

**CHARACTERIZATION OF SOLID LEWIS ACIDS IN BIOMASS CONVERSION
REACTIONS**

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ABSTRACT

CHARACTERIZATION OF SOLID LEWIS ACIDS IN BIOMASS CONVERSION REACTIONS

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Solid Lewis acids can be very selective in many important biomass reactions. Unfortunately, our understanding of solid Lewis acidity is very poor, making it difficult to design and select specific catalysts for a particular reaction. In this dissertation, solid Lewis acids were characterized using Temperature-Programmed Desorption (TPD)/Thermogravimetric Analysis (TGA), calorimetry, and a multiphase continuous flow reactor. A number of important catalyst families were examined in this work, including bulk metal oxides, ion-exchanged zeolites and framework substituted Lewis acid zeolites. It has been shown that the adsorption properties obtained from TPD-TGA and calorimetry experiments are very helpful in understanding reaction results. Adsorption studies are able to determine Lewis site density, relative adsorption strength and activation energies of monomolecular reactions, providing are extremely valuable information for catalysts. Biomass reactions over Lewis acid catalysts occur through multiple, complicated steps. My studies provide a basis for understanding solid Lewis acidity in biomass reactions.

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Chapter 1. Introduction

1.1 Background

Acid-catalyzed biochemical transformations are among the most important biomass conversion reactions. While these reactions are usually carried out with homogeneous phase acids, heterogeneous solid acids would have significant advantages since the solids are less corrosive, more environmentally friendly and easily separated from reactants. Much work has gone into understanding solid Brønsted acids due to their importance in refinery reactions, such as hydrocarbon cracking, olefin oligomerization, and aromatic alkylations. However, Brønsted sites tend to be unselective for many reactions involving biomass molecules due to the molecules being highly functionalized. Highly functionalized molecules tend to polymerize on the surface of Brønsted sites.

By comparison, solid Lewis acids can be very selective. Unfortunately, our understanding of solid Lewis acidity is very poor, making it difficult to design and select specific catalysts for a particular reaction. The goal of my Ph.D. research is to develop a better understanding of solid Lewis acids in biomass conversion and to devise methods for characterizing solid Lewis acidity. To study this, I built instruments for simultaneous Temperature-Programmed Desorption (TPD)/Thermogravimetric Analysis, calorimetry, and a multiphase continuous flow reactor for characterization and examination of solid Lewis acids. I used these techniques to characterize a number of important catalyst families were examined in this work, including bulk metal oxides, ion-exchanged zeolites and framework substitution Lewis acid zeolites. These advances will help in predicting reactions and broadening the application of solid Lewis acids in the future.

1.2 Definition

A brief review of definitions for Brønsted and Lewis acids is necessary before discussing methods and approaches. Brønsted acids are defined as proton donors [1]:



In aqueous solutions, the strength of an acid is usually defined by the equilibrium constant: $pK_a = -\log_{10} K_a$ where K_a is the equilibrium constant for Equation 1.1). For gas-phase acids, Brønsted acidity is measured in terms of proton affinity (PA= ΔH of Equation 1.1)) or gas-phase basicity (GB= ΔG of Equation 1.1)). Although GB should be directly related to pK_a , solvent effects often dominate the energetics of proton transfer in solutions. In most cases, PA and GB are used to extract information on the effects of the solvent.

Lewis acids are electron-pair acceptors, as shown in Equation 1.2).



Similar to Brønsted acidity, the energetics of Equation 1.2), either ΔH or ΔG , can be used to define the strength of a Lewis acid [2]. However, problem of Equation 1.2) is that it can be used to describe any chemical reaction, making the definition so broad that it is not always useful. For example, reactions as dissimilar as CO adsorption on Ni and benzene interacting with $AlCl_3$ can be considered as Lewis acid/base reactions. For quantification purposes, the reference base is also critically important in Lewis acidity. Unlike protons in Brønsted acids, electrons are not independent of the Lewis base; consequently there is no universal scale of Lewis acidity [3].

1.3 Solid Lewis Acids in Biomass Reactions

A major challenge in developing bio-based chemical industry is the development of selective, stable and active catalysts. In recent years, several Lewis catalytic systems have been successfully used for transformations of biomass into commercially available chemicals. In this section, I will

introduce the main solid Lewis catalyst families for biomass conversion reactions and several important examples to illustrate their applications.

1.3.1 Bulk Metal Oxides

Metal oxides are the traditional choice for dehydration catalysts [4], and have also been successfully applied in isomerization reactions in biomass conversion. One important example is that of $\gamma\text{-Al}_2\text{O}_3$, which has been used to carry out alcohol dehydration to olefins without leading to undesired side reactions, such as isomerizations or double-bond shifts [5]. Also, ZrO_2 and anatase TiO_2 are reported to be active for isomerization of glucose and fructose in hot-compressed water at 473 K and further dehydration reaction into 5-hydroxymethyl-2-furaldehyde (HMF) [6].

1.3.2 Framework Substituted Lewis Acid Zeolites

Zeolites are widely used solid catalysts with high surface area, thermal stability, and usually strong Brønsted acidity. When aluminum atoms inside zeolites are substituted with tetravalent Lewis acidic metal atoms like Sn or Ti, the zeolite becomes a pure solid Lewis acid in the absence of Brønsted acid sites. Framework-substituted, Lewis-acid zeolites are found to be extremely effective in many biomass conversion reactions. For example, for the isomerization of glucose, SnBEA (zeolite with BEA topology containing framework Sn) gives product yields of approximately 46% glucose, 31% fructose and 9% mannose after 12 min at 413K [7]. Sn and Zr BEA are also very active catalysts for Meerwein-Ponndorf-Verley (referred as MPV) reduction reaction and Baeyer-Villiger oxidation reactions which will be introduced in later sections [8,9].

1.3.3 Ion-exchange Zeolites

Although framework substituted zeolites are attractive catalysts, many of these materials can be difficult to synthesize. Ion-exchange provides an easy and convenient way to replace the proton in Brønsted-acid zeolites with metal cations. Although alkali-ion-exchanged zeolites are

normally thought of as basic materials, there is indeed evidence that using ion-exchanged zeolites may act as solid Lewis acid. For example, Huang and Kaliaguine reported that alkali-ion-exchanged ZSM-5 was active for the transformation of propene to aromatics and the dehydrogenation of cyclohexane [10]. Tago, et al. found that activity of alkali-ion-exchanged BEA zeolites for the production of isobutylene from acetone followed the order of the acidity of the cations [11]. It is also reported by Davis et al. that Na-exchanged SnBEA would shift the reaction pathway toward glucose-fructose-mannose isomerization.

1.4 Mechanisms of solid Lewis acids as catalysts in biomass reactions

As pointed earlier, the nature of solid Lewis acids is not well understood in many cases. Here, I will briefly introduce some of the mechanisms that have been proposed in biomass conversion reactions for the interaction of Lewis sites and functional groups in biomass molecules. Some of these will be very helpful in understanding the characterization of Lewis acids I have carried out in my thesis.

1.4.1 Glucose Isomerization, MPV reaction and Baeyer-Villiger oxidation reaction over Sn-BEA

Isomerization of glucose into fructose has played a crucial role in the biomass-derived chemical platforms [12]. The reaction is limited by equilibrium and typically catalyzed by an immobilized enzyme [13]. However, the narrow range of operating conditions for enzymes limits their application. As mentioned earlier, SnBEA was shown to be active over wide temperature range in acid solutions. Moreover, SnBEA showed superb stability over multiple cycles after calcination.

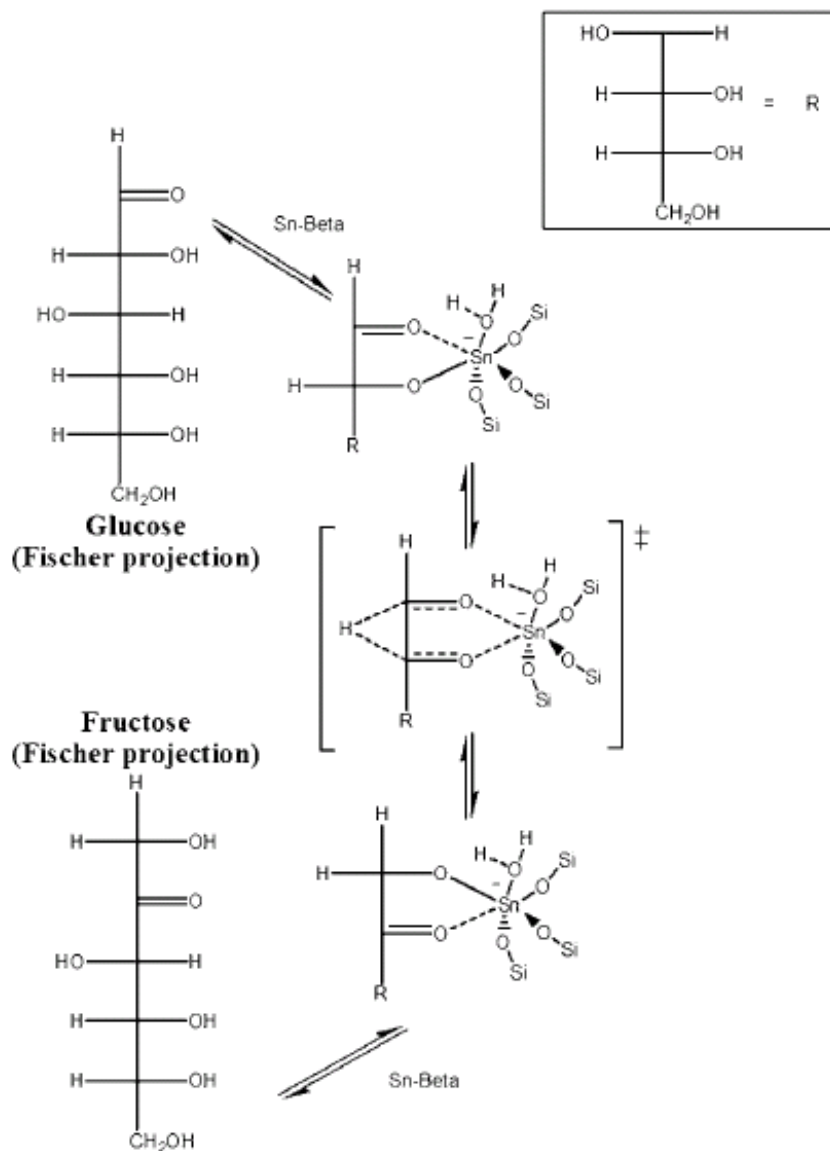


Figure 1.1: Glucose isomerization mechanism by way of intramolecular hydride transfer in presence of SnBEA [14]

A ^1H and ^{13}C NMR spectroscopy study by Davis et al. demonstrated that the isomerization reaction in the presence of SnBEA occurred through an intramolecular hydride shift, as shown in Fig. 1.1 [14]. With isotopically labeled glucose molecules, it was shown that Sn

atoms in zeolite act as a six-member center which connect the carbonyl group at the C1 position and the hydroxyl group at the C2 position. The intrinsic hydride transfer then occurs between the C1 and C2, completing the transformation from glucose to fructose.

As shown by Corma et al., the MPV reaction can also be catalyzed by SnBEA via a very similar mechanism [15,16]. In Fig. 1.2, co-adsorption of ketone and secondary alcohol on the Sn center makes it possible for carbon-carbon hydride transfer between two molecules through the catalyst. The difference between isomerization of glucose and the MPV reaction is that the former is an intramolecular reaction. The high electronegativity of Sn gives it a strong ability to interact with the carbonyl group, making the activity of SnBEA much higher than that of Al-BEA or Ti-BEA in several MPV reduction reactions [15].

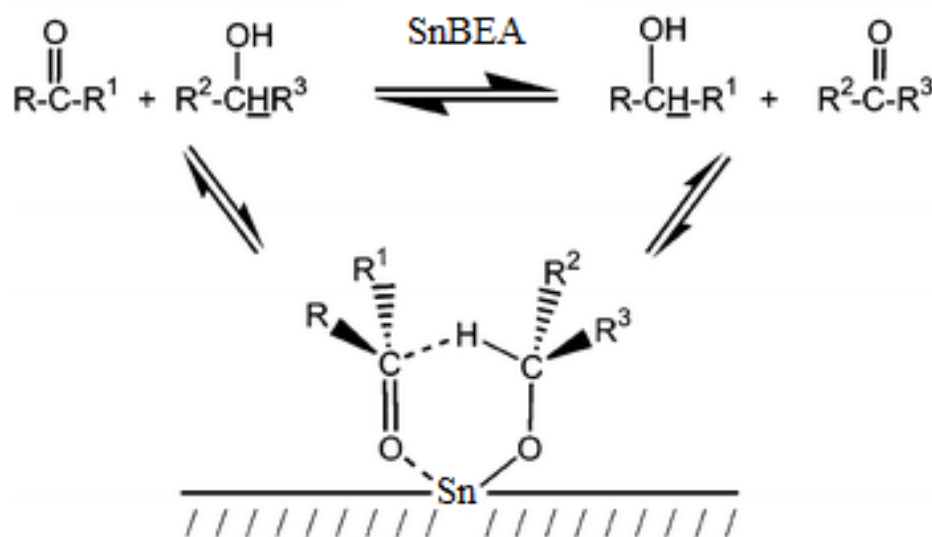


Figure 1.2: Mechanism of MPV reaction through SnBEA [16].

