4 Discussion

Zn-exchanged ZSM-5 zeolites show promise as catalysts for endothermic reforming in hypersonic aircraft. Compared to zeolites having only Brønsted-acid sites, the increased production of H\textsubscript{2} and aromatics observed with the metal-exchanged zeolites significantly improves the endothermicity of the reactions. The increased production rates of H\textsubscript{2} and aromatic species is consistent with the investigations of Biscardi et al.\textsuperscript{145} on Zn-exchanged ZSM-5 catalysts on the propane aromatization reaction at atmospheric pressure. At high pressures, reaction rates on the Zn-exchanged ZSM-5 materials are reasonably high and the stabilities against coking appear to be comparable to that found with the normal acidic H-ZSM-5.

Previously, there have been suggestions\textsuperscript{145,146} that each Zn\textsuperscript{2+} cation balances the charge of two framework Al sites. An alternative explanation involves the formation of (ZnOH)\textsuperscript{+}.\textsuperscript{147} Our results do not appear to be consistent with either of those pictures. Regarding Zn\textsuperscript{2+} balancing the charge of two framework sites, for smaller Zn contents, our TPD-TGA results for 2-propanamine indicate that one Brønsted site is displaced for each added Zn and that one new amine-reaction site is formed for each lost Brønsted site. Furthermore, if Zn was simply acting as a divalent ion, Brønsted sites should have also been removed by the addition of Sr\textsuperscript{2+}. Furthermore, we found no evidence that the Zn is present as a compound ion (e.g., Zn(OH)\textsuperscript{+1}) from IR spectroscopy. Although Zn\textsuperscript{1+} compounds are relatively rare, evidence for their formation has been reported in confined environments, such as microporous zeolites.\textsuperscript{148-151} For example, Tian et al.\textsuperscript{150} reported the existence of mononuclear Zn\textsuperscript{1+} species in the SAPO-CHA zeolite by electron spin resonance (ESR) spectroscopy and magnetic susceptibility measurements. More recently, Qi et al.\textsuperscript{151} found evidence for stable, isolated Zn\textsuperscript{1+} ions by ESR in Zn-exchanged ZSM-5.

The present study also indicates that reactions on the Zn-exchange sites are not independent of reactions that occur on the Brønsted sites. Even though the presence of Zn sites changed the product selectivity, conversions declined linearly with the concentration of Brønsted sites. If the observed products were simply a linear combination of reactions at Zn sites and...
Brønsted sites, the chemistry occurring at Brønsted sites should dominate the product distribution. This is indeed what happens in the case of H(Li)-ZSM-5. Because the Li sites are unreactive, the rates decrease linearly with Li addition but there is no effect on the product distribution. One possibility for explaining the product distributions on H(Zn)-ZSM-5 is that they result from products formed at Brønsted sites undergoing further reaction at Zn sites. Unfortunately, because we were unable to prepare a Zn-ZSM-5 without Brønsted sites, it was not possible for us to test the reaction chemistry in the absence of Brønsted sites. An alternative explanation is that the Zn sites affect the chemistry that occurs at Brønsted sites. To picture how this might occur, consider the methanol-to-olefins reaction in H-ZSM-5.152 This reaction occurs via a “carbon-pool” mechanism, in which the intermediates formed within the pores can be very large. It is possible that Zn sites simply affect the products that are formed by these carbon-pool intermediates without changing the overall rates for n-hexane conversion. This last explanation for how Zn affects product selectivity may explain the similarities between H(Zn)-ZSM-5 and H(Ga)-ZSM-5. The overall results for the two materials are very similar, even though one would expect Ga\(^{3+}\) and Zn\(^{2+}\) to be very different. If the main role of these cations is to act as a Lewis acid that polarizes a large intermediate, it is reasonable that both would show similar chemistries. Despite the extensive literature, there is obviously still much to learn about the nature of metal-exchanged zeolites and the effect of the metal sites on hydrocarbon reactions. The fact that these materials are able to modify the product selectivities for alkane cracking so dramatically makes their continued study important, particularly for application to endothermic reforming in hypersonic aircraft.

6.5 Summary

In this chapter, I have demonstrated that the addition of Zn to an H-ZSM-5 catalyst greatly increases the rates of H\(_2\) and aromatics production from the reaction of n-hexane, even though rates for n-hexane conversion decrease linearly with Brønsted-site concentrations. The added Zn
cations are present at ion-exchange sites within the zeolite and each Zn cation displaces one Brønsted site at low Zn coverages. The ion-exchanged Zn cations form Lewis-acid sites that polarize adsorbed CD$_3$CN in a similar manner to what is observed in other solid Lewis acids. We suggest that Zn sites act in combination with Brønsted sites to alter the product distributions in alkane cracking.
Chapter 7. Study of Zn and Ga Exchange in H-[Fe]ZSM-5 and H-[B]ZSM-5 Zeolites

7.1 Introduction

Results in Chapter 5 and 6 showed that both Ga- and Zn-exchanged ZSM-5 zeolites may be sufficiently active and stable for endothermic reforming. In addition to demonstrating that the addition of Ga or Zn greatly enhances the formation of H\textsubscript{2} and small aromatics from the reaction of n-hexane, the work also showed that Brønsted sites were at least partially removed by exchange with either Ga or Zn and stoichiometrically replaced by new sites with dehydrogenation and Lewis-acid properties. The loss of Bronsted-acid sites and formation of sites with dehydrogenation activity were observed by TPD/TGA of 2-propanamine. 2-Propylammonium ions formed by adsorption of the amine at Bronsted-acid sites react to propene and ammonia through Hoffman elimination between 575 and 650 K.\textsuperscript{64} Addition of either Ga or Zn to H-ZSM-5 replaced the Brønsted-acid-site desorption feature in TPD with a peak at higher temperature that includes dehydrogenation products.\textsuperscript{153} That the metal sites have Lewis acid character was observed in Zn-exchanged materials by Fourier transform infrared (FTIR) spectroscopy of adsorbed CD\textsubscript{3}CN.\textsuperscript{15}

Because Brønsted-acid sites play a critical role in dehydrocyclization reactions that occur in Zn- and Ga- exchanged zeolites, it is interesting to consider what effect acid-site strength has on both the metal sites and the reaction chemistry. One method for varying the zeolite deprotonation energy, and therefore the acid strength, involves framework substitution of silicates with the MFI (ZSM-5) structure by substitution with framework Al, Fe, and B. Similarly to the aluminosilicate, H-[Al]ZSM-5, the ferrosilicate, H-[Fe]ZSM-5, has been shown to have a Brønsted-acid-site concentration equal to the framework Fe concentration.\textsuperscript{154} Whereas the heats of adsorption for NH\textsubscript{3} and pyridine on H-[Fe]ZSM-5 and H-[Al]ZSM-5 are indistinguishable,\textsuperscript{155} the deprotonation energy of H-[Fe]ZSM-5 is significantly higher, implying that the acid sites are much
weaker, a fact that is observed as much lower rates for some reactions. The turnover frequencies for n-hexane cracking were reported to be a factor of at least 30 lower on sites in H-[Fe]ZSM-5 compared to H-[Al]ZSM-5. The Brønsted-acid sites in H-[Fe]ZSM-5 are active for the oligomerization of olefins and the esterification of acetic acid, but the rates for hydride-transfer reactions in H-[Fe]ZSM-5 are much lower. This leads to a significant reduction in coke formation during olefin oligomerization reactions in H-[Fe]ZSM-5 compared to H-[Al]ZSM-5. Because it is critically important to avoid coking in the endothermic reforming application, this property is of great potential interest. The protonic sites in H-[B]ZSM-5 are not able to protonate strong bases such as 2-propanamine, implying that the proton affinity of the sites in this material are even higher.

The present Chapter will demonstrate that the metal-exchange sites in [Fe]ZSM-5 exhibit adsorption properties very similar to those present in [Al]ZSM-5 for 2-propanamine but that no similar sites are formed in [B]ZSM-5. However, because the acid sites in H-[Fe]ZSM-5 are not able to activate alkanes, no dehydrocyclization chemistry occurs in metal-exchanged [Fe]-ZSM-5, supporting the conclusion that Brønsted-acid sites play a critical role in the reaction chemistry.

### 7.2 Experimental Section

#### 7.2.1 Materials.

The [Al]ZSM-5 sample, with a Si/Al ratio of 50 (CBV 5524G), was received in its ammonium-ion form from Zeolyst. The [Fe]ZSM-5 sample (Si/Fe ratio of 60) was part of the same batch as used in a previous study, and a complete description of the synthesis procedure and characterization have been described in detail in Chapter 2. The as-synthesized sample was white, and it remained off-white after calcination in dry flowing air at 750 K. The [B]ZSM-5 sample was synthesized using a recipe from the literature. Table 7.1 provides some of the important characteristics of these samples.
Table 7.1 Zeolite Samples Used in This Study

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/M₂</th>
<th>Pore volume with n-hexane (cm$^3$/g)</th>
<th>Brønsted-acid site densities (µmol/g)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-[Al]ZSM-5</td>
<td>50</td>
<td>0.19</td>
<td>500</td>
</tr>
<tr>
<td>H-[Fe]ZSM-5</td>
<td>56$^a$</td>
<td>0.16</td>
<td>420</td>
</tr>
<tr>
<td>H-[B]ZSM-5</td>
<td>120$^a$</td>
<td>0.15</td>
<td>30</td>
</tr>
</tbody>
</table>

$^a$ Determined by ICP-OES analysis.