Another important reaction is the Baeyer-Villiger oxidation of ketones for the selective formation of the corresponding lactones which can also be catalyzed through SnBEA zeolite [17]. Similar to the reactions shown above, Sn sites still perform as a co-adsorption center for ketone

and H_2O_2 in this reaction, which occurs via an oxygen insertion through a seven-member ring intermediate [18].

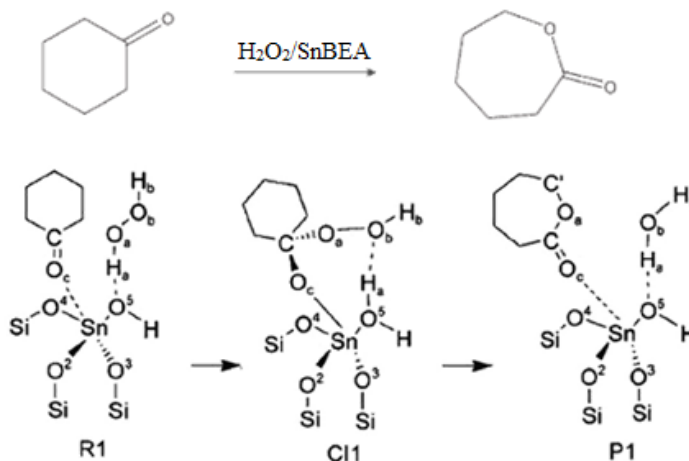


Figure 1.3: SnBEA catalyzed Baeyer–Villiger reaction mechanism [18]

For all these important reactions over SnBEA and other framework substituted zeolite catalysts, the most important step in each of the mechanisms is the adsorption of different functional groups onto Lewis-site centers. These mechanisms provide us an important view for Lewis acidity in biomass conversion reactions.

1.4.2 Alcohol dehydration over $\gamma\text{-Al}_2\text{O}_3$

Oxygen removal is required for converting lignocellulosic biomass to hydrocarbon fuels. Dehydration is one of the most common methods for oxygen removal from molecules. Since Brønsted acidity in solid acids can lead to undesired side reactions with different functional groups in biomass molecules, dehydration through solid Lewis acids in biomass upgrading is more attractive [12]. However, even for the simplest dehydration reaction, for example the alcohol dehydration over $\gamma\text{-Al}_2\text{O}_3$, our understanding is still very limited.

Dehydration of a series of alcohols over γ -Al₂O₃ by Roy, et al. showed that both experimental and theoretical results indicate a linear relationship between dehydration activation energy of alcohol and the proton affinity of corresponding carbenium-ion. This is shown in Fig. 1.4 [19]. The relationship indicates that the dehydration mechanism involves a carbenium-like transition state during the reaction.

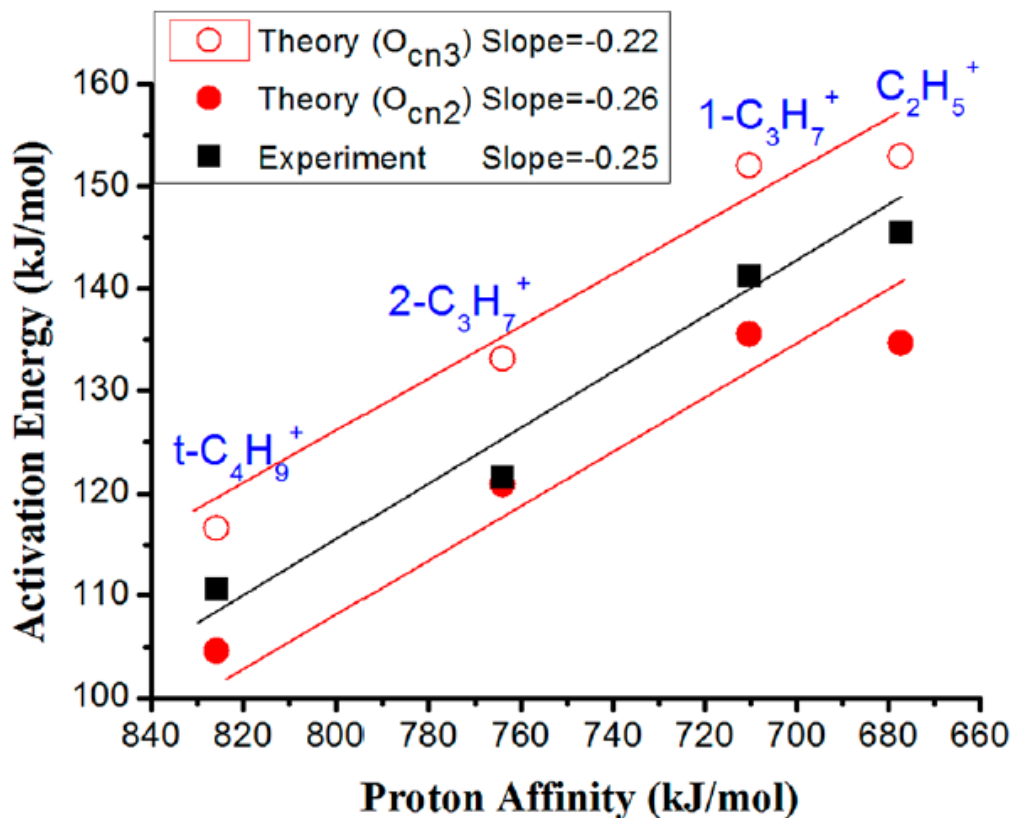


Figure 1.4: Activation energy of experimental results (■), theoretical results involving dehydration on a two-coordinated (●) and three-coordinated (○) O atom vs PA [19]

After investigating various dehydration mechanisms, they reported that a concerted E2-type, dehydration mechanism explains the energy barrier obtained from experiments [19]. From the mechanism for dehydration of 1-propanol over γ -Al₂O₃, shown in Fig. 1.5, the first step is the

alcohol adsorption on the Al-Lewis site; then, in the next step, H is transferred from the secondary carbon of the alcohol to a surface O atom of the alumina. After that, alkene is formed and desorbs from the surface to the gas-phase. Finally, water is formed from the remaining H and OH groups and desorbs into the gas-phase.

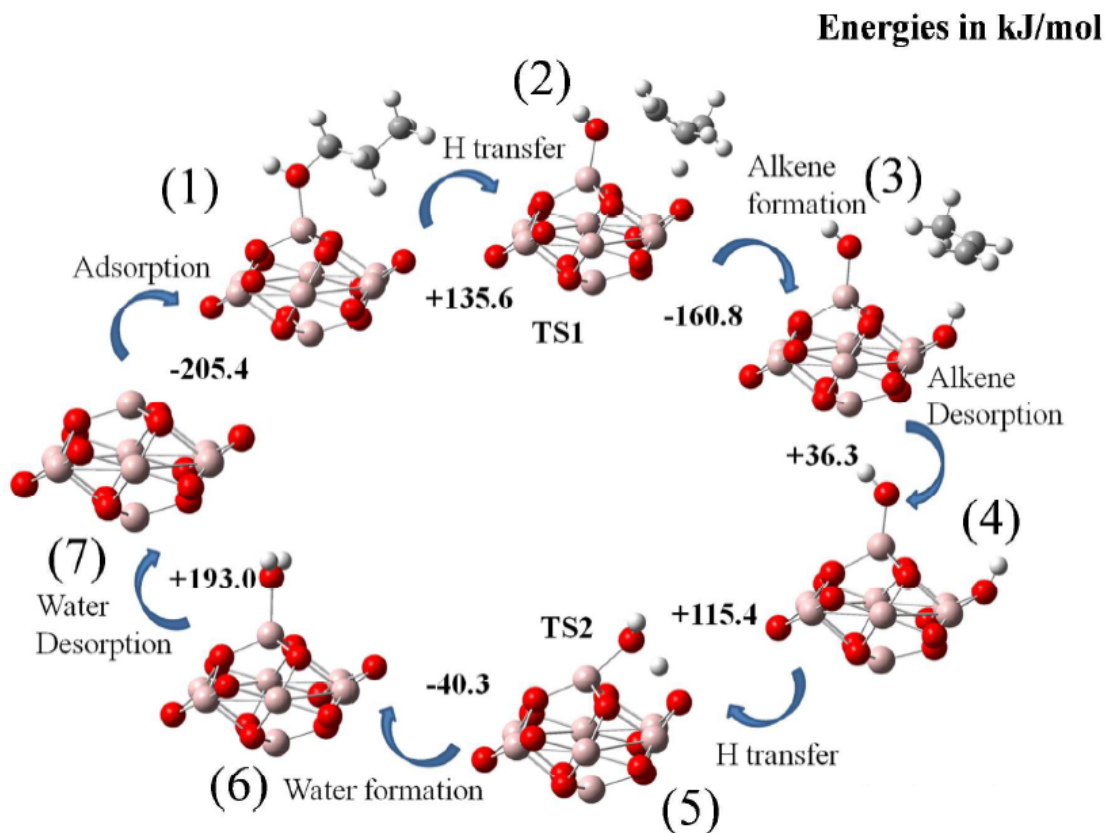


Figure 1.5: Scheme of 1-propanol dehydration reaction involving a tri-coordinated Al Lewis-acid site and a two-coordinated O of γ - Al_2O_3 . The steps are: 1) adsorption, 2) dehydration TS, 3) Alkene formation, 4) Alkene desorption, 5) water formation TS, 6) water formation, and 7) water desorption.

1.4.3 Summary of mechanisms for Lewis acids in Biomass reactions

From the mechanisms introduced above, it can be concluded that the adsorption of molecules onto Lewis-acid centers, especially the adsorption of functional groups onto catalysts, is crucial in biomass conversion reactions. Therefore, understanding adsorption of typical biomass molecules on Lewis sites is important for characterization of solid Lewis acids. Some methods that have been developed to study the adsorption properties will be discussed in the next section.

1.5 Approaches to Study Solid Brønsted Acidity by Adsorption Measurements

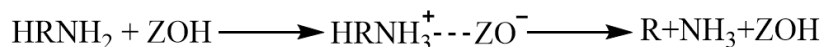
The systematic studies of zeolite Brønsted acidity by Gorte et al. [20,21] provide a good background for discussing Brønsted sites and demonstrate methods for understanding and predicting catalytic chemistry from adsorption properties. A review of these approaches provides a path for understanding and characterizing solid Lewis acidity and will be described in this section.

1.5.1 Site densities and stoichiometric adsorption complexes

Determination of the concentration of acid sites is essential before one can begin to describe reactions on Brønsted-acid sites. ^{27}Al NMR together with elemental analysis is able to determine the framework Al content in zeolites. However, the equipment is expensive and the method suffers from the problem that not all framework Al in zeolites are accessible to reactant molecules [22]. Another widely used methods for obtaining Brønsted site densities is Temperature Programmed Desorption (TPD) of ammonia. Ammonia TPD results are often ambiguous because adsorption of ammonia is not specific to Brønsted sites [23].

An easy and effective method for measuring Brønsted site densities is simultaneous temperature programmed desorption (TPD) and thermogravimetric analysis (TGA) measurements of reactive amines [24–27]. Details about TPD-TGA instrument are given in Chapter 2. The idea

behind the technique is that alkyl-ammonium ions can be formed by protonation of amines at Brønsted sites. At high temperatures, these react via a Hoffman elimination reaction to form an alkene and ammonia in a very narrow temperature range, as shown below:



The reaction of one molecule per framework Al has been observed on H-MFI samples with different Al contents for a variety of amines small enough to enter the pores of zeolites. Since the reaction is from the 1:1 complexes, TGA results are very useful to determine whether there is a residual mass remaining on the sample and to quantify the amount of reacting amines by monitoring the mass change over the temperature at which reaction occurs. An investigation of a series of FAU showed a linear correlation between site density determined by TPD-TGA of 2-propylamine and framework Al content, which can be used as an additional evidence that the measurement of site density is accurate in zeolites [28].

It is also important to know the stability and chemical structure of reactants, products and intermediates at the catalytic sites in order to describe a surface-catalyzed reaction. TPD-TGA is one of the clearest methods to observe the 1:1 complexes. TPD-TGA results provide information on the adsorption complexes from the TGA results. Many types of molecules including alcohols [29,30], amines [31], nitriles [32], pyridines [33], ketones [34,35], and diethyl ether [32] have been demonstrated to form 1:1 adsorption complexes on H-MFI.

1.5.2 Calorimetric measurements

As described in Section 1.2, the definition of Brønsted acidity in either solution phase or gas phase can be scaled into a universal form from the change of free energy of the protonation reaction. Thus, calorimetric measurements of stoichiometric adsorption complexes can be used as

a powerful method for defining solid acidity by comparing thermodynamic properties in zeolites to thermodynamic properties in homogeneous acids [21].

The microcalorimeter used in my thesis is a home-built instrument which is able to simultaneously measure the heats of adsorption and adsorption isotherms. The instrument is described in detail in Chapter 2. To demonstrate how it can be used to quantify acidity, it is useful to consider the data in Fig. 1.6. The figure shows the differential heats for pyridine on three different H-MFI samples with different Si/Al ratios at 480 K. The differential heats are 200 kJ/mol up to the coverage of one per site and the heats fall rapidly to around 70 kJ/mol at the coverage above one per site [36]. Taking the difference between these values, one can calculate the enthalpy change for the proton-transfer reaction to be 130 kJ/mol in the zeolite. By comparison, $-\Delta H_{\text{pro,que}}$ is approximately 20 kJ/mol in aqueous solution. This difference between solution phase and the zeolite can have a huge impact on reaction kinetics.

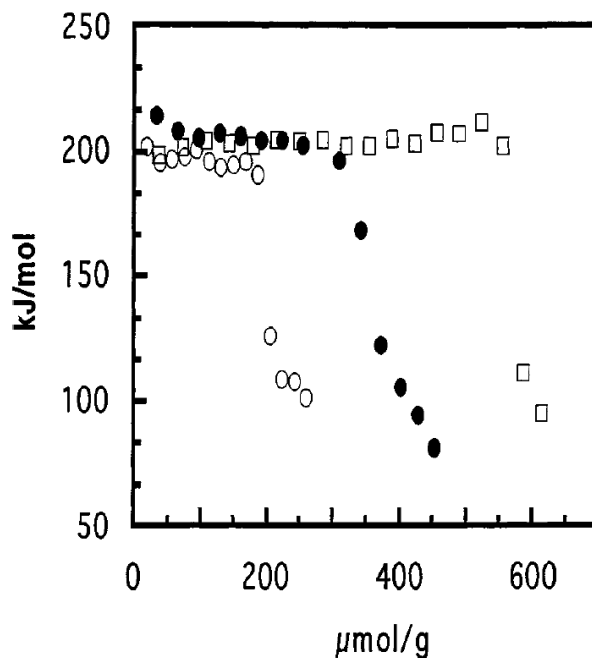


Figure 1.6: Differential heats of adsorption for pyridine on three H-MFI samples with varying Al contents. The drops in the heats occur at the Brønsted site densities for each sample [36]

The comparison of differential heats for a series of molecules including amines, ring-substituted pyridines and nitriles with their protonation heats in aqueous solution and gas phase is shown in Fig. 1.7(a) and 1.7(b) [32,33,37]. It is obvious from this data that the correlation between the differential heats in H-MFI and gas-phase proton affinities (PA) in 1.7(b) is much better than that for the differential heats with effective pK_a in aqueous solution in 1.7(a). Moreover, the linear correlation between differential heats and proton affinities has a slope of one. This strong correlation suggests that the $\Delta H_{\text{binding}}$ for Brønsted acid sites with different base molecules (including pyridine, amines) should be a constant. These experiments provide strong evidence that solution-phase definition as pK_a 's, are not be useful in predicting chemistry in zeolites. Even if the zeolite is placed in the aqueous phase, one should not expect for the same binding energy for Brønsted-acid sites in zeolites to be the same as hydrogen ion with base molecules in water.

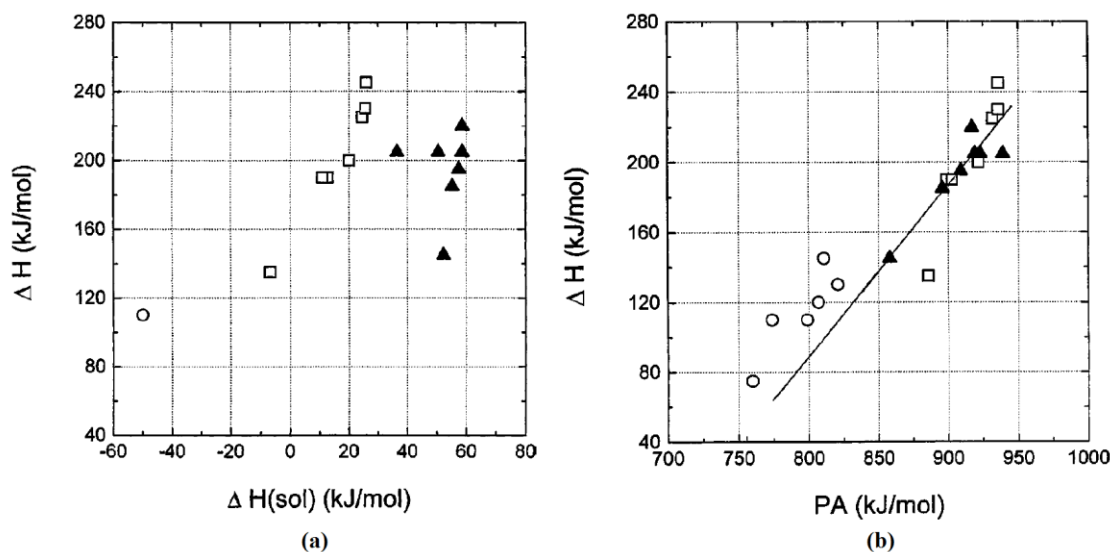
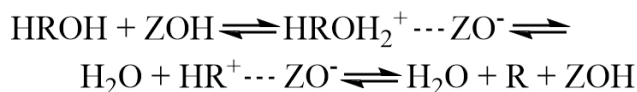


Figure 1.7: Plot of the heat of formation of the 1:1 complex in H-MFI versus ($\square$) pyridines ($\blacktriangle$) amines, and ($\circ$) acetonitrile for their (a) the enthalpy of protonation in aqueous solutions; (b) the gas-phase proton affinities

The intent in this section was to demonstrate that microcalorimetry provides a powerful framework for understanding Brønsted acidity in zeolites. The approach to extending these concepts to reaction chemistry will be discussed in the next section.

1.5.3 Reaction Chemistry

In this section, the alcohol dehydration reaction, catalyzed by H-MFI, will be shown as a practical application to demonstrate that the proton-affinity picture, together with the concept of stoichiometric adsorption complexes, is useful in predicting chemistry. The reaction pathway for alcohol dehydration can be simplified as follows:



Adsorption studies demonstrated that 1:1 complex can be formed by adsorption of various alcohols onto zeolite. Dehydration happens through formation of water and a zeolite-bound carbenium ion, which finally decomposes back to the zeolite and an olefin. If we use the conclusion from calorimetric studies that the heats of formation for complexes on the zeolite can be calculated from tabulated proton affinities of olefins and alcohols and the linear correlation in Fig. 1.7 (b), energies of all transition states during dehydration for different alcohols can be determined. The result of this calculation is shown in Fig. 1.8.

Fig. 1.8 allows us to predict alcohol dehydration reactions in H-MFI. Based on the potential energy diagram, one would expect that each of the gas-phase alcohols should adsorb onto the Brønsted acid sites and form oxonium-ion adsorption complexes. The energy differences between oxonium-ion complexes for different alcohols with H-MFI are very small. However, the energy differences for forming the carbenium ions from their corresponding oxonium ions are very large. If one assumes the activation barrier for dehydration is equal to the energy difference

between the oxonium ion and carbenium ion, one would expect a dramatic difference in the reaction chemistries. For example, in the case of methanol, the formation of the methyl carbenium-ion is extremely unfavorable, requiring more than 55 kcal/mol from the oxonium ion. By contrast, the energy difference between the oxonium and carbenium ions for t-butanol is only 8 kcal/mol.

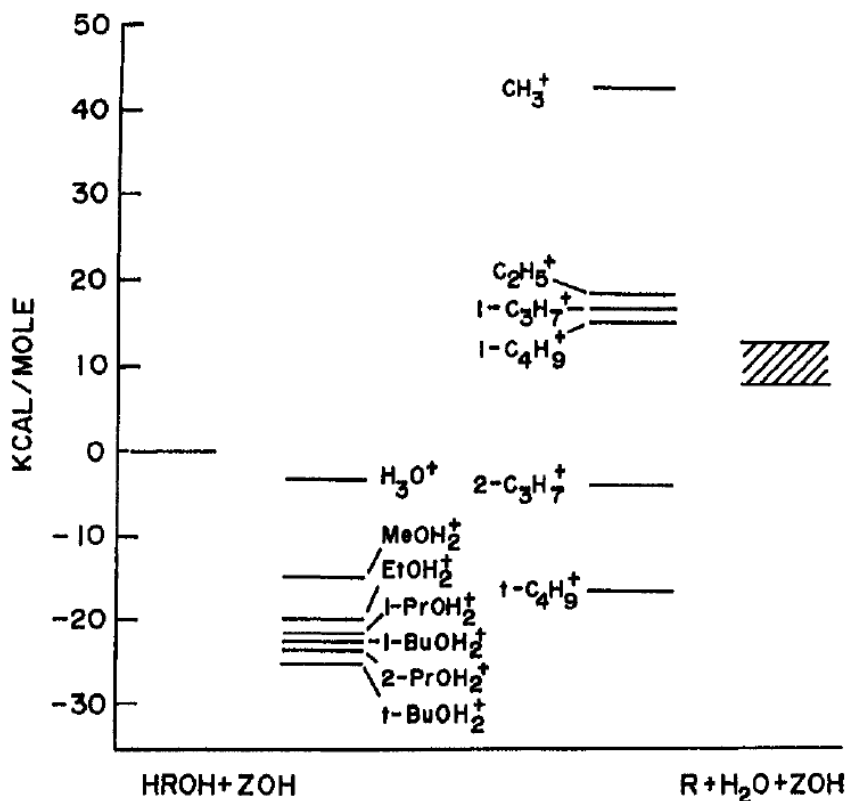


Figure 1.8: Potential energy diagram of alcohol/H-MFI interactions. The adsorption of alcohols and olefins on the zeolite is assumed to occur through proton transfer, allowing the use of known proton affinities to calculate relative heats of formation [30]

The predictions for alcohol dehydration based on adsorption studies correspond well with observations from adsorption studies [30]. From TPD-TGA experiments, the 1:1 complex for isopropanol decomposes into propene and water at ~400 K while dehydration of t-butanol happens at room temperature.

In summary, these approaches provide a proper understanding of the nature of solid acidity. By determining structures and energies of all species along a reaction coordinate from adsorption measurements, one can describe and predict a surface-catalyzed reaction.

1.5.4 The Approaches to study solid Lewis Acidity

The success in understanding solid Brønsted acidity encouraged us to seek a better understanding of solid Lewis acidity for purposes of predicting Lewis-catalyzed biomass reactions. The main methods and approaches for studying solid Lewis acidity were similar to that used in characterizing solid Brønsted acidity.

1.6 Scope of the Thesis

This thesis is divided into 7 chapters. Chapter 2 provides descriptions of the characterization techniques and preparation methods of catalysts in this work.

Chapter 3 focuses on the characterization of metal oxides and metal oxides over SBA-15 support. The acidity of each material was examined by adsorption and reaction studies. The relationship between Lewis acidity, Brønsted acidity and the etherification reaction of 5-hydroxymethylfurfural (HMF) with 2-propanol was also described.

In Chapter 4, the possibility of using alkali-exchanged BEA zeolites as Lewis-acid catalysts was examined using temperature-programmed desorption (TPD)/thermogravimetric analysis (TGA) measurements of adsorbed pyridine, 2-propanamine, diethyl ether, 2-methyl-2-propanol, and acetonitrile, FTIR of pyridine and CD₃CN, calorimetry of CO, and reaction rates for reductive etherification of 5-hydroxymethyl furfural (HMF) with 2-propanol. Adsorption on the alkali cations occurs through ion-dipole interactions, as evidenced by the fact that adsorption is strongest on Li, followed by Na and K. Adsorption of all the probe molecules was much stronger on Li-BEA than on acid sites formed by framework Sn in SnBEA; however, the alkali-

exchanged BEA samples were not catalytically active for alcohol dehydration or reductive etherification of HMF. The implications of these results for the characterization of solid Lewis acidity are discussed.

In Chapter 5, 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 to 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. on adsorption studies of methane over ZSM-5, MOR, and ZSM-12 using calorimetric measurements and DFT calculations.

In Chapter 6, the adsorption and reaction properties of H-BEA, SnBEA, ZrBEA, and siliceous BEA were examined in order to understand the reaction of 2,5-dimethylfuran (DMF) with ethene to produce p-xylene. Temperature-programmed desorption (TPD) of diethyl ether, DMF, 2,5-hexanedione, and p-xylene on each of the zeolites demonstrated that the Brønsted sites in H-BEA are much more reactive than the Lewis sites in SnBEA and ZrBEA and tend to promote oligomerization of DMF and 2,5-hexanedione, even at 295 K; however, adsorbed 2,5-hexanedione is converted to DMF at both Lewis- and Brønsted-acid sites. H-BEA, SnBEA, and

ZrBEA were all able to catalyze the reaction to p-xylene with high selectivity in a continuous flow reactor, with all three showing rates that are first-order in both DMF and ethene. H-BEA was found to deactivate rapidly due to coking, while ZrBEA and SnBEA were both very stable. The implications of these results for practical applications are discussed.

Finally in Chapter 7, overall results and conclusions of this work are summarized.