$^b$ Measured by TPD-TGA of 2-propanamine.

Metals were added to the H$^+$ forms of the molecular sieves by incipient wetness with aqueous solutions of either Zn(NO$_3$)$_2$ (98%, extra pure, Acros Organics) or Ga(NO$_3$)$_3$ (99.999% purity, Sigma-Aldrich). Samples are identified by the weight percentages of metal that they contain, in parentheses; for example, H-[Al]ZSM-5 containing 4.0 wt % Zn is denoted as H(Zn)-[Al]ZSM-5(4.0). The metal-containing samples are listed in Table 7.2, together with some important properties.

In addition to crystalline molecular sieves, we also examined metal exchange into an amorphous silica-alumina made by infiltrating alumina into SBA-15, a mesoporous silica with 5.0-nm channels, to determine possible effects of structure on metal sites. The sample, designated here as Al$_2$O$_3$(10)/SBA-15, had 10 wt % Al$_2$O$_3$ added to it by mixing 1.23 g of aluminum nitrate nonahydrate (98.0-102.0%, Alfa Aesar) together with 1.5 g of SBA-15 in 100 mL of water and then evaporating the water and heating to 773 K for 4 h.$^{160}$ Zn-containing materials with 4 wt % Zn, Zn(4)/SBA-15 and Zn(4)/Al$_2$O$_3$(10)/SBA-15, were then prepared by incipient wetness with aqueous solutions of Zn(NO$_3$)$_2$ to have Zn loadings of 4 wt %. Some characteristics of these samples are also reported in Table 7.2.
Table 7.2 Metal-Containing Zeolite Samples Used in This Study

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Bronsted-acid site densities (µmol/g)</th>
<th>Metal content (µmol/g)</th>
<th>Metal content (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(Zn)-[Al]ZSM-5(4.0)</td>
<td>110</td>
<td>610</td>
<td>4.0</td>
</tr>
<tr>
<td>H(Zn)-[Fe]ZSM-5(4.0)</td>
<td>30</td>
<td>610</td>
<td>4.0</td>
</tr>
<tr>
<td>H(Zn)-[B]ZSM-5(4.0)</td>
<td>10</td>
<td>610</td>
<td>4.0</td>
</tr>
<tr>
<td>H(Ga)-[Al]ZSM-5(4.0)</td>
<td>400</td>
<td>570</td>
<td>4.0</td>
</tr>
<tr>
<td>H(Ga)-[Fe]ZSM-5(4.0)</td>
<td>330</td>
<td>570</td>
<td>4.0</td>
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<tr>
<td>H(Ga)-[B]ZSM-5(4.0)</td>
<td>10</td>
<td>570</td>
<td>4.0</td>
</tr>
<tr>
<td>SBA-15</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Al₂O₃(10)/SBA-15</td>
<td>200</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Zn(4)/SBA-15</td>
<td>0</td>
<td>610</td>
<td>4.0</td>
</tr>
<tr>
<td>Zn(4)/Al₂O₃(10)/SBA-15</td>
<td>90</td>
<td>610</td>
<td>4.0</td>
</tr>
</tbody>
</table>

*Measured by TPD-TGA of 2-propanamine.

7.2.2 Characterization Techniques

A Rigaku Smartlab diffractometer was used to record X-ray diffraction (XRD) patterns on the calcined H-[B]ZSM-5. The XRD pattern for this sample, shown in Figure 7.1, exhibits the characteristic peaks associated with the MFI structure, with no indication of broadening due to amorphous impurities.\textsuperscript{161,162} For the [Fe]-ZSM-5 and [B]ZSM-5 samples, bulk compositions were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis and are reported in Table 7.1.

A Mattson Galaxy FTIR spectrometer with a diffuse reflectance attachment was used to collect Fourier transform infrared (FTIR) spectra. To remove adsorbed water, the samples were heated to 573 K in He that was flowing at 0.5 cm\textsuperscript{3}/s, before any spectra were recorded. The FTIR spectra were all collected at room temperature at 8 cm\textsuperscript{-1} resolution. After the samples had been exposed to a saturation dose of CD\textsubscript{3}CN, excess CD\textsubscript{3}CN was removed in flowing He before the collection of FTIR spectra. Additional spectra were measured at various temperatures as the sample was heated to 473 K in flowing He.
Simultaneous TPD-TGA measurements were performed to identify the types of sites present in the catalysts. A detailed description of this system can be found in Chapter 2. Rate measurements used the same flow reactor as in previous Chapters. There was no evidence of any catalyst deactivation during the 4 h required to perform rate measurements. Additional evidence that coking did not occur under our conditions came from the observation that the catalysts remained off-white upon removal from the reactor. An online gas chromatograph was used to monitor the reaction products.

7.3 Results

7.3.1 Characterization of Protonic Sites in Solids

Alkyl amines are strong bases that are easily protonated by Brønsted-acid sites. In TPD, the resulting alkylammonium ions decompose by the Hofmann elimination reaction into an olefin and ammonia at a temperature that depends only on the alkyl group. Consequently, Brønsted-
acid site densities can be easily determined from TPD-TGA measurements by quantifying the amounts of the adsorbed amines that react. In the case of 2-propanammonium ions, reaction to propene and ammonia occurs between 575 and 650 K.\textsuperscript{97,154}

The TPD-TGA results for 2-propanamine on H-[Fe]ZSM-5 and H-[B]ZSM-5 are shown in Figure 7.2. (Because the analogous data for the H-[Al]ZSM-5 sample have been reported previously, we include data for that sample in the Figure 7.3.) The results for H-[Fe]ZSM-5 in Figure 7.2a are similar to what was published for H-[Al]ZSM-5. As shown in Figure 7.2a and Figure 7.3, hydrogen-bonded 2-propanamine (m/e = 17, 41, and 44) desorbs unreacted below approximately 500 K. The amount of 2-propanamine desorbing in this lower-temperature feature depends on the evacuation time and the concentration of hydroxyl defects in the sample. The 2-propanamine that is bound to Brønsted-acid sites decomposes between 575 and 650 K to propene (m/e = 41) and ammonia (m/e = 17). The results for H-[Al]ZSM-5 and H-[Fe]ZSM-5 differ only in the amounts that are formed in each of the two observed desorption features. Based on the amounts of amine that react, the Brønsted-acid site densities for H-[Al]ZSM-5 and H-[Fe]ZSM-5 were determined to be 500 and 420 μmol/g, respectively. These values are somewhat less than the bulk Al and Fe densities for these samples, namely, 670 and 560 μmol/g, respectively, possibly because of the presence of non-framework Al or Fe and possibly because of steric interactions between amine molecules at adjacent sites in zeolites with relatively low Si/M\textsubscript{2} ratios.
Figure 7.2 TPD-TGA of 2-propanamine over (a) H-[Fe]ZSM-5 and (b) H-[B]ZSM-5. The peaks correspond to ammonia (m/e = 17), propene (m/e = 41), and 2-propanamine (m/e = 17, 41, and 44).

Figure 7.3 TPD-TGA of 2-propanamine over H-[Al]ZSM-5. The peaks correspond to ammonia (m/e =17), propene (m/e = 41), and 2-propanamine (m/e =17, 41, and 44).
The TPD-TGA data for the H-[B]ZSM-5 sample, presented in Figure 7.2b, again show desorption of physically adsorbed amine molecules below 500 K. However, in this case, additional unreacted 2-propanamine leaves the sample in a feature between 500 and 575 K, similar to what was reported previously for 2-propanamine desorption from H-[B]ZSM-5. The coverage of this additional desorption feature is close to one molecule per B atom, ~250 μmol/g. The fact that there is no reaction of the amine implies that these molecules are not protonated by the protonic sites in H-[B]ZSM-5 but, rather, are simply hydrogen-bonded to the hydroxyl sites. The TPD-TGA results in Figure 7.2b do exhibit a small reaction feature between 575 and 650 K, with a coverage of ~30 μmol/g; however, we suggest that this is due to Al impurities introduced from the silica source used in the synthesis of the [B]ZSM-5. The Al composition in this sample was determined by ICP-OES analysis to be ~10 μmol/g. Although this is less than the site density measured by TPD-TGA with 2-propanamine, it appears that each Al site catalyzes the reaction of more than one amine molecule as a result of the overlap of the reaction feature with that of the amine molecules desorbing from the B sites. Additional support for the conclusion that the reaction feature in TPD is due to Al sites comes from the reaction rates for n-hexane cracking, as discussed later.