Chapter 2. Experimental Techniques

This chapter will describe the various techniques used to characterize the catalysts, including the continuous-flow reactor designed for biomass conversion, as well as the pretreatment methods used in preparing the catalysts.

2.1 Characterization Techniques

2.1.1 TPD-TGA measurement

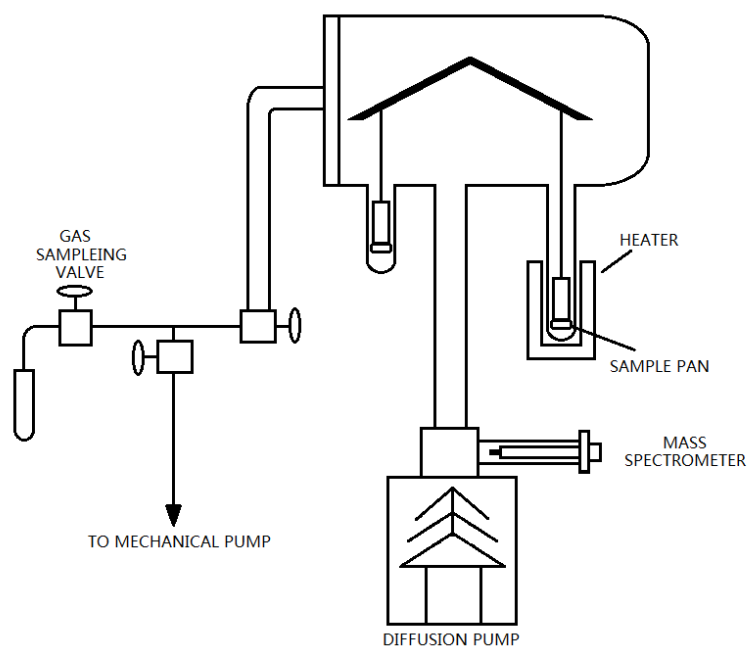


Figure 2.1: Schematic diagram of TPD-TGA system

Simultaneous thermogravimetric analysis (TGA) and temperature programmed desorption (TPD) was found to be one of the most useful methods available for the initial characterization of adsorption complexes. A schematic of the equipment is shown in Fig. 2.1. The

TGA unit in this system has an accuracy of 0.01 mg and allows the measurement of weight changes as small as 0.01%. After exposure to the vapors of interest, the sample can be evacuated by a diffusion pump, which ensures that the pressure above the sample is low enough to minimize secondary reactions. Desorbing species can be monitored with high sensitivity by a mass spectrometer. From the TPD-TGA results, one can quantify the desorption amount and determine whether there is a reaction on the sample during desorption.

In a typical TPD-TGA experiment, the sample is first heated to 830 K in vacuum to remove water and other impurities. After cooling to room temperature, the sample is exposed to several Torr of the probe molecule of interest. After evacuation, the temperature is then ramped at 10 K/min to 830 K, while the sample mass and desorbing products are monitored.

If readsorption is negligible, the rate of desorption from a unit surface area can be written as:

$$N(t) = -\frac{d\sigma}{dt} = v_n \sigma^n \exp\left(\frac{-E}{RT}\right) \quad 2.1)$$

Where: N is the desorption rate

σ is the surface coverage (molecules/cm²)

n is the order of the reaction

v_n is the rate constant

E is the activation energy of reaction(kJ/mol)

Because the temperature is linearly ramped to 830 K, temperature of the system can be written as a function of time $T = T_0 + \beta t$. If we assume that the reaction is first order and the activation energy E is independent of σ , then the expression of peak temperature T_p below can be obtained by solving $dN/dt = 0$:

$$\frac{E}{RT_p^2} = \frac{v_1}{\beta} \exp\left(\frac{-E}{RT_p}\right) \quad 2.2)$$

While this description is not appropriate for desorption from porous catalysts due to readsorption effects, the approach is useful for describing decomposition reactions where the products leave the sample once they are formed [20]. In this circumstance, the activation energy of the reaction may be obtained from the peak temperature of the products using Eqn 2.2. For example, a TPD-TGA of 1-propanol over TiO_2 is shown in Fig. 2.2. The dehydration reaction of 1-propanol into propylene and water occurs during TPD and propylene cannot readsorb on titania. Using the peak temperature for propylene of 596 K, the activation energy for dehydration of 1-propanol can be calculated to be 171 kJ/mol by assuming a normal reaction pre-exponential of 10^{13} s^{-1} .

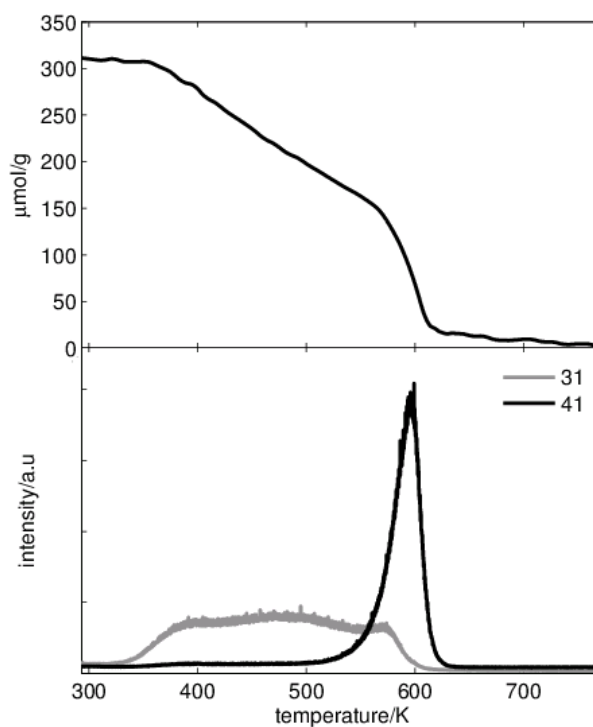


Figure 2.2: TPD-TGA of 1-propanol over TiO_2

2.1.2 Calorimetric measurement

Calorimetry is a direct method for measuring heats of adsorption for gaseous adsorbates on acid sites. Our home-built, Calvent-type calorimeter allows the use of relatively large samples (0.5g~1g) spread into very thin beds (~1 mm thick) for rapid adsorption and heat transfer. As shown in Fig. 2.3, the calorimeter cell is surrounded on five of six sides by highly sensitive thermopiles which generate a voltage proportional to the heat flow released by adsorption. The calorimeter cell is enclosed in a large aluminum block, which in turn is kept within a Styrofoam cooler, to maintain isothermal conditions. A dosing loop is connected to a six-port valve which allows calibrated volumes of gas to be admitted into the calorimeter cell. Two pressure transducers are separately positioned on the dosing system, which is used to fill the dosing loop, and the calorimeter cell.

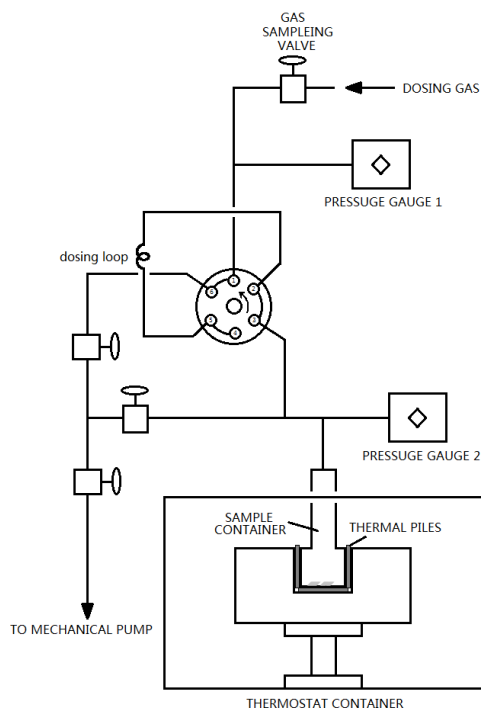


Figure 2.3: Schematic diagram of calorimetric system.

The dosing procedure involves switching the six-port valve to the dosing side, filling the dosing loop with the adsorbate gas, and then switching the six-port valve to the calorimeter side. Usually, adsorption equilibrium is achieved in approximately 20 min. The amount of gas introduced to the dosing loop and the amount remaining at equilibrium can be determined by the volume, pressure, and the temperature.

In a typical measurement, the samples were heated in the evacuated calorimeter cell to ~600 K overnight to clean the sample before beginning to expose the sample to gaseous adsorbates. Aliquots of adsorbate were then dosed onto the sample by switching the six-port valve from dosing side to the calorimeter side. Dosing continued until saturation coverage was reached. The adsorption isotherm was obtained simultaneously with the heats by measuring the amount of gas remaining at equilibrium with the pressure above the sample.

2.1.3 FTIR

Fourier Transform Infrared Spectroscopy (FTIR) is another useful technique to study the adsorption properties on the catalyst. Comparing spectra before and after adsorption of certain probe molecules provides a convenient method to characterize solid Lewis acid catalysts. The spectra were recorded using Mattson Galaxy 2020 FTIR spectrometer which has an accuracy of 2 cm^{-1} resolution. A Spectra-Tech diffuse-reflectance accessory (Collector II), which allowed programmed heating during measurements on powder samples, was available on the FTIR spectrometer.

2.2 Tubular flow reactor

A schematic diagram of the continuous-flow, tubular reactor used in my studies of the biomass conversion reaction is shown in Fig. 2.4. Detailed kinetic studies are easier to interpret in continuous flow reactors comparing to batch reactors because they operate at steady state. In most cases, a specified amount of catalyst was packed in the middle of a 20 cm-long, stainless-steel

tube and held by glass wool. A stainless-steel stick was placed downstream from the catalyst in the tube in order to reduce the empty volume of the reactor and hold the catalyst bed. A solution of reactants from a feed reservoir was introduced into the reactor by a HPLC pump (Series III, Scientific System) at a controllable flow rate from 0.05 ml/min to 1.0 mol/min. A back-pressure regulator (KPB series, Swagelok) was placed downstream from the reactor in order to control the pressure. The pressure inside the system can also be measured by the HPLC pump. A gas tank equipped with a high pressure delivery regulator was used to introduce gas into the system through 7 ft of 0.002-in. ID capillary tube (Valco Instruments). The relationship between pressure drop across the capillary tube and the gas flow rate can be determined by calibration.

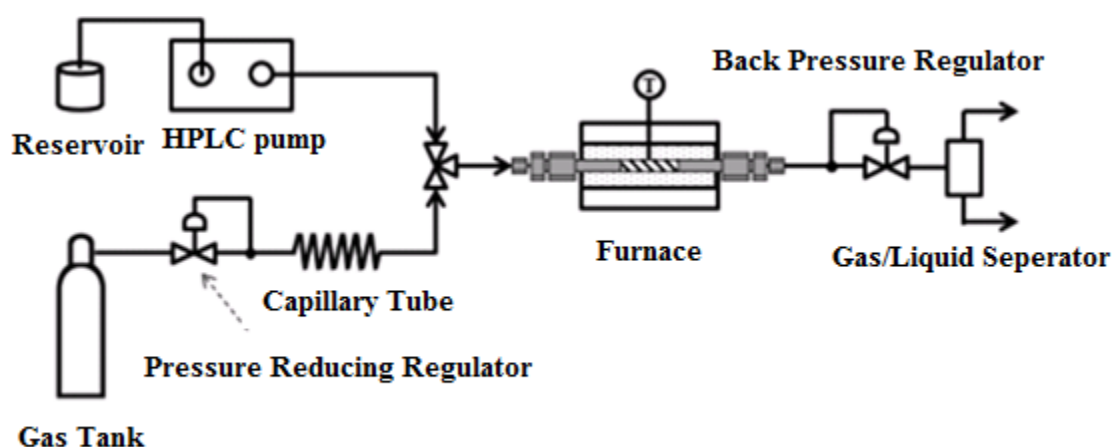


Figure 2.4: Schematic diagram of continuous flow reactor

2.3 Catalyst Preparation

In my work, I started with commercially available zeolites. However, some of these materials were modified by alkali exchange to change the nature of the sites and by dealumination to remove Brønsted acid sites. In this section, general treatment methods will be

discussed, while the details of the preparation procedures will be described in corresponding chapters.

2.3.1 Alkali-exchanged zeolite

Alkali-ion exchange replaces Brønsted-acid sites in zeolites into alkali-ion sites. As discussed in Chapter 1, alkali-ion-exchanged zeolites can be viewed as solid Lewis acids. To obtain the alkali (M^+) form, 1 g of the NH_4^+ or H^+ form of the zeolite was stirred with a 300 mL solution that was 0.1 MCl and 0.001 MOH for four hours, followed by filtering. As a final step, the sample was calcined at 550°C under flowing air for four hours to remove surface impurities.

2.3.2 Dealumination of a BEA zeolite

The activity of zeolites is related to the ion-exchange sites in the framework. The removal of framework Aluminum atoms provides a zeolite sample with the same topology of the original one but essentially no acid sites. Dealuminated zeolites can be used as a precursor in synthesizing framework Lewis acids.

To obtain dealuminated BEA zeolite without losing its original crystallinity, 3 g of BEA zeolite was mixed with 60 ml 13 mol/L nitric acid for 4 h at 373 K, with stirring. The suspension was then filtered and washed multiple times to remove any remaining acid. Finally, the sample was dried at 373 K overnight.

Chapter 3. Lewis acidity of metal-oxides and metal-oxides over SBA-15 and the effect of acidity on HMF etherification reaction

3.1 Introduction

The conversion of cellulosic biomass into liquid fuels, or fuel additives, would be attractive if it could be performed economically. While potential processes exist for taking cellulose to C-5 and C-6 sugars, and these can in turn be converted into furfural and 5-hydroxymethylfurfural (HMF), additional processing is required in order to stabilize furfural and HMF because they remain highly functionalized. Since H_2 is expensive to produce and compress and is not economically renewable, processes that avoid its use and minimize its consumption are preferred. One interesting approach for upgrading furfural and HMF that avoids the need for gas-phase H_2 involves reactions with alcohols or aldehydes to produce higher molecular weight products that can be used in diesel fuel, either directly or after minor additions of hydrogen [38,39]. One example where this has been accomplished involves cross-aldol condensation with acetone [40] and hydroxylation [41].

An alternative approach to aldol condensation involves etherification of HMF with an alcohol. The direct etherification of HMF to form the mono-ether furfural can be catalyzed by Brønsted acids, including H_2SO_4 [38] and H-zeolites [42], as shown in Fig. 3.1(a). However, the remaining carbonyl functional group in the mono-ether furfurals reduces the stability of the molecule compared to the corresponding alcohols [38,43]. Formation of di-ethers from 2,5-bis(hydroxymethyl)-furan (BHMF) has been demonstrated but this requires a two-step process in which the carbonyl group is first reduced [44]. Reductive etherification, in which the carbonyl is hydrogenated and then reacted to form the di-ether, avoids this problem. In a demonstration of this chemistry, Balakrishnan et al. [38] reported the one-pot reductive etherification of HMF to

form 2,5-bis(alkoxymethyl)furan, shown in Fig. 3.1(b). This reaction requires H_2 to reduce the carbonyl group, increasing the material and process cost.

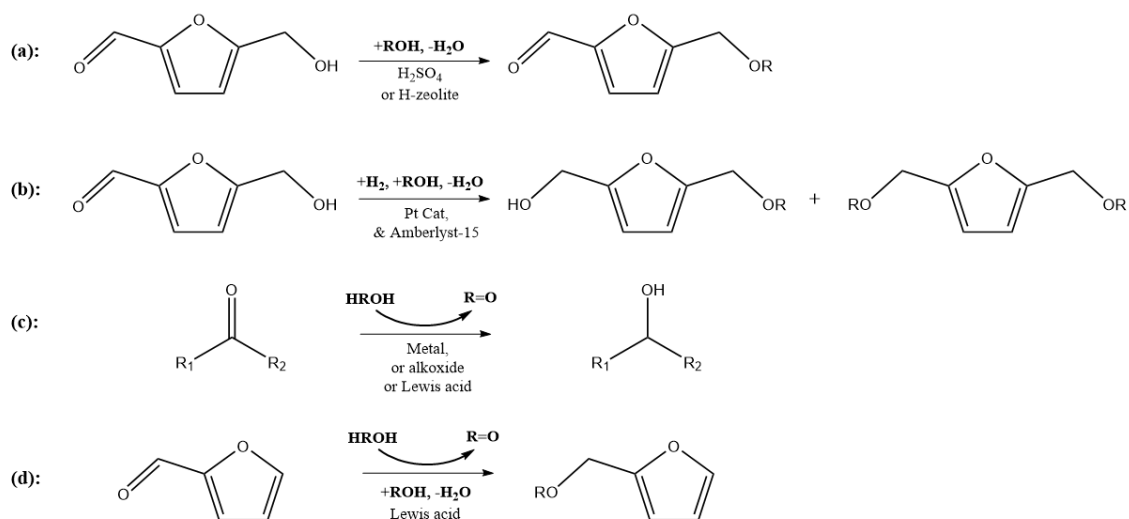


Figure 3.1: (a) Direct etherification of HMF, (b) one-pot reductive etherification of HMF via hydrogenation, (c) transfer hydrogenation via Meerwein–Ponndorf–Verley reaction, and (d) reductive etherification of HMF via transfer hydrogenation

Transfer hydrogenation via the Meerwein–Ponndorf–Verley (MPV) reaction, shown in Fig. 3.1(c), provides the opportunity for an interesting variation on reductive etherification, since the alcohol used as the reactant for making the ether can also be used as the hydrogen source. The aldehyde or ketone produced by oxidation of the alcohol would need to be hydrogenated in a separate step, but this subsequent reaction could be carried out in the gas phase and would not require high-pressure H_2 [45]. Alternatively, the aldehyde or ketone produced could be used in aldol-condensation of HMF. Some examples where transfer hydrogenation has been used include the following: Petra et al. [46] performed transfer hydrogenation over ruthenium(II) for the reduction of acetophenone; Mollica et al. [47] reported the reduction of aromatic and aliphatic

aldehydes using isopropanol as hydrogen donor and ytterbium triflate as the catalyst; Misra et al. [48] applied bimetallic alkoxides of praseodymium and neodymium to carry out the transfer hydrogenation of octanone. Of particular interest, transfer hydrogenation has been shown to be catalyzed by solid, inexpensive oxides. For example, Dumesic and coworkers [49] showed that ZrO_2 can be effective for transfer hydrogenation of levulinic acid/ethyl levulinate to γ -valerolactone. Similarly, Corma et al. [16] reported the reduction of cyclohexanone to cyclohexanol in large-pore zeolites with framework Sn or Zr. Presumably, the oxides in these examples are acting as solid Lewis acids. An additional benefit of using solid acids to catalyze transfer hydrogenation is that the acids may also catalyze the etherification reactions. The feasibility of this has been demonstrated by Bui et al. [50] and Jae et al. [51], who performed the sequential transfer hydrogenation and etherification of furfural to furfuryl ether over zeolite BEA with framework Zr, Sn and Ti, using an alcohol as hydrogen donor. This reaction is shown in Fig. 3.1(d). Metal oxides exhibit Lewis acid properties for reaction involving alcohols [4,52–56]. There are even questions concerning whether the active sites are Brønsted- or Lewis-acid in nature, especially in the presence of water, which is a product of the reaction.

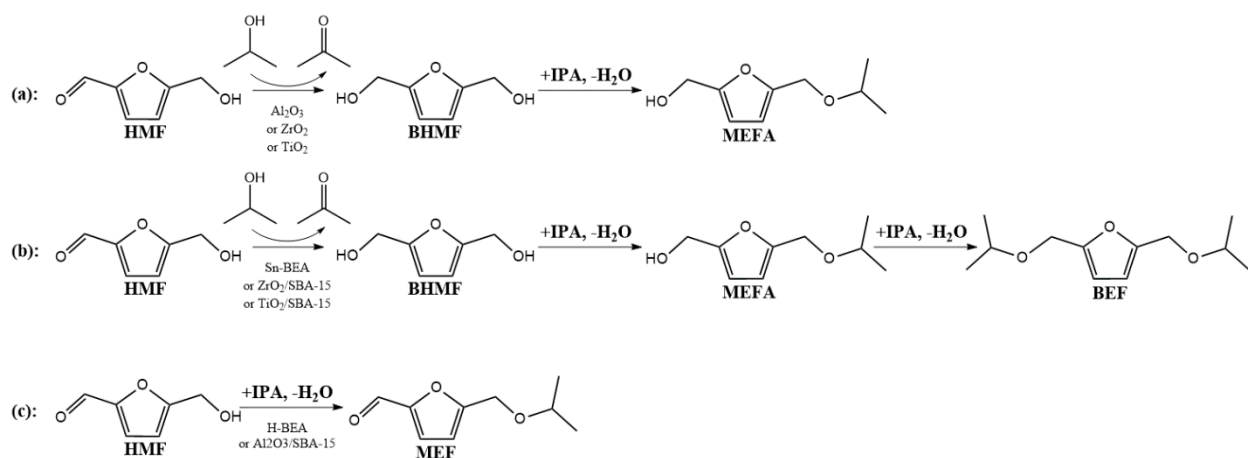


Figure 3.2: Reaction schemes of HMF etherification with isopropanol over solid acid catalysts. Compounds: 5-(hydroxymethyl)furfural (HMF), 2,5-bis(hydroxymethyl)furan (BHMF), 5-[(1-

methylethoxy) methyl]furfural (MEF), 5-[(1-methylethoxy)methyl]-2-furanmethanol (MEFA), 2,5-bis[(1-methylethoxy)methyl]furan (BEF)

In the present work, we combine TPD–TGA experiments and the performance of a range of solid acids for the reaction of HMF with 2-propanol in the liquid phase in order to gain insights into what properties are most desirable for carrying out transfer hydrogenation and the subsequent etherification reactions. We examined both solid Lewis acids (Al_2O_3 , ZrO_2 , TiO_2 , and Sn-BEA) and solid Brønsted acids (H-BEA, $\text{Al}_2\text{O}_3/\text{SBA-15}$, and $\text{ZrO}_2/\text{SBA-15}$). What we will show is that each of the materials showed activity but that the product selectivities varied strongly with the oxide acidities (Fig. 3.2).

3.2 Experimental methods

3.2.1 Materials

The $\gamma\text{-Al}_2\text{O}_3$ (99%, Alfa Aesar) was pre-treated with a 1 mol L⁻¹ NH_4NO_3 solution in order to remove Na impurities [19]. In the NH_4NO_3 treatment, 500 mg of $\gamma\text{-Al}_2\text{O}_3$ was stirred with 300 mL of the solution at 353 K for 3 hours, then calcined to 773 K. The TiO_2 was purchased from Aeroxide (99%) and used without additional pretreatment. The ZrO_2 sample was prepared by drying an aqueous solution of zirconyl nitrate hydrate (99%, Aldrich), followed by calcination at 773 K for 4 h. The surface areas of the samples were determined from N_2 isotherms using the Brunauer–Emmett–Teller (BET) method at 78 K, after evacuation of the sample at 500 K, and are reported in Table 3.1.

The Sn-BEA, with Si/Sn ratio of 118, was prepared by the procedure described by Corma et al. [16]; characterization of this material has been described elsewhere [51,57]. First, 13.6 g of TEOS (Sigma Aldrich, 98%) were hydrolyzed in 13.01 g of TEAOH (40 wt%, Sigma Aldrich) with stirring at room temperature. To this solution, 0.1840 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (Strem Chemicals,

98% reagent grade) in 0.92 g of DI water were added, after which the mixture was again stirred at room temperature until the solution had decreased in weight by 12 g because of ethanol evaporation. To the resulting clear solution, 1.47 g of HF (48 wt%) were added, causing the formation of a thick paste. Next, 0.152 g of calcined, siliceous zeolite Si-Beta in 0.73 g of DI water was added as seed crystals. The final gel composition was as follows: 1.0 SiO₂ : 0.0083 SnO₂ : 0.54 TEAOH: 7.5 H₂O: 0.54 HF. The crystallization was carried out in rotating, Teflon-lined, stainless-steel autoclaves at 413 K for 28 days. The solid produced by this process was then calcined in air using a heating ramp of 3 K min⁻¹ to 853 K and held at this temperature for an additional 3 h.

SBA-15-supported Al₂O₃, ZrO₂, and TiO₂ were also prepared and tested. The SBA-15 was a mesoporous silica, with 5.0 nm, uniform, mono-dimensional channels and has been described elsewhere [58]. Al₂O₃/SBA-15 was synthesized to have 10 wt% Al₂O₃ by mixing 1.46 g aluminum nitrate nonahydrate (98.0% to 102.0%, Alfa Aesar) with 1.8 g SBA-15 in 100 mL of water for 2 h at 353 K, followed by evaporation of the water and calcination of the solid at 773 K. The 10 wt% ZrO₂/SBA-15 sample was prepared in the same manner, with a zirconia nitrate aqueous solution (99%, Aldrich). For the 10 wt% TiO₂/SBA-15 sample, 1.8 g SBA-15 powder was stirred with 0.88 mL titanium iso-propoxide (97%, Aldrich) in 100 mL tetrahydrofuran under a N₂ atmosphere. After removing the solvent by evaporation, the solid was again calcined at 773 K for 4 h.

3.2.2 Experimental

The reactions of HMF with 2-propanol were carried out in a high-pressure, continuous-flow reactor similar to that described in Chapter 2 [59]. The tubular reactor was a 20 cm long, stainless-steel tube with a 4 mm ID and 1/4 inch OD, passed through a tube furnace. The liquid feed, a mixture of 1 g HMF (99%, Sigma-Aldrich) and 100 mL isopropanol (99.9%, Fisher

Scientific), was introduced into the reactor using an HPLC pump (Series I+, Scientific Systems Inc.) with a fixed feed rate at 0.2 mL min⁻¹. For these measurements, the reactor pressure was maintained at 69 bar using a back-pressure regulator (KPB series, Swagelok). Product analysis was carried out by means of a GC-Mass Spectrometer (QP-5000, Shimadzu), equipped with a capillary column (HP-Innowax, Agilent Technologies). The HMF quantification was achieved by GC/MS using standard solutions with different concentrations. Due to the lack of commercial standards for ethers, the GC sensitivity for the products was assumed to be equal to that for HMF. Due to the uncertainties in the calibration factors, the total GC area for all products was used to normalize product selectivities.