To investigate the effect of structure on the nature of protonic sites, we also examined an amorphous silica-alumina formed by introducing alumina onto SBA-15. The TPD-TGA data for 2-propanamine on SBA-15 and Al₂O₃(10)/SBA-15 are shown in Figure 7.4. Because SBA-15 has no Brønsted-acid sites, only hydrogen-bonded 2-propanamine is observed leaving the sample below about 450 K (Figure 7.4a). Data for the Al₂O₃(10)/SBA-15 sample (Figure 7.4b) show the desorption of additional unreacted amine between 450 and 550 K, which is likely associated with alumina that has not been inserted into the silica framework.137 More interesting for the present investigation, approximately 200 μmol/g of the amine reacted to propene and ammonia between 575 and 650 K. These Brønsted-acid sites must be formed by the incorporation of Al³⁺ into tetrahedral positions in the siliceous matrix.
Figure 7.4 TPD-TGA of 2-propanamine over (a) SBA-15, and (b) Al$_2$O$_3$(10)/SBA-15. The peaks correspond to ammonia (m/e =17), propene (m/e = 41), and 2-propanamine (m/e =17, 41, and 44).

To further elucidate the nature of the protonic sites in the three ZSM-5 molecular sieves, FTIR measurements were performed, with the results shown in Figure 7.5. The protonic sites in the H-[Al]ZSM-5, H-[Fe]ZSM-5, and H-[B]ZSM-5 samples exhibited hydroxyl stretches at 3605, 3620, and 3718 cm$^{-1}$, respectively, in good agreement with the literature.$^{163}$ All three samples also exhibited a vibrational band near 3735 cm$^{-1}$, which was shown to be due to external silanols.$^{164}$ Because the H-[B]ZSM-5 sample was composed of very large crystallites, as shown in Figure 7.6, this external-silanol band is relatively weak and appears as a shoulder on the hydroxyl stretch associated with framework B.
Figure 7.5 DRIFTS spectra of the following samples: (a) H-[Al]ZSM-5, (b) H-[Fe]ZSM-5, and (c) H-[B]ZSM-5.

Figure 7.6 Optical microscope images of the H-[B]ZSM-5 sample.
7.3.2 Examination of Zn Exchange with Protonic Sites

Previously, we showed that Zn could displace Brønsted-acid sites in H-[Al]ZSM-5 with a nearly 1:1 stoichiometry.\textsuperscript{15} To explore the effect of the acid-site strength on the Zn exchange process, we investigated Zn incorporation into the H-[Fe]ZSM-5 and H-[B]ZSM-5 zeolites. \textbf{Figure 7.7a} shows the TPD–TGA results for 2-propanamine from H(Zn)-[Fe]ZSM-5(4.0), the H-[Fe]ZSM-5 sample with 4 wt % Zn (610 μmol of Zn/g), which has excess Zn compared to the protonic site concentrations in the unmodified material. For comparison purposes, we present the analogous data for H(Zn)-[Al]ZSM-5(4.0) in the \textbf{Figure 7.8a}. Similarly to the results for H-[Fe]ZSM-5, hydrogen-bonded 2-propanamine desorbs from the sample below 550 K, leaving approximately 400 μmol/g, a value close to the Brønsted-acid site density of the parent sample, remaining in the sample. Similar to what was reported for H(Zn)-[Al]ZSM-5, the amine molecules that desorb at higher temperatures leave the zeolite in two regions. The small propene (m/e = 41) and ammonia (m/e = 17) features between 575 and 650 K, corresponding to about 30 μmol/g, can be assigned to molecules adsorbed on Brønsted-acid sites; however, the additional desorption above 650 K must be associated with Zn. The products formed above 650 K are also not simply propene and ammonia, as demonstrated by the fact that the relative intensities of the peaks in the mass spectrum were different. Detailed product distributions are difficult to determine using these mass spectra, but our previous report suggested that the products formed at the higher temperatures in the Zn-exchanged H-[Al]ZSM-5 include dehydrogenation products, such as acetonitrile.\textsuperscript{15} To a first approximation, the sum of the concentrations of Zn sites and Brønsted-acid sites is equal to the concentration of Brønsted-acid sites in the parent material, implying that Zn sites that react with 2-propanamine in TPD are produced at the expense of Brønsted-acid sites.

The TPD-TGA results for H(Zn)-[B]ZSM-5(4.0) are shown in \textbf{Figure 7.7b}. With the exception that the small concentration of Brønsted-acid sites associated with Al impurities has been almost completely removed and replaced by higher-temperature Zn-related features, the desorption curves on this sample are nearly identical to those observed on the parent H-[B]ZSM-
5. There is no evidence for the formation of Zn sites in H-[B]ZSM-5 similar to those formed upon addition of Zn into H-[Al]ZSM-5 or H-[Fe]ZSM-5.

To determine whether the solid structure affects the adsorption properties of Zn exchange sites, we performed adsorption measurements with SBA-15 and Al₂O₃(10)/SBA-15 samples, each with 4 wt % of added Zn. The TPD-TGA data for Zn(4)/SBA-15 are shown in Figure 7.7c. The only effect of adding Zn to the siliceous SBA-15 was the additional desorption of unreacted 2-propanamine in a tail to slightly higher temperatures, with approximately 200 μmol/g desorbing between 450 and 550 K. This is likely associated with adsorption on ZnO incorporated in the pores and is clearly very different from the high-temperature reaction feature observed for adsorption on Zn incorporated into either H-[Fe]ZSM-5 or H-[Al]ZSM-5. The results for amine adsorption in Zn(4)/Al₂O₃(10)/SBA-15, shown in Figure 7.7d, are more similar to what is typically observed for Zn-exchanged zeolites. Again, only unreacted 2-propanamine is observed to leave the sample below 550 K. Similar to what was observed following Zn incorporation into H-[Al]ZSM-5, there is a significant reduction in the Brønsted-acid site density, from 200 to 90 μmol/g, on Al₂O₃(10)/SBA-15. Finally, the desorption feature associated with Brønsted-acid sites is replaced by a high temperature desorption feature, above 650 K, that can be assigned to Zn sites. One difference in the case of Al₂O₃(10)/SBA-15 is that the Zn exchange for Brønsted-acid sites was less efficient on the amorphous catalyst, possibly because some of the Zn cations were able to interact with alumina that did not produce Brønsted acidity.
Figure 7.7 TPD-TGA of 2-propanamine over (a) H(Zn)-[Fe]ZSM-5(4.0), (b) H(Zn)-[B]ZSM-5(4.0), (c) Zn(4)/SBA-15, and (d) Zn(4)/Al$_2$O$_3$(10)/SBA-15. The peaks correspond to ammonia (m/e =17), propene (m/e = 41, 42), and 2-propanamine (m/e = 17, 41, 42, and 44).
Figure 7.8 TPD-TGA of 2-propanamine over (a) H(Zn)-[Al]ZSM-5(4.0), (b) H(Ga)-[Al]ZSM-5(4.0). The peaks correspond to ammonia (m/e = 17), propene (m/e = 41, 42), and 2-propanamine (m/e = 17, 41, 42, and 44).

Previously, FTIR spectra following CD₃CN adsorption on Zn exchange sites in H-[Al]ZSM-5 were found to exhibit a υ(CN) stretch centered at 2310 cm⁻¹.¹⁵ A band at this vibrational frequency has been used as a fingerprint for Lewis acid sites formed by framework Sn in BEA zeolites.¹⁴³,¹⁶⁵

Figure 7.9 shows FTIR results for CD₃CN adsorbed on H-[Fe]ZSM-5, H-[B]ZSM-5, 4 wt % Zn-exchanged H-[Fe]ZSM-5 (H(Zn)-[Fe]ZSM-5(4.0)), and 4 wt % Zn-exchanged H-[B]ZSM-5 (H(Zn)-[B]ZSM-5(4.0)). (Figure 7.10 reproduces the FTIR results for CD₃CN on Zn-exchanged H-[Al]ZSM-5.) The spectra of CD₃CN on H-[Fe]ZSM-5 (Figure 7.9a) are essentially indistinguishable from those on H-[Al]ZSM-5, in agreement with previous reports.¹⁴⁴ Spectra measured with excess CD₃CN showed two υ(CN) stretching bands, near 2267 and 2298 cm⁻¹, but mild heating inflowing He removed the lower-frequency band. In agreement with previous interpretations,¹⁴⁴ the band near 2298 cm⁻¹ can be assigned to the adsorption of CD₃CN on Brønsted sites formed by either
framework Fe or framework Al. When the spectrum was measured at higher temperatures, the band at 2298 cm\(^{-1}\) shifted to 2291 cm\(^{-1}\). The spectra of adsorbed CD\(_3\)CN on H-[B]ZSM-5, reported in Figure 7.9b, do not show evidence for multiple bands. The \(\nu(CN)\) frequency shifted gradually, from 2267 to 2271 cm\(^{-1}\), as the coverage decreased. Because this frequency is similar to what is observed on purely siliceous materials,\(^{144}\) there does not appear to be any special interaction between CD\(_3\)CN and the protonic sites in H-[B]ZSM-5.