To avoid large pressure drops in the reactor, the catalyst samples were first pressed into thin wafers, which were then broken into small pieces before placing them into the reactor. The rectangular wafers had a characteristic size of 1–2 mm and a thickness of approximately 0.3 mm. The catalyst was loosely packed in the reactor, so that the length of the bed was approximately 1 cm for a 0.1 g loading, and 4 cm for a 0.4 g loading. Based on the volumetric flow rate, the linear velocity of the liquid feed was determined to be 1.6 cm min⁻¹. For differential conversions, it was possible to calculate rates from the measured conversions, although characteristic diffusion times ($\delta^2/D \sim (0.015 \text{ cm})^2/10^{-6} \text{ cm}^2 \text{ s}^{-1} \sim 200 \text{ s}$) could affect this somewhat. However, channeling of the reaction fluid around the catalyst particles prevents measurement of rates at higher conversions. In this study, catalyst loading was varied in order to determine the effect of increasing conversion on the selectivity and cannot be used as a measure of reaction rates.

To determine the effect of temperature, reactions were carried out with 0.1 g of catalyst at 413 K and 453 K. (For the H-BEA and Sn-BEA catalysts, reactions were also measured with 0.05 g at 413 K in order to maintain differential conversions.) The conversions were negligible in the absence of a catalyst and also with unmodified SBA-15. For each of the catalysts examined in

this study, conversions and selectivities remained unchanged over the period of several hours required to make the measurements. The typical run time was 3 h, and the outlet products were sampled every 30 min. In all cases, minimal changes were observed in the conversion and selectivity; and representative data was typically chosen from the second or third measurement (40 to 60 min after starting the reaction).

3.3 Results and discussion

3.3.1 Isopropylamine adsorption

Brønsted-acid site concentrations were determined from TPD-TGA results following room-temperature adsorption of 2-propanamine, as shown in Fig. 3.3, which were measured on metal oxides and metal oxides over SBA-15 samples. On γ - Al_2O_3 , it has previously been reported that all of the amine desorbs intact over a broad temperature range, from room temperature to 700 K [19]. The high desorption temperature demonstrates that adsorption is strong but the fact that there is no reaction implies a complete absence of Brønsted-acid sites. This result is in sharp contrast to that found for the Al_2O_3 /SBA-15 sample. Following exposure to the amine and evacuation, approximately $200 \mu\text{mol g}^{-1}$ of the amine reacts to propene and ammonia between 575 and 650 K. Although the Brønsted-site concentration on Al_2O_3 /SBA-15 is significantly lower than the Al concentration ($\sim 2000 \mu\text{mol g}^{-1}$), it is much higher than is normally found on amorphous silica–alumina catalysts [27,59]. We suggest that the amorphous silica walls making up the SBA-15 are exceptionally capable of incorporating Al^{3+} into tetrahedral positions in the siliceous matrix.

The TPD-TGA results for 2-propanamine on pure and SBA-15-supported ZrO_2 and TiO_2 were unexpectedly similar to that found for Al_2O_3 . Again, the pure oxides showed no Brønsted acidity, while the SBA-15-supported oxides both showed significant concentrations of Brønsted-acid sites, $130 \mu\text{mol g}^{-1}$ for ZrO_2 /SBA-15 and $30 \mu\text{mol g}^{-1}$ for TiO_2 /SBA-15, as determined by

the reaction of the amine between 575 and 650 K. Evidence for Brønsted acidity in some zirconia silicates has been presented previously, based on isomerization of butane and on the formation of pyridinium ions in FTIR measurements [60]. Obviously, the nature of Brønsted-acid sites formed by Zr^{4+} and Ti^{4+} in silica is not expected to be similar to that of sites formed by tetrahedral Al^{3+} .

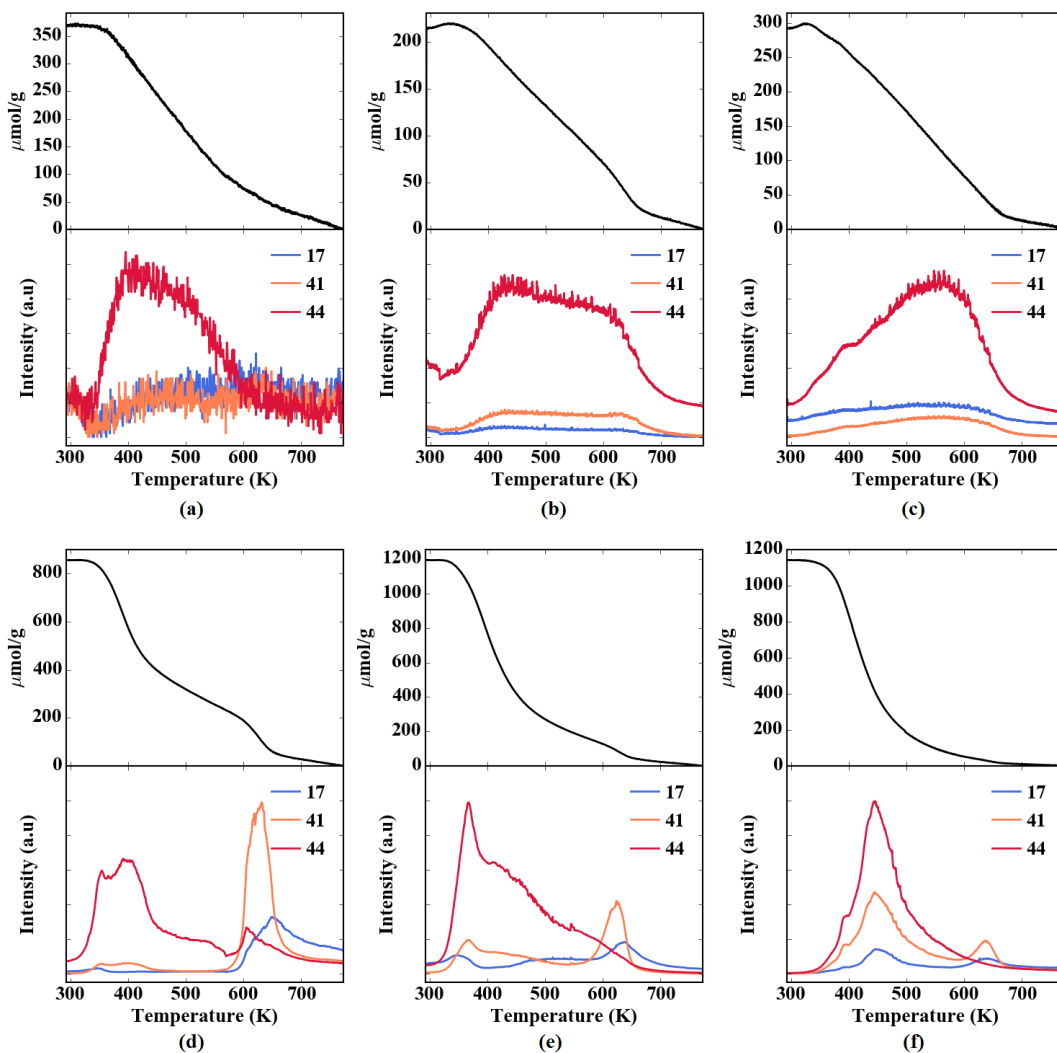


Figure 3.3: TPD-TGA for 2-propylamine over (a) $\gamma\text{-Al}_2\text{O}_3$ (b) ZrO_2 (c) TiO_2 (d) 10 wt% $\text{Al}_2\text{O}_3/\text{SBA-15}$ (e) 10 wt% $\text{ZrO}_2/\text{SBA-15}$ (f) 10 wt% $\text{TiO}_2/\text{SBA-15}$. For 2-propylamine, the peaks correspond to 2-propylamine ($m/z=44$), propene ($m/z=41$) and amine ($m/z=17$)

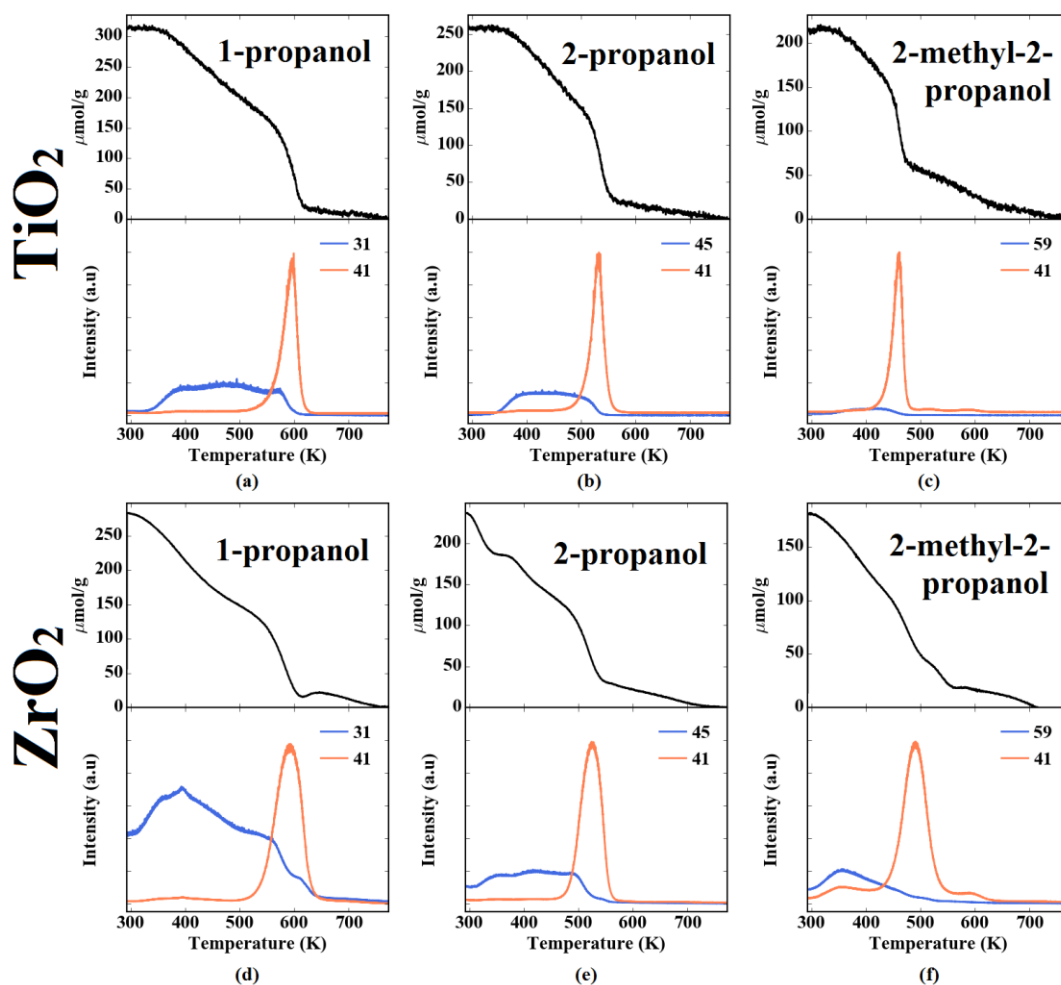


Figure 3.4: TPD-TGA results for 1-propanol, 2-propanol and 2-methyl-2-propanol over TiO_2 and ZrO_2 . The corresponding TPD-TGA results over $\gamma\text{-Al}_2\text{O}_3$ can be found in ref [19]. For 1-propanol, the peaks correspond to 1-propanol ($m/z=31$) and propene ($m/z=41$); for 2-propanol, the peaks are for 2-propanol ($m/z=45$) and propene ($m/z=41$); for 2-methyl-2-propanol, the peaks are 2-methyl-2-propanol ($m/z=59$) and butane ($m/z=41$)

3.3.2 Alcohol dehydration over metal oxides

TPD-TGA experiments were performed with 1-propanol, 2-propanol, and 2-methyl-2-propanol on TiO_2 , ZrO_2 and $\gamma\text{-Al}_2\text{O}_3$ [19]. Fig. 3.4 shows results for 1-propanol, 2-propanol, and 2-methyl-2-propanol on the TiO_2 and ZrO_2 samples. For 1-propanol (Fig. 3.4(a) and (d)) the

initial coverages are $300 \mu\text{mol g}^{-1}$ and $250 \mu\text{mol g}^{-1}$, respectively. Both of these correspond to a specific surface coverage of 3×10^{18} molecules m^{-2} , which is close to what would be expected for a monolayer and essentially the same as that reported for $\gamma\text{-Al}_2\text{O}_3$ in a previous study [19]. The TPD results indicate that desorption occurred in two temperature regions, with unreacted 1-propanol ($m/z = 31$) leaving the sample below 550 K and propene ($m/z = 41$) desorbing in a peak centered at ~ 590 K. (Desorption features for water were too broad to observe.) Propene ($m/z = 41$) desorption peaks on the two oxides were narrow, implying that the reaction sites on each material are nearly catalytically identical. Mass changes associated with propene desorption indicate that approximately $150 \mu\text{mol g}^{-1}$ 1-propanol reacted to propene and water on TiO_2 and $120 \mu\text{mol g}^{-1}$ on ZrO_2 . It is also interesting to note that reaction to propene and water occurred at ~ 550 K on $\gamma\text{-Al}_2\text{O}_3$ [19].

Table 3.1: TPD-TGA desorption peaks of the alkenes, experimental activation energies and BET surface areas of the oxides. The values of alcohol dehydration on $\gamma\text{-Al}_2\text{O}_3$ have been taken from ref [19]

Oxide	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Alcohol	Alkene desorption peak T(K)	Activation energy (kJ mol^{-1})
TiO_2	50	1-propanol	596	171
		2-propanol	533	153
		2-methyl-2-propanol	461	128
ZrO_2	40	1-propanol	595	171
		2-propanol	525	150
		2-methyl-2-propanol	491	140
$\gamma\text{-Al}_2\text{O}_3$	120	1-propanol	550	141
		2-propanol	490	121
		2-methyl-2-propanol	435	110

TPD–TGA experiments for 2-propanol and 2-methyl-2-propanol on both TiO_2 and ZrO_2 are also shown in Fig. 3.2. The data are qualitatively similar to those obtained for 1-propanol, with similar initial coverages and similar fractions of the alcohols reacting on each oxide. The only major difference is in the temperatures at which the olefin products form. With 2-propanol, the propene formed in a sharp peak at 533 K on TiO_2 and 525 K on ZrO_2 . With 2-methyl-2-propanol, olefin products were formed at 490 K on TiO_2 and 460 K on ZrO_2 . Again, these temperatures are significantly higher than what was observed with $\gamma\text{-Al}_2\text{O}_3$ in previous study [19]. The desorption peak-temperature data are summarized in Table 3.1, together with reaction activation energies calculated using the Redhead equation [61], assuming a normal reaction pre-exponential of 10^{13} s^{-1} .

TPD-TGA measurements of 1-propanol are complementary in that the alcohol reacts on both Lewis- and Brønsted-acid sites. Results for H-ZSM-5 zeolite [30] have been published elsewhere. As with 2-propanamine, some of the adsorbed 1-propanol leaves the sample unreacted. On H-ZSM-5, molecules associated with the Brønsted sites react at approximately 460 K. TPD-TGA data for $\gamma\text{-Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3/\text{SBA-15}$ are shown in Fig. 3.5 a&b and are qualitatively more similar to the results for H-ZSM-5. On $\gamma\text{-Al}_2\text{O}_3$, 1-propanol molecules at Lewis-acid sites undergo dehydration over a narrow temperature range centered at approximately 550 K. Approximately $800 \mu\text{mol g}^{-1}$ of the alcohol remains on the sample following room-temperature exposure, followed by evacuation for 1 h. During the temperature ramp, $360 \mu\text{mol g}^{-1}$ of the alcohol react over a broad temperature range centered at 480 K. Because this is close to the reaction temperature observed with Brønsted sites on H-ZSM-5, we suggest that the lower dehydration temperature on $\text{Al}_2\text{O}_3/\text{SBA-15}$ compared to $\gamma\text{-Al}_2\text{O}_3$ is associated with reaction on Brønsted-acid sites. The increased width of the reaction feature on $\text{Al}_2\text{O}_3/\text{SBA-15}$ may be due to the presence of a mixture of Brønsted- and Lewis-acid sites, since the concentration of sites able

to react 1-propanol was larger than the concentration of Brønsted acid sites determined by 2-propanamine adsorption.

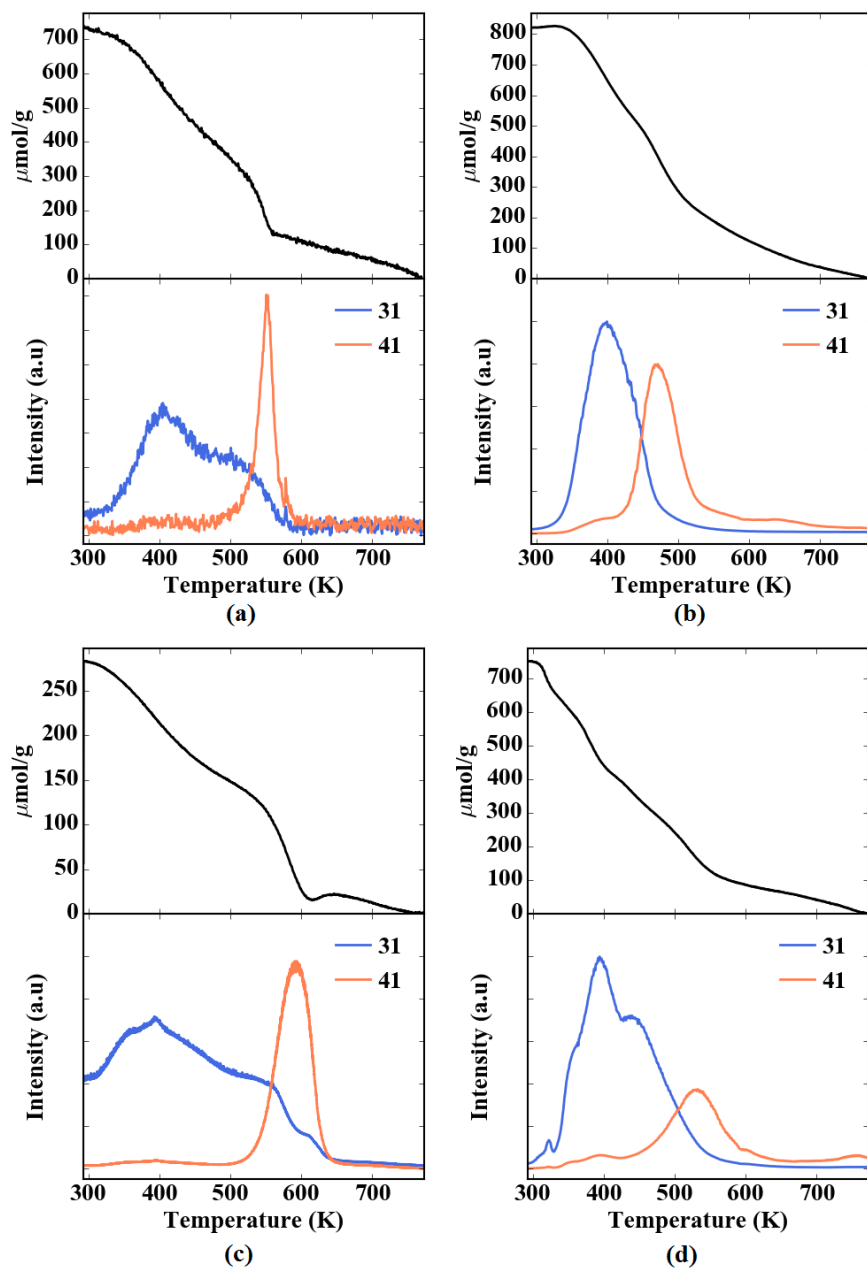


Figure 3.5: TPD-TGA results for 1-propanol over (a) γ - Al_2O_3 (b) Al_2O_3 -SBA15 (c) ZrO_2 (d) ZrO_2 -SBA15. For 1-propanol, the peaks correspond to 1-propanol ($m/z=31$) and propene ($m/z=41$)

TPD-TGA curves for the 1-propanol adsorption on ZrO_2 and $\text{ZrO}_2/\text{SBA-15}$ are shown in Fig. 3.5 c&d. The acid-site concentrations, as determined by the amount of 1-propanol that dehydrates, were 120 and 200 $\mu\text{mol g}^{-1}$ on these two samples, respectively. The peak temperature for propene formation on pure ZrO_2 was 590 K, which is approximately 40 K higher than with $\gamma\text{-Al}_2\text{O}_3$, implying that the Lewis-acid sites on ZrO_2 are somewhat weaker. Because the concentration of sites able to dehydrate 1-propanol on $\text{ZrO}_2/\text{SBA-15}$ was similar to the

Brønsted-acid site concentration, most of the 1-propanol reacting on this sample are likely associated with Brønsted sites, which may explain the lower reaction temperature on this sample, ~540 K. Previously, changes in the peak temperature for dehydration of alcohols at Brønsted sites associated with framework Fe or Al in siliceous zeolites has been shown to correlate with the activity of those sites [25]. Therefore, using the dehydration temperature as a measure of site strength, the Brønsted sites in $\text{ZrO}_2/\text{SBA-15}$ must be significantly weaker than those in $\text{Al}_2\text{O}_3/\text{SBA-15}$.

Results for adsorption of 1-propanol on TiO_2 and $\text{TiO}_2/\text{SBA-15}$ are not shown because they were similar to that obtained with ZrO_2 and $\text{ZrO}_2/\text{SBA-15}$. The site density as determined by the amount of 1-propanol that reacted was slightly higher on TiO_2 compared to ZrO_2 , 150 $\mu\text{mol g}^{-1}$ versus 120 $\mu\text{mol g}^{-1}$; but the dehydration temperatures were identical within experimental error. The SBA-15 support had less effect on the dehydration peak temperature with TiO_2 (The dehydration peak temperature on $\text{TiO}_2/\text{SBA-15}$ was 620 K.), which is likely due to the fact that the Brønsted site concentration was much lower on $\text{TiO}_2/\text{SBA-15}$ than on $\text{ZrO}_2/\text{SBA-15}$. A summary of the most important properties for each of the materials used in this study is given in Table 3.2.

Table 3.2: Site densities and BET surface area of the catalyst sample used in this study

Materials	TPD-TGA of 1-propanol ($\mu\text{mol g}^{-1}$)	TPD-TGA of 2-propylamine ($\mu\text{mol g}^{-1}$)	Site density for TOF calculation ($\mu\text{mol g}^{-1}$)	BET surface area ($\text{m}^2 \text{g}^{-1}$)
$\gamma\text{-Al}_2\text{O}_3$	200	0	200	150
ZrO_2	120	0	120	40
TiO_2	150	0	150	50
10 wt% Al_2O_3 /SBA-15	360	200	360	480
10 wt% ZrO_2 /SBA-15	200	130	200	560
10 wt% TiO_2 /SBA-15	260	30	260	480
SBA-15	0	0	-	650
H-BEA	-	100	100	-
Sn-BEA	-	0	100 ^a	-

^a The active site density of SnBEA was obtained from TPD-TGA measurement adsorbing acetonitrile

3.3.3 HMF etherification reaction studies

The liquid-phase reaction (69 bar) of HMF with 2-propanol (1 g HMF dissolved in 100 mL of 2-propanol) on each of the catalysts was characterized using a fixed feed rate of 0.2 mL min^{-1} . The measurements were carried out with 0.1 g of each catalyst at 413 and 453 K to determine the effect of temperature on conversion and selectivity and with 0.4 g of each catalyst at 453 K to determine how selectivity changed with conversion at this temperature. All of the catalysts were stable over the period of several hours used in making the measurements and no conversion was observed in the absence of a catalyst. While we have focused on the products formed from HMF, we also observed formation of acetone from the 2-propanol in amounts equal to that required for the transfer hydrogenation rates. The data at 413 K emphasizes the initial products formed at low conversions and is shown in Table 3.3. (Note: the data in Table 3.3 for H-

BEA and SnBEA were determined using a catalyst loading of 0.05 g in order to maintain the conversion below 10%.) All of the reaction results are summarized in graphical form in Fig. 3.6.

Table 3.3: Turnover rates and product selectivities of HMF etherification with IPA at 413 K^a

Materials	Conv. (%)	TOF (10 ⁻³ molec per site s ⁻¹)	Product selectivity (%)			
			MEF	BHMF	MEFA	BEF
γ -Al ₂ O ₃	11.1	1.45	-	55.4	44.7	-
ZrO ₂	7.1	1.56	-	91.0	9.0	-
TiO ₂	3.7	0.65	-	79.4	20.6	-
10 wt%Al ₂ O ₃ /SBA-15	11.4	0.83	91.5	-	-	8.5
10 wt%ZrO ₂ /SBA-15	12.1	1.60	-	-	31.4	68.6
10 wt%TiO ₂ /SBA-15	6.9	0.7	31.7	-	20.5	47.9
H-BEA	14.6	7.20	97.9	-	-	2.1
Sn-BEA	12.8	6.71	9.8	-	7.4	82.5

^a The active site density of Sn-BEA was obtained from TPD-TGA measurement adsorbing acetonitrile

Since the conversions in Table 3.2 were all less than 10%, these data appear to represent the initial products that are formed in the reaction. Several clear trends appear. H-BEA and Al₂O₃/SBA-15 have strong Brønsted-acid sites and are both highly selective for MEF. As expected based on literature reports, these catalysts are highly active for ether formation but less active for transfer hydrogenation. By contrast, the pure oxides, which exhibit purely Lewis acidity, are much more active for transfer hydrogenation reactions. On ZrO₂, the selectivity for the di-alcohol, 2,5-bis(hydroxymethyl)furan (BHMF), was over 90%. BHMF can go on to form the monoetheralcohol, 5-[(1-methylethoxy)methyl]-2-furanmethanol (MEFA), and the di-ether, 2,5-bis[(1-methylethoxy)methyl]furan (BEF), on the more acidic oxides. The Lewis-acid sites on

SnBEA were the most active, showing a high selectivity to 2,5-bis[(1-methylethoxy)methyl]furan (BEF) even at low total conversions. Interestingly, ZrO₂ and TiO₂ on SBA-15 were also quite selective towards formation of BEF, presumably by carrying the MPV interhydride transfer from 2-propanol to the carbonyl of HMF on the Lewis acid sites followed by etherification on the Brønsted acid sites of the catalyst.