Figure 7.9 DRIFTS spectra of (a) H-[Fe]ZSM-5, (b) H-[B]ZSM-5, (c) H(Zn)-[Fe]ZSM-5(4.0), and (d) H(Zn)-[B]ZSM-5(4.0) : (I) in He flow with CD\(_3\)CN vapor at RT; (II) in pure He flow at RT immediately removing CD\(_3\)CN vapor; (III) in He flow after heating to 373 K; (IV) in He flow after heating to 423 K; (V) in He flow after heating to 473 K.
Figure 7.10 DRIFTS spectra of H(Zn)-[Al]ZSM-5(4.0) : (I) in He flow with CD$_3$CN vapor at RT; (II) in pure He flow at RT immediately removing CD$_3$CN vapor; (III) in He flow after heating to 323 K; (IV) in He flow after heating to 373 K; (V) in He flow after heating to 473 K.

The spectra changed significantly following the addition of 4wt % Zn to H-[Fe]ZSM-5 (Figure 7.9c). Upon exposure to CD$_3$CN vapor, two υ(CN) stretching regions were again observed, but the higher-frequency band was now centered near 2308 cm$^{-1}$. Upon removal of excess CD$_3$CN, only the 2308 cm$^{-1}$ peak remained. These results closely resemble what has been observed on Sn-containing zeolites, suggesting that the ion-exchanged Zn cations have Lewis-acid character on both the aluminosilicate and ferrosilicate zeolites. By contrast, the FTIR results for CD$_3$CN adsorbed on Zn-incorporated H-[B]ZSM-5, shown in Figure 7.9d, did not exhibit a peak near 2310 cm$^{-1}$. The primary vibrational band on this material was centered near 2267 cm$^{-1}$ and did not shift as the coverage decreased. The small shoulder near 2310 cm$^{-1}$ on H(Zn)-[B]ZSM-5(4.0) is likely associated with residual Al impurities in this sample.

Both the TPD-TGA and FTIR results indicate that Zn cations that displace Brønsted-acid sites in [Fe]ZSM-5 and [Al]ZSM-5 have special adsorption properties that are very different from those of normal Zn cations in materials such as silica. Furthermore, these special properties,
although indistinguishable on [Fe]ZSM-5 and [Al]ZSM-5, are not duplicated in [B]ZSM-5. Finally, the fact that similar Zn sites could be formed from Brønsted-acid sites on an amorphous Al₂O₃/SiO₂ sample implies that the local structure of the site is not a determining factor in producing the special Zn sites.

7.3.3 Examination of Ga Exchange with Protonic Sites

The addition of Ga to H-[Al]ZSM-5 was found to give rise to adsorption and reaction properties similar to those found with Zn, although the replacement of Brønsted-acid sites by Ga was less efficient in that more Ga had to be added to achieve a significant reduction in Brønsted-acid sites.⁹ To determine whether similar Ga sites could be formed in either H-[Fe]ZSM-5 or H-[B]ZSM-5, we performed TPD-TGA experiments with 2-propanamine on both of these materials after the incorporation of 4 wt % Ga. The results are shown in Figure 7.11.

Figure 7.11 TPD-TGA of 2-propanamine over (a) H(Ga)-[Fe]ZSM-5(4.0), and (b) H(Ga)-[B]ZSM-5(4.0). The peaks correspond to ammonia (m/e =17), propene (m/e = 41, 42), and 2-propanamine (m/e =17, 41, 42, and 44).
The results for 2-propanamine on Ga-exchanged H-[Fe]-ZSM-5 (Figure 7.11a) are very similar to the analogous results for Ga-exchanged H-[Al]ZSM-5 (Figure 7.8b). Similar to the case for Zn exchange, the addition of Ga replaced some of the propene-ammonia desorption feature between 575 and 650 K with a second high-temperature reaction feature above 650 K. Again, the products formed above 650 K were not simply additional propene and ammonia, as demonstrated by the fragmentation patterns in the mass spectra. The TPD-TGA results for 2-propanamine on Ga-exchanged H-[B]ZSM-5, shown in Figure 7.11b, were not significantly affected, indicating that the Ga sites associated with B do not have special adsorption properties.

7.3.4 Catalytic Properties of Zn- and Ga-Exchanged H-ZSM-5

To determine how exchanged Zn and Ga cations affect catalytic properties, the reaction of n-hexane was measured at 1 bar and 773 K, under conditions of differential conversions. Table 7.3 reports the rates of n-hexane conversion and the turnover frequencies (TOFs) for the unmodified zeolites and for zeolites with either 4 wt % Zn or 4 wt % Ga. (Note that the TOFs were based on Bronsted-acid site densities determined from the amount of 2-propanamine that reacted between 575 and 650 K by TPD-TGA.) The TOF for H-[Al]ZSM-5 was 0.30 s⁻¹, a value that agrees well with data from previous work for the reaction of n-hexane under these conditions.⁶,⁹ The TOF on H-[B]ZSM-5, calculated from the reaction feature in the TPD-TGA of 2-propanamine, was a similar value, 0.24 s⁻¹. Given that alkane-cracking rates on H-[Al]ZSM-5 are reported to increase linearly with Al content,⁹¹,⁹² this result supports the conclusion that the Brønsted-acid sites in this material are due to Al impurities. Finally, the rates on H-[Fe]ZSM-5 were so low that they were difficult to measure. The TOF was less than 0.01 s⁻¹, which is a factor of 30 lower than the TOF determined for Brønsted-acid sites formed from framework Al, in agreement with previous reports.¹⁵⁵
Table 7.3 Turnover Frequencies (TOFs) and Rates of n-Hexane Conversion at 773 K and 1 bar

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>TOF (molecules/site·s)(^a)</th>
<th>Rates (×10(^{-4})) (mol/g·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-[Al]ZSM-5</td>
<td>0.30</td>
<td>1.5</td>
</tr>
<tr>
<td>H-[Fe]ZSM-5</td>
<td>&lt; 0.01</td>
<td>&lt; 0.04</td>
</tr>
<tr>
<td>H-[B]ZSM-5</td>
<td>0.24</td>
<td>0.07</td>
</tr>
<tr>
<td>H(Zn)-[Al]ZSM-5(4.0)</td>
<td>0.32</td>
<td>0.4</td>
</tr>
<tr>
<td>H(Zn)-[Fe]ZSM-5(4.0)</td>
<td>&lt; 0.06</td>
<td>&lt; 0.02</td>
</tr>
<tr>
<td>H(Zn)-[B]ZSM-5(4.0)</td>
<td></td>
<td>0.06</td>
</tr>
<tr>
<td>H(Ga)-[Al]ZSM-5(4.0)</td>
<td>0.31</td>
<td>1.2</td>
</tr>
<tr>
<td>H(Ga)-[Fe]ZSM-5(4.0)</td>
<td>&lt; 0.01</td>
<td>&lt; 0.03</td>
</tr>
<tr>
<td>H(Ga)-[B]ZSM-5(4.0)</td>
<td></td>
<td>0.06</td>
</tr>
</tbody>
</table>

\(^a\)Normalized to Brønsted-site concentrations determine from TPD-TGA.

Table 7.4 Molar Selectivities (%) for n-Hexane Cracking over H-[Al]ZSM-5, H(Zn)-[Al]ZSM-5(4.0), and H(Ga)-[Al]ZSM-5(4.0) at 137 bar and 633 K

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>BTX products (%)</th>
<th>H(_2) (%)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-[Al]ZSM-5</td>
<td>7.7</td>
<td>5.2</td>
<td>6.2</td>
</tr>
<tr>
<td>H(Zn)-[Al]ZSM-5(4.0)</td>
<td>20.9</td>
<td>22.3</td>
<td>5.8</td>
</tr>
<tr>
<td>H(Ga)-[Al]ZSM-5(4.0)</td>
<td>19.4</td>
<td>15.3</td>
<td>5.2</td>
</tr>
</tbody>
</table>

For H(Zn)-[Al]ZSM-5 and H(Ga)-[Al]ZSM-5, the rates of n-hexane conversion decreased because of the decrease in Brønsted-acid site density, but the TOFs remained essentially the same. However, the product distribution (see Table 7.4) changed dramatically upon the addition of either Zn or Ga for n-hexane conversion at high pressures. The addition of either Zn or Ga to H-[Al]ZSM-5 significantly increased the production of BTX products (benzene, toluene, and xylenes) and H\(_2\). The conversions of n-hexane on the Zn- and Ga-containing [Fe]ZSM-5 and [B]ZSM-5 remained negligible. Both of these observations imply that the Ga and Zn sites, by themselves, are
not able to activate the n-hexane molecules. Strong Brønsted-acid sites are required to initiate the reaction. Because H-[Fe]ZSM-5 is able to oligomerize olefins,\textsuperscript{154} we also examined the adsorption of propene on H-[Fe]ZSM-5 and H(Zn)-[Fe]ZSM-5(4.0) using TPD-TGA measurements. For the data in Figure 7.12, the samples were exposed to 10 Torr of propene at room temperature, ramped at 10 K/min in propene to 323 K, evacuated for 1 h, and then cooled to room temperature before the TPD measurements were performed. The results for adsorption on H-[Fe]ZSM-5 (Figure 7.12a) are similar to those reported previously.\textsuperscript{154} The initial coverage after evacuation was approximately 900 μmol of propene/g, a value equal to twice the site density. In TPD, a small amount of unreacted propene desorbed at 350 K, but most desorption occurred from a peak centered at about 460 K. Because the mass spectra showed peaks with m/e values greater than the molecular weight of propene, this desorption feature must result from the decomposition of oligomers that form at the Brønsted-acid sites. The absence of a peak at m/e = 78 shows that the desorption products did not include benzene, in agreement with a previous study of propene adsorption in H-[Fe]ZSM-5 and in contrast to results following the adsorption of propene in H-[Al]ZSM-5.\textsuperscript{154}

![Figure 7.12 TPD-TGA of Propene over (a) H-[Fe]ZSM-5, and (b) H(Zn)-[Fe]ZSM-5(4.0). The peaks correspond to propene (m/e = 41), oligomers (m/e = 41, 56, 69), and benzene (m/e = 78).]
The TPD–TGA results following propene adsorption in H(Zn)-[Fe]ZSM-5(4.0) (Figure 7.12b) exhibited surprising differences. For the same propene exposure, the initial coverage was lower, only 300 μmol of propene/g; however, because the Brønsted-acid site density was less than 10% of that on the parent H-[Fe]ZSM-5, only 30 μmol/g, the coverage of propene per Brønsted-acid site was actually significantly larger. Also, the desorption products and temperatures were very different. First, a significant fraction of the adsorbed propene desorbed unreacted at about 400 K on H(Zn)-[Fe]ZSM-5(4.0). Because propene oligomerizes on Brønsted-acid sites and is easily evacuated from siliceous ZSM-5, we suggest that there must be some attraction between propene and the Zn sites. Although the quantity of propene leaving the sample in the 400 K peak was less than the Zn-site concentration (∼350 μmol/g) of this sample, the peak temperature was low enough that some fraction of propene adsorbed at Zn sites would likely be removed during evacuation. Second, the oligomers that formed were removed at a higher temperature, between 500 and 600 K. Again, the higher peak temperature might be due to interactions between the Zn sites and the larger olefins formed by oligomerization. Finally, a nontrivial amount of benzene (m/e = 78) was observed in a peak near 650 K. All of these results suggest that there is a relatively strong interaction between the Zn sites and olefinic species and that these interactions are responsible for the dehydrocyclization reaction.

7.4 Discussion

The results from our study of Zn and Ga exchange into H-[Al]ZSM-5, H-[Fe]ZSM-5, and H-[B]ZSM-5 provide several important insights into the nature of the sites responsible for aromatics formation in Zn- and Ga-exchanged [Al]ZSM-5. First, the 2-propanamine adsorption studies indicate that protonic sites are removed in both H-[Al]ZSM-5 and H-[Fe]ZSM-5 upon the addition of either Zn or Ga. The exact nature of this exchange process is uncertain. Because one metal site forms for the removal of each Brønsted-acid site, it is unlikely that the metal cations are coordinated
to multiple framework exchange sites. Furthermore, a previous attempt to displace Brønsted-acid sites in H-[Al]ZSM-5 with another multivalent ion, Sr$^{2+}$, showed no loss of Brønsted acidity. Therefore, the metal cations must either be present as compound cations [e.g., Zn(OH)$^+$] or be reduced to their univalent states. Both of these possibilities were suggested previously.$^{15}$ Although identification of the cation oxidation states would seem to be straightforward by techniques such as X-ray absorption near-edge structure (XANES) spectroscopy, a recent publication showed that the interpretation of the spectra might not be simple.$^{166}$

Whatever the chemical nature of the Zn and Ga cations that exchange with Brønsted-acid sites in H-[Al]ZSM-5 and H-[Fe]ZSM-5, it is different from that of the cations that form upon simple infiltration into amorphous silica, such as SBA-15, or into borosilicates such as H-[B]ZSM-5. The metal cations that displace Brønsted-acid sites in both H-[Al]ZSM-5 and H-[Fe]ZSM-5 are able to adsorb 2-propanamine and promote the dehydrogenation reactions of the amine molecules at high temperatures, whereas there was no evidence for the adsorption of the amine on the Zn or Ga sites in H-[B]ZSM-5 or in purely siliceous materials. Based on the fact that a similar reactive adsorption occurs with Zn cations that exchange for Brønsted-acid sites on amorphous silica-alumina, the zeolite structure does not appear to be a critical factor for achieving these special properties. Because Zn cations at exchange sites in [Al]ZSM-5 and [Fe]ZSM-5 appear to have similar adsorption properties, the proton affinity of the framework anion does not appear to be a major factor, so long as it is low enough to produce a Brønsted-acid site, which [B]ZSM-5 cannot.

The inability of Zn-exchanged H-[Fe]ZSM-5 to catalyze the reaction of n-hexane confirms previous reports that the exchanged metal sites are not able to activate alkanes. Although the Brønsted-acid sites in H-[Fe]ZSM-5 are able to protonate amines in a manner similar to the sites in H-[Al]ZSM-5, they are not able to catalyze alkane cracking for reasons discussed by Deshlahra and Iglesia.$^{157}$ In the absence of these Brønsted-acid catalyzed reactions, the metal sites are not able to promote reactions of alkanes.
It seems likely that the selectivity changes observed for reactions of alkanes in Zn- and Ga-exchanged zeolites are initiated by the production of olefins at Brønsted-acid sites, at least locally, and that it is the interaction of olefins with the metal sites that leads to dehydrogenation activity. In H-[Al]ZSM-5, olefins oligomerize rapidly upon adsorption, even at room temperature, making it very difficult to study the interaction of olefins with metal sites in the aluminosilicate when any Brønsted-acid sites are present. Because complete exchange of the Brønsted-acid sites with Zn or Ga is difficult, adsorption studies of olefins on the metal-exchanged [Al]ZSM-5 samples is difficult. However, as shown in this and earlier studies, olefin oligomerization is much slower in H-[Fe]ZSM-5, offering the possibility of observing olefin interactions with the metal sites. Based on our present propene adsorption results, olefins do indeed appear to interact with the metal sites. Exactly how this leads to dehydrogenation is uncertain.

It is interesting to ask whether there is a relationship between Zn- and Ga-exchanged zeolites and Mo-exchanged materials. Mo-exchanged ZSM-5 has received a great deal of attention recently because of its ability to form aromatics from reactions with natural gas. In that case, isolated molybdenum oxide species are reported to agglomerate and convert into molybdenum carbide nanoparticles under the reaction conditions. We are not aware of evidence for a similar conversion of Zn or Ga species during the reaction, but the possibility exists that species formed during the reaction are different from those observed prior to the reaction.

Obviously, there is still much to learn about the nature of metal-exchange sites in zeolites. The need for new technologies to perform endothermic reforming and produce aromatics from lighter feedstocks suggests that continued work on these materials is required.

7.5 Summary

In this chapter, based on the adsorption of 2-propanamine, I have shown that the nature of Zn and Ga cations exchanged into [Fe]ZSM-5 is similar to that of the cations in Al-containing zeolites. The sites are able to hold the amine to high temperatures and promote dehydrogenation
reactions. By contrast, Zn and Ga cations in a purely siliceous material, such as SBA-15, and in H-[B]ZSM-5 do not exhibit these special properties. Although the Zn and Ga sites in exchanged H-[Fe]ZSM-5 are not capable of activating alkanes, they do interact with olefins and are capable of forming aromatics from olefins.
Chapter 8. Heat-Flow Measurements for n-Hexane Reactions on
H-ZSM-5 and H(Zn)-ZSM-5: Implications for Endothermic Reforming
in Hypersonic Aircraft

8.1 Introduction

In the above Chapters, conclusions concerning the endothermicity of reactions over H-ZSM-5 and H(Zn)-ZSM-5 were based on product selectivities. Furthermore, the product selectivities could only be accurately determined at low conversions. This raises many questions, especially concerning the effect of higher fuel conversion. In the present Chapter, I developed a system to measure the heats of reaction at high temperature and pressures and then used this to characterize the thermal effects of n-hexane cracking on the acidic zeolite H-ZSM-5 and of aromatization on the Zn-exchanged H(Zn)-ZSM-5. To avoid the effects of homogeneous pyrolysis reactions, which can also be endothermic, experiments were performed at temperatures below 773 K. I will demonstrate that the heats of reaction under these conditions are a strong function of conversion. While reactions over H(Zn)-ZSM-5 show promise, the acid-catalyzed reactions were found to be thermoneutral at low conversions to exothermic at high conversions.

8.2 Experimental Section

8.2.1 Materials

The ZSM-5 sample with a Si/Al₂ ratio of 50 (CBV 5524G), and the Zn-promoted zeolite, H(Zn)-ZSM-5, with 1.3 wt % Zn (200μmol of Zn/g) were the same as used in previous Chapter. Characterization of the Brønsted-acid and Zn sites in H-ZSM-5 and H(Zn)-ZSM-5 has been
discussed in detail previously. Most significant was the information obtained from TPD-TGA measurements of 2-propanamine, which are reproduced in Figure 8.1 and Figure 8.2. These showed that amine molecules adsorbed at Brønsted-acid sites decompose to propene and ammonia between 575 K and 650 K, via the Hoffman-Elimination reaction, while amine molecules adsorbed on Zn sites decomposed to a mixture of dehydrogenation products above 650 K.

Figure 8.1 TPD-TGA of 2-propanamine over H-ZSM-5. The peaks correspond to ammonia (m/e =17), propene (m/e = 41), and 2-propanamine (m/e =17, 41, and 44).
Figure 8.2 TPD-TGA of 2-propanamine over H(Zn)-ZSM-5. Below 550 K, the peaks correspond to 2-propanamine (m/e =17, 41, 42, and 44). Between 575 and 650 K, the peaks are due to ammonia (m/e =17) and propene (m/e = 41 and 42). Above 650 K, the peaks at m/e =17 and 41 correspond to a range of dehydrogenation products.

From the TPD-TGA data, the Brønsted-acid site density for the H-ZSM-5 sample was shown to be 500 μmol/g, close to the Al content of the zeolite, as expected. After the addition of 1.3 wt % Zn (200 μmol of Zn/g), the H(Zn)-ZSM-5 had 300 μmol/g of Brønsted-acid sites and 200 μmol/g of Zn sites, implying that each Zn cation removed one Brønsted-acid site and replaced it with a Zn site. As discussed in the earlier study,\textsuperscript{15} this one-for-one replacement of Brønsted sites with Zn sites was a general observation for ZSM-5 samples with Zn loadings below ~0.5 Zn/Al.\textsuperscript{15} Key properties for the H-ZSM-5 and H(Zn)-ZSM-5 samples used in the present study are summarized in Table 8.1.
Table 8.1 Summary of Properties for the Zeolite Samples Used in This Study

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al</th>
<th>Metal content (wt %)</th>
<th>Metal content (µmol/g)</th>
<th>Brønsted-acid site density (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5</td>
<td>50</td>
<td>0</td>
<td>0</td>
<td>500</td>
</tr>
<tr>
<td>H(Zn)-ZSM-5</td>
<td>50</td>
<td>1.3</td>
<td>200</td>
<td>300</td>
</tr>
</tbody>
</table>

*Measured by TPD-TGA of 2-propanamine.

8.2.2 Apparatus for Measuring Heats of Reaction

The design of the apparatus used to measure heats of reaction was based loosely on the equipment described for a similar study by Huang et al.\(^1\) and is shown schematically in Figure 8.3.

![Figure 8.3 Schematic diagram of the apparatus used in the heat-flow measurements.](image)

Liquid n-hexane (>99% purity, Acros Organics) was fed to the system using an HPLC pump and the pressure in the reactor was controlled by a back-pressure regulator near the reactor exit. The HPLC pump maintained a constant flow rate while simultaneously measuring the pressure. The feed was introduced first to a preheater furnace, where its temperature was increased to either
573 K or 673 K. The preheated n-hexane then entered the reactor, which was a 3/8 in. outer diameter (OD), 7.8 mm inner diameter (ID), stainless-steel tube, 20 cm long, inserted in a second tube furnace that was operated at the reaction temperature. Because the flow of cooler n-hexane from the preheater to the reactor caused the reactor temperature to decrease slightly, additional heat was supplied directly to the reactor through a Nichrome wire that was wrapped around the stainless-steel reactor tube. Current was passed through the Nichrome wire, using a DC power supply in order to maintain the reactor at a constant temperature. The reactor temperature was measured using a thermocouple positioned in the middle of the catalyst bed, as shown in Figure 8.3. Additional thermocouples were placed at the front and back of the reactor to ensure that temperature gradients were negligible. The power required to maintain the temperature of the reactor was simply read from the DC power supply. The accuracy of the power requirements was estimated to be within ∼5%, based on measurements with the reactor in the absence of catalyst.

To minimize the pressure drop in the reactor, the catalyst powders were pressed into 0.5-mm-thick wafers, broken into pieces, and then loaded into the middle of the reactor tube. The length of the catalyst bed varied from 0.5 to 5 cm, depending on the catalyst loading. The catalyst wafers were held in the middle of the reactor tube, using glass wool. Products from the reactor were analyzed with the same online gas chromatograph in previous Chapters. While the production rates of lighter hydrocarbons could be determined with reasonable accuracy, the complexity of the product distribution at high conversions made a detailed analysis of the heavier products impossible, so that production rates for these were determined by difference.

Stability was not an issue in these experiments. Figure 8.4 shows the normalized conversion of n-hexane reaction over H-ZSM-5 and H(Zn)-ZSM-5 at 60 bar as a function of time at two different temperatures and demonstrates that deactivation was negligible for at least 3 h. A measurement of the catalyst weight after 4 h of reaction in n-hexane at high conversion and 773 K showed a weight increase of only 5%. Moreover, for the measurements used in this study, only two or three data points were taken before replacing the catalyst with a fresh sample.
Figure 8.4 Normalized conversion of n-hexane reaction over (a) H-ZSM-5, and (b) H(Zn)-ZSM-5 at 60 bar as a function of time at 673 K (■), and 773 K (▲).

8.3 Results

In order to verify the heat-flow measurements, the initial experiments were performed using the reactor without catalyst. Figure 8.5 shows the power requirement for maintaining constant reactor temperature, as a function of liquid n-hexane flow rate at a pressure of 60 bar. In Figure 8.5a, the n-hexane was preheated to 573 K before entering the reactor, then heated to 673 K in the reactor. In Figure 8.5b and Figure 8.5c, the n-hexane was preheated to 673 K and left the reactor at 723 and 773 K, respectively. In all three plots, the power requirement increases linearly with n-hexane flow rate, as expected. A simple energy balance shows that the slopes of the lines in these three plots can be used to calculate the heat capacity of n-hexane, averaged over the temperature range that the n-hexane is heated. Based on those calculations and Figure 8.5a, the averaged heat capacity for n-hexane between 573 and 673 K was determined to be $270 \pm 18 \text{ J/(mol K)}$, in reasonable agreement with NIST data ($259 \text{ J/(mol K)}$). Between 673 K and 723 K, the averaged heat capacity was $288 \pm 15 \text{ J/(mol K)}$, compared to the NIST value of $279 \text{ J/(mol K)}$. Finally, the averaged heat capacity in the temperature range from 673 K to 773 K was determined
to 313 ± 20 J/(mol K) from Figure 8.5c, compared to 286 J/(mol K) from the NIST website. The agreement between these values provides confidence that the system is capable of measuring heat flows due to reaction.

![Graphs showing power required to maintain a constant temperature as a function of flow rate for heating n-hexane at 60 bar from (a) 573 K to 673 K, (b) 673 K to 723 K, and (c) 673 K to 773 K.](image)

Figure 8.5 Power required to maintain a constant temperature, as a function of flow rate for heating n-hexane at 60 bar from (a) 573 K to 673 K, (b) 673 K to 723 K, and (c) 673 K to 773 K.

8.3.1 H-ZSM-5

Because heat-flow results were found to be dependent strongly on conversion, measurements on the acidic zeolite were performed as a function of flow rate for two catalyst loadings at both 673 K and 773 K. Data at 673 K are shown in Figure 8.6a and Figure 8.6b for H-ZSM-5 loadings of 0.3 and 0.9 g of catalyst, respectively. These results are also summarized, together with the conversion and a rough product distribution, in Table 8.2. Considering first the case for 0.3 g of catalyst in Figure 8.6a, the difference between results for the empty reactor and for one with H-ZSM-5 is negligible, except for the lowest flow rate, for which the reaction was actually exothermic. In part, this is due to low conversions at the higher flow rates; however, the conversions were significant at the lower flow rates, reaching 98%. With the higher catalyst loading (Figure 8.6b), the reaction was always exothermic.
Figure 8.6 Power required to maintain constant temperature, as a function of flow rate for n-hexane reacting over H-ZSM-5 at 60 bar and 673 K with (a) 0.3 g and (b) 0.9 g of catalyst. The n-hexane entered the reactor at 573 K.

Because conversion varies with residence time in the reactor, the data in Table 8.2 are organized by the weight hourly space velocity (WHSV, g n-hexane/g catalyst h). Table 8.2 also shows the heats of reaction per mole of n-hexane converted, determined from the difference between heat flows in the empty reactor and the reactor with catalyst, divided by the conversion. The heats of reaction vary from slightly endothermic (+5 kJ/mol) at the lowest conversion to mildly exothermic at the highest conversions (between -16 kJ/mol and -25 kJ/mol). The change in the heats of reaction with conversion are due to changes in the product distributions. At the lowest conversions, most of the products were light alkanes and alkenes, shown as <C6, together with a significant amount of benzene, toluene, and xylene (BTX). As discussed in a previous publication, alkene production was relatively low, due to hydride-transfer reactions, so that the reaction is only slightly endothermic. At the higher conversions, most of the products were high-molecular-weight
species (C7+) that we were unable to identify in detail. These large products almost certainly account for the decrease in endothermicity of the reaction.

Table 8.2 n-Hexane reactions at 60 bar and 673 K over H-ZSM-5 and H(Zn)-ZSM-5

<table>
<thead>
<tr>
<th>Flow Rate (mL/min)</th>
<th>0.30</th>
<th>0.53</th>
<th>0.88</th>
<th>0.30</th>
<th>1.10</th>
<th>1.31</th>
<th>0.53</th>
<th>0.88</th>
<th>1.10</th>
<th>1.31</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst Amount (g)</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.3</td>
<td>0.9</td>
<td>0.9</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>WHSV (g n-hexane/g-catalyst-hr)</td>
<td>13</td>
<td>23</td>
<td>38</td>
<td>39</td>
<td>48</td>
<td>57</td>
<td>69</td>
<td>115</td>
<td>144</td>
<td>172</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>H-ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; C6 (%)</td>
</tr>
<tr>
<td>BTX (%)</td>
</tr>
<tr>
<td>C7+ (%)</td>
</tr>
<tr>
<td>Conversion (%)</td>
</tr>
<tr>
<td>Heat of Reaction (kJ/mol)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>H(Zn)-ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; C6 (%)</td>
</tr>
<tr>
<td>BTX (%)</td>
</tr>
<tr>
<td>C7+ (%)</td>
</tr>
<tr>
<td>Conversion (%)</td>
</tr>
<tr>
<td>Heat of Reaction (kJ/mol)</td>
</tr>
</tbody>
</table>

Conclusions from results for reaction at 773 K, shown in Figure 8.7 and Table 8.3, are essentially the same. In this case, the catalyst loadings were decreased to 0.02 and 0.15 g in order to maintain lower conversions. The reactions were again thermoneutral at lower conversions and exothermic at higher conversions. Possibly because the rates are higher at 773 K, the reaction had a tendency to be more exothermic, reaching values as large in magnitude as -40 kJ/mol.
Table 8.3 n-Hexane reactions at 60 bar and 773 K over H-ZSM-5 and H(Zn)-ZSM-5

<table>
<thead>
<tr>
<th>Flow Rate (mL/min)</th>
<th>0.30</th>
<th>0.53</th>
<th>0.88</th>
<th>0.30</th>
<th>0.53</th>
<th>0.88</th>
<th>1.31</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst Amount (g)</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>WHSV (g n-hexane/g catalyst·hr)</td>
<td>79</td>
<td>139</td>
<td>230</td>
<td>589</td>
<td>1041</td>
<td>1729</td>
<td>2573</td>
</tr>
</tbody>
</table>

H-ZSM-5

| < C6 (%) | 9 | 19 | 25 | 30 | 41 | 86 |
| BTX (%)  | 1 | 1 | 3 | 4 | 3 | 4 |
| C7+ (%)  | 90 | 80 | 72 | 66 | 56 | 10 |

| Conversion (%) | 98 | 88 | 60 | 75 | 50 | 25 | 5 |
| Heat of Reaction (kJ/mol) | -40 | -34 | -1 | -5 | -10 | -8 | 0 |

H(Zn)-ZSM-5

| < C6 (%) | 4 | 6 | 7 | 15 | 34 | 65 |
| BTX (%)  | 0.5 | 0.7 | 1 | 5 | 8 | 10 |
| C7+ (%)  | 95 | 94 | 92 | 80 | 58 | 25 |

| Conversion (%) | 98 | 90 | 83 | 67 | 50 | 20 | 7.3 |
| Heat of Reaction (kJ/mol) | -32 | 0 | 1 | 31 | 46 | 42 | 45 |

Figure 8.7 Power required to maintain constant temperature as a function of flow rate for n-hexane reaction over H-ZSM-5 at 60 bar and 773 K with (a) 0.02 g and (b) 0.15 g of catalyst. The n-hexane entered the reactor at 673 K.
8.3.2 H(Zn)-ZSM-5

The heat-flow and reaction results for the H(Zn)-ZSM-5 catalyst at 673 K are shown in Figure 8.8 and Table 8.2. The heat-flow measurements with 0.3 g of catalyst (Figure 8.8a) showed the reaction to be endothermic in all cases. For the larger catalyst loading (Figure 8.8b), the reaction changed from endothermic at high flow rates to exothermic at the lowest flow rates. The low flow rates and high catalyst loading again correspond to high conversions. Table 8.2 shows that the heats of reaction are significantly endothermic for all conversions approaching 90% (in the range of 30-50 kJ/mol). These values agree very well with heats of reaction previously calculated from the product distributions at differential conversions for n-hexane on H(Zn)-ZSM-5.\textsuperscript{15} For comparison, the enthalpy change under standard conditions associated with heating n-hexane by 200 K is also 50 kJ/mol. In addition, Table 8.2 shows that the major difference between H(Zn)-ZSM-5 and H-ZSM-5 is the high rate of BTX production on the Zn-containing material. In previous work, it was demonstrated that BTX production was accompanied by H\textsubscript{2} production, which was not measured in the present study. At the highest conversions, the reaction does become exothermic. The product distribution shows that this is accompanied by consumption of the BTX. Results for H(Zn)-ZSM-5 at 773 K, reported in Figure 8.9 and Table 8.3, lead to similar conclusions as those reached at 673 K. Because of the higher temperatures, the conversions were higher and the system exhibited an increased tendency to become exothermic.
Figure 8.8 Power required to maintain constant temperature as a function of flow rate for n-hexane reaction over H(Zn)-ZSM-5 at 60 bar and 673 K with (a) 0.3 g and (b) 0.9 g of catalyst. The n-hexane entered the reactor at 573 K.

Figure 8.9 Power required to maintain constant temperature as a function of flow rate for n-hexane reaction over H(Zn)-ZSM-5 at 60 bar and 773 K with (a) 0.02 g and (b) 0.15 g of catalyst. The n-hexane entered the reactor at 673 K.
As noted earlier, interpretation of the heat-flow curves is somewhat complex because of the fact that the power required to maintain a constant temperature is affected by both the flow rate (the amount of material that must be heated) and the conversion, both of which change with flow rate. A more useful way to visualize the results is from plots of the heats of reaction versus conversion, shown for 673 K in Figure 8.10a and for 773 K in Figure 8.10b. Results are reported for both H-ZSM-5 and H(Zn)-ZSM-5. At both temperatures, acid-catalyzed cracking on H-ZSM-5 is thermoneutral at best, becoming slightly exothermic at high conversions. The reaction on H(Zn)-ZSM-5 is significantly endothermic, so long as the conversion is maintained below 70%.

Figure 8.10 Heats of reaction for n-hexane conversion at 60 bar over HZSM-5 and H(Zn)-ZSM-5: (a) 673 K and (b) 773 K.

8.4 Discussion

The results from this study reinforce a previous report that the product distribution, not simply fuel conversion, is the critical issue for determining whether or not a reaction is going to be endothermic. While results may well be dependent on the nature of the fuel, the H-ZSM-5, acid-catalyzed cracking of n-hexane will clearly not be effective as a reaction for cooling aircraft engines in hypersonic flight. As discussed in the previous publications, saturation of olefins due to
bimolecular, hydride transfer reactions appears to have an important and deleterious (for this application) effect on the heats of reaction. The addition of Zn to promote aromatization reactions improves the product distribution to the point that the reactions can be endothermic enough to provide significant cooling. However, high conversions are not desirable, because this situation promotes further reaction of the favorable products, which are responsible for the desired heats of reaction. This was most noticeable by the large decrease in the production of BTX observed at high conversions on H(Zn)-ZSM-5. We suggest that these small aromatics react to form polyaromatics at high conversions, and it is the production of these polyaromatic compounds that is responsible for the reaction becoming exothermic.

It is important to reconcile the above conclusions with other reports which have found acid-catalyzed cracking reactions to be endothermic. One possibility is that the endothermic reactions in previous work were actually the result of homogeneous pyrolysis. Pyrolysis of alkanes can produce significant quantities of ethylene, which would be highly desirable for this application. The homogeneous reactions will only be important at higher temperatures, a primary reason we chose to work at temperatures below 800 K. In the work of Huang et al., homogeneous, endothermic reactions with n-octane as fuel became significant above ~873 K, even at high fuel flow rates. In another example, Saldana and Bogin reported that 10% of n-pentane is converted in 0.6 s at 923 K.

It is interesting to compare H(Zn)-ZSM-5-catalyzed, endothermic reforming to homogeneous endothermic reforming. The catalyzed reactions occur at lower temperatures, implying that heat from fuel reactions can be removed at lower temperatures. Because the same homogeneous reactions that produce olefins can also lead to tar formation that can “plug” fuel lines, this would seem to be an advantage for the catalyzed reactions. Using the results of Huang et al. as a measure of how much heat can be removed by the homogeneous reaction, a maximum cooling of ~950 kJ/kg was achieved with n-octane, compared to cooling of ~600 kJ/kg in our study with n-hexane. Finally, since the catalyzed reactions occur at lower temperatures, it may be possible to
use a combination of catalyzed reactions at lower temperatures and homogeneous reactions at higher temperatures by proper placement of the catalyst in select places within the fuel lines.

One clear result of the present study, with regard to the development of new catalysts, is that careful attention must be paid to the product distribution. To be effective, the catalyst must generate products, such as H₂, small aromatic compounds, and small olefins, which make the reactions more endothermic. We suggest that optimization of the catalyst could indeed lead to changes in the product selectivity that would further increase the cooling capacity of the catalyzed reactions. For example, it is well-known that product selectivities for catalytic cracking are strongly dependent on zeolite structure and the same is likely true for aromatization catalysts. There may also be differences due to the choice of fuels. This is still a relative new application with opportunities for improvement.

8.5 Summary

In this chapter, I have demonstrated that the acid-catalyzed cracking of n-hexane over H-ZSM-5 zeolite catalysts was shown to be ineffective for endothermic reforming applications. For reaction at 60 bar and both 673 and 773 K, the reactions were found to be mildly endothermic at low conversions and exothermic at high conversions. Aromatization reactions over H(Zn)-ZSM-5 exhibit much better endothermicities under these conditions at conversions of <70% but can also become exothermic at very high conversions. In the development of new catalysts, careful attention must be paid to the product selectivities.
Chapter 9. Conclusions

This thesis focused on the metal-exchanged zeolites for application to endothermic reforming of the fuels, using well-defined experimental conditions to determine which factors are important in these reactions. The results presented in this thesis make a significant contribution towards a better understanding of the active sites in metal-exchanged zeolites and demonstrated that careful attention must be paid to the product distribution in the development of new catalysts.

In Chapter 3, CH₄ adsorption was studied experimentally and theoretically on ZSM-5, MOR, and ZSM-12 zeolites using calorimetric measurements at 195 K and plane wave DFT calculations. Differential heats measured on four different H-ZSM-5 samples were determined to be 22.5 ± 1 kJ/mol, independent of Brønsted site density or defect concentration. However, DFT calculations performed using various functionals and on the most stable Brønsted site indicated that CH₄ should bind to this site by an additional 1-7 kJ/mol, a discrepancy that is due to the inability of standard DFT methods to capture hydrogen-bonding effects accurately with CH₄. Differential heats for CH₄ in MOR were 30 ± 1 kJ/mol at low coverages, falling to 25 kJ/mol for coverages above one molecule per 8-membered-ring side pocket, while differential heats on ZSM-12 were initially 22.5 kJ/mol, decreasing to 21 kJ/mol with coverage. DFT calculations on the siliceous form of the zeolites were able to predict these values within 5 kJ/mol in most cases. The results indicate that CH₄ is an excellent probe molecule for characterizing the pore structure of zeolites.

In Chapter 4, the adsorption of a series of small alkanes was studied experimentally on H-ZSM-5 zeolites using calorimetric measurements in order to determine their interactions with the Brønsted sites. Differential heats measured on four ZSM-5 samples with different Si/Al₂ ratio and with different defect concentrations were found to depend strongly on the Brønsted-site density but not on the presence of defects. The interactions for CH₄ with the Brønsted sites were minimal but the effect was significant (up to 11 ± 2 kJ/mol extra heats) for larger alkanes, such as n-C₆H₁₄. The affinity of the alkanes with the Brønsted sites increased with the gas-phase proton affinity of the
alkanes and the calculated affinity of the alkanes for the strong acid, fluorosulfonic acid. The extra heats of adsorption in H-ZSM-5 over its siliceous counterparts can therefore be associated with the strength of hydrogen bonding between the adsorbed alkane and the Brønsted sites, which in turn increases with molecular size. Specifically, extra heats were found to vary linearly with acid affinity corrected for dispersion interactions. The comparison of the experimental and computational results, therefore, indicates that the hydrogen bonded interaction theory describes the effect of Brønsted sites for alkane adsorption on zeolites.

In Chapter 5, the supercritical, high-pressure reaction of n-hexane over H-ZSM-5, with and without the addition of Pt and Ga, has been studied for application to endothermic reforming in scramjet engines. The endothermicities of the reactions were determined from the product distributions. For unpromoted H-ZSM-5, the product distribution indicated that the endothermicity is low and decreases with increasing pressure. The addition of Ga to H-ZSM-5 has a relatively small effect on n-hexane conversion but significantly increases the endothermicity of the reaction by increasing the selectivity to form small aromatics. The H(Ga)-ZSM-5 catalyst showed no deactivation for at least 5 h at 633 K and 137 bar of n-hexane. By contrast, the addition of Pt had a minor effect on both the rate and the reaction endothermicity.

In Chapter 6, the addition of Zn to H-ZSM-5 zeolites was studied for application to endothermic reforming in hypersonic aircraft engines. Temperature programmed desorption (TPD) and thermogravimetric-analysis (TGA) measurements with 2-propanamine on two H(Zn)-ZSM-5 samples showed that at low ion-exchange levels, less than 0.5 Zn/Al, each Zn cation displaces one Brønsted-acid site. Although rates for n-hexane conversion at 633 and 823 K and at a pressure of 137 bar decreased with the loss of Brønsted sites, Zn promotion greatly increased the production of H₂ and the formation of small aromatic molecules. FTIR of adsorbed acetonitrile-d₃ and calorimetric measurements of adsorbed CO at 195 K indicate that the exchanged Zn cations form Lewis-acid centers. A model in which the Zn cations, acting as Lewis-acid centers, polarize intermediates formed at Brønsted sites is presented as a way of understanding the observations.
In Chapter 7, the catalytic properties of H-[Fe]ZSM-5 and H-[B]ZSM-5 were explored after addition of Zn or Ga. TPD–TGA of 2-propanamine adsorbed on Zn and Ga-exchanged H-[Fe]ZSM-5 showed a decrease in Brønsted-acid site densities and the formation of new dehydrogenation sites, similar to what is observed following exchange in H-[Al]ZSM-5 and in amorphous silica-alumina. Exchanged Zn cations in [Fe]ZSM-5 also exhibited Lewis-acid character, as demonstrated by the appearance of a $\nu$(CN) stretch at 2310 cm$^{-1}$ upon adsorption of CD$_3$CN. By contrast, the sites in H-[B]ZSM-5 were not capable of protonating 2-propanamine, did not form dehydrogenation sites when Zn or Ga were added, and showed no evidence for sites with Lewis-acid character from the FTIR spectroscopy of CD$_3$CN. Neither H(Zn)-[Fe]ZSM-5 nor H(Zn)-[B]ZSM-5 catalyzed reactions of n-hexane at 773 K, but the TPD–TGA of adsorbed propene on H(Zn)-[Fe]ZSM-5 showed strong interactions between the Zn and olefins that might be responsible for the dehydrocyclization of light alkanes in Zn-exchanged, Al-containing zeolites.

In Chapter 8, the heat flows associated with conversion of n-hexane on H-ZSM-5 and H(Zn)-ZSM-5 were measured for reaction at 60 bar and both 673 and 773 K for application to endothermic reforming for hypersonic flight. The heat flows were determined by measuring the power required to maintain a constant reactor temperature upon introduction of flowing n-hexane. The acid-catalyzed reactions over H-ZSM-5 were found to be only mildly endothermic (<10 kJ/mol) at low conversions and exothermic at all conversions above 50%. The reactions on H(Zn)-ZSM-5 were significantly more endothermic (40-50 kJ/mol) for conversions of <70%; however, the reactions also became exothermic at very high conversions. Measurements of the product distributions showed that the reaction endothermicity for H(Zn)-ZSM-5 at lower conversions was likely due to the formation of significant amounts of benzene, toluene, and xylene, but that these were converted to higher-molecular-weight products at high conversions. Implications of these results for preparing improved endothermic-reforming catalysts is discussed.
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