Turnover frequencies, based on HMF consumption, were estimated for each of the catalysts using site densities calculated from the amount of 1-propanol that reacted in TPD-TGA measurements. The only obvious trend is that both H-BEA and Sn-BEA were much more active than either the pure oxides or the oxides supported on SBA-15. This might suggest that the zeolite cavities have a confining effect that increases the reaction rates. Alternatively, change in coordination of the metal atom may also play a role in the observed turnover frequencies.

As shown in Fig. 3.6, increasing the temperature to 453 K did not change the overall picture. As expected, the conversions increased and selectivities for MEFA and BEF increased at the expense of BHMF formation on those catalysts that are active for transfer hydrogenation. Similarly, increasing the catalyst loading did not significantly alter the conclusions, other than to suggest that MEFA and BEF can undergo additional reactions to form unidentified side products. This was especially noticeable with ZrO₂/SBA-15. Interestingly, MEF does not seem to undergo additional reactions on H-BEA or Al₂O₃/SBA-15, since the selectivity for MEF remained high at the higher conversions. Once MEF is formed, further reaction to the desired product, BEF, does not occur.

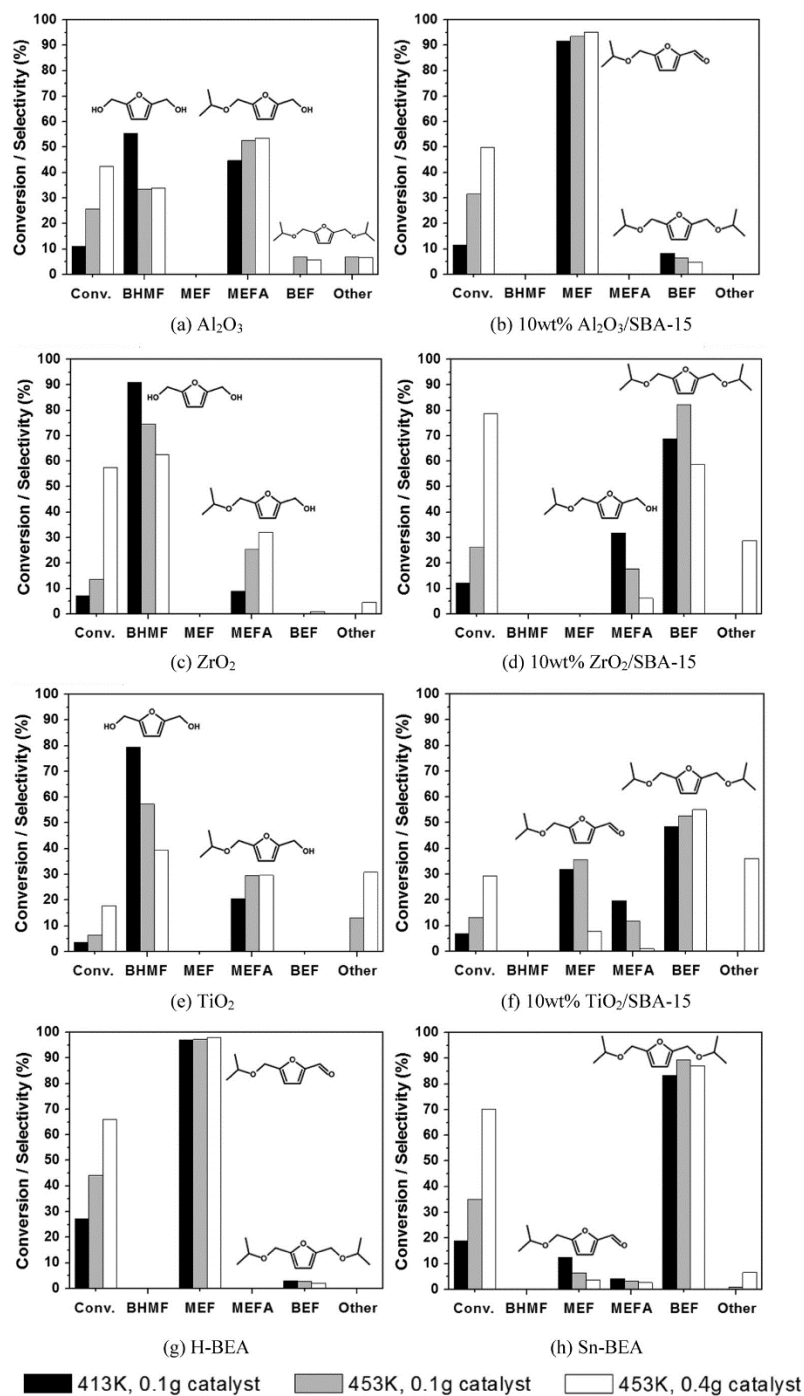


Figure 3.6: HMF conversion and product distributions over different catalysts as a function of temperature and catalyst loading

Overall, the results from this study show surprisingly simple product distributions for the reaction of HMF with 2-propanol over a variety of solid catalysts, although the selectivities were

remarkably different depending on the nature of the oxide. Lewis acidity appears to be essential for transfer hydrogenation, since the reaction was almost completely absent on H-BEA and $\text{Al}_2\text{O}_3/\text{SBA-15}$, which are primarily Brønsted acids. These strong Brønsted acids produce the mono-ether (MEF), which appears to be resistant to transfer hydrogenation. Bulk ZrO_2 and TiO_2 , which are Lewis acids only, were both reasonably active for hydrogen transfer but less active for the etherification reactions. The weak Brønsted acidity that was added by supporting these oxides on SBA-15 enhanced that activity substantially; however, Brønsted acidity is clearly not required for etherification, given that Sn-BEA was very active and selective for production of the di-ether.

One very interesting question arising from this work involves how to characterize Lewis acidity and then relate it to catalytic activity. A previous adsorption study with alcohols on Sn-BEA showed that tert-butanol adsorbed at Sn sites started to undergo dehydration beginning at ~ 370 K in TPD-TGA [57]. By comparison, the same dehydration reaction on $\gamma\text{-Al}_2\text{O}_3$ commenced above 400 K [19]. On the other hand, diethyl ether, which is expected to have a similar reactivity to ethanol or 1-propanol given that reaction involves a primary carbenium ion, desorbed from the Sn sites unreacted, while $\gamma\text{-Al}_2\text{O}_3$ was able to promote dehydration prior to desorption.

The difference here may be simply due to the ability of on $\gamma\text{-Al}_2\text{O}_3$ to hold the alcohols to high temperatures, which does not itself seem to be a good measure of acid strength.

Finally, it is worth noting that the chemistries observed in this study were all possible without having a precious metal or gaseous hydrogen. There was also no attempt to optimize the materials used in this study; the addition of dopants to modify the acidic properties could well lead to improved selectivities. This is still a relatively new avenue for research.

3.4 Summary

Using TPD–TGA measurements, we investigated the dehydration of different alcohols on TiO_2 , ZrO_2 and $\gamma\text{-Al}_2\text{O}_3$. Our results demonstrate that $\gamma\text{-Al}_2\text{O}_3$ is a better dehydration catalyst than TiO_2 and ZrO_2 , with the latter two oxides showing similar dehydration performance. The liquid-phase reaction of HMF with 2-propanol can be catalyzed by a wide range of oxide catalysts. $\gamma\text{-Al}_2\text{O}_3$, ZrO_2 , and TiO_2 are all Lewis acids that are able to carry out transfer hydrogenation of the aldehyde functionality in HMF, as well as form a mono-ether. Strong Brønsted sites, present in H-BEA and $\text{Al}_2\text{O}_3/\text{SBA-15}$, catalyze formation of a mono-ether without hydrogenation of the carbonyl. Weak Brønsted sites are formed when ZrO_2 and TiO_2 are supported on SBA-15 and these promote ether formation following transfer hydrogenation. Sn-BEA, which contains only Lewis acid sites, was the most active catalyst for transfer hydrogenation and ether formation.

Chapter 4. An Examination of Alkali-Exchanged BEA Zeolites as Possible Lewis-Acid Catalysts

4.1 Introduction

There has recently been a great deal of interest in the development of solid Lewis acids for the processing of complex organic molecules, particularly for reactions involving biomass, [50,51,62–65]. Solid Lewis acids selectively catalyze a number of important reactions that are not effectively carried out by Brønsted acids, such as glucose-fructose isomerization [7] and the Meerwein-Ponndorf-Verley (MPV) reactions [16,49]. Some solid Lewis acids, such as TiO_2 [66] and ceria [67], are even effective in water. One of the big advances in the development of solid Lewis acids has come from the recognition that highly active catalytic sites can be formed by framework substitution of metals like Sn [16,68,69], Ti [70,71], Zr [51,72], and Hf [72] into siliceous zeolites. Unfortunately, many of these materials can be difficult to synthesize and characterize. Although great progress has been made in our understanding of these metal-substituted zeolites [73,74], there are still questions about the exact nature of the active sites.

It is noteworthy that gas-phase alkali cations “are generally considered as archetypal Lewis acids because the full positive charge of the naked cation allows strong binding with classical Lewis bases [3]”. This leads to the question whether simple, alkali-exchanged zeolites might be used as solid Lewis acids. It is known that the hydrogen forms of zeolites have Brønsted-acid sites with characteristics that are very different from solution-phase Brønsted acids due in part to the fact that solvent interactions with the protonated base are limited by the nanopore structure of the zeolite. For example, for bases with proton affinities greater than that of ammonia, heats of adsorption at zeolite Brønsted sites tend to scale in a nearly 1:1 manner with the proton affinities of the bases [20,37], while heats of protonation in solution-phase are much more dependent on the structure of the molecule and the solvent. One manifestation of this is that

pyridine is a much weaker base than ammonia in aqueous solutions, while it has a much higher proton affinity and interacts much more strongly with Brønsted sites in zeolites [36]. Although alkali cations in solution would not be considered Lewis acids, the environment in the zeolite pores could reduce solvent effects in the alkali-exchanged materials so that alkali cations could interact with Lewis bases in a similar manner to that observed in the gas phase.

However, alkali-exchanged zeolites are normally thought of as basic materials; and, in agreement with this, alkali-exchanged faujasites have been shown to exhibit catalytic properties that correlate with the basicity of the alkali hydroxide [75–78]. For example, Li, et al [76] found that the condensation of propionic acid and formaldehyde to form methacrylic acid increased with the basicity of the cation, with $\text{NaX} < \text{KX} < \text{CsX}$. The properties in this case would appear to be dominated by the basicity of the framework oxygens. While this may be a general feature in zeolites, it should be recognized that many of the alkali cations in the faujasite structure will not be accessible to adsorbates, depending on the cation size and the Si/Al ratio of the zeolite [79,80]. By contrast, all of the cations should be accessible to adsorbates in high-silica zeolites like BEA and MFI and these cations should exhibit Lewis-acid character, even if the oxygens are basic. There is indeed evidence that this may sometimes occur. For example, Huang and Kaliaguine reported that alkali-exchanged ZSM-5 was active for the transformation of propene to aromatics and the dehydrogenation of cyclohexane [10]. Tago, et al [11] found that activity of alkali-ion-exchanged BEA zeolites for the production of isobutylene from acetone followed the order of the acidity of the cations. Other evidence that alkali cations in solids could have Lewis-acid character comes from a recent study that showed encapsulated Li^+ ions in C_{60} are active catalysts for the Diels-Alder reactions [81].

In the present work, we set out to investigate more completely the idea that alkali-exchanged BEA zeolites could be used as Lewis-acid catalysts and to compare the nature of the

sites to those formed in SnBEA. We will show that, based on studies of selected probe molecules on Li-, Na-, and K-exchanged BEA zeolites, adsorption is dominated by interactions with the alkali cations. Based on pyridine adsorption, Li-BEA would appear to be as strong a Lewis acid as SnBEA; however, the reactivities of selected probe molecules in TPD measurements suggest that the alkali-exchanged zeolites are not good catalysts, a result that is confirmed by the lack of reaction between 5-hydroxymethyl furfural (HMF) and 2-propanol in flow-reactor measurements.

4.2 Experimental

The reactions of HMF with 2-propanol were carried out in the high-pressure, flow reactor described in Chapter 3. The tubular reactor was a 20-cm long, stainless-steel tube with a 4-mm ID and 1/4-inch OD, passed through a tube furnace. The liquid feed, a mixture of 1 g HMF (99%, Sigma-Aldrich) and 100 mL 2-propanol (99.9%, Fisher Scientific), was introduced into the reactor using an HPLC pump (Series I+, Scientific Systems Inc). The reactor pressure was maintained at 69 bar using a back-pressure regulator (KPB series, Swagelok), and product analysis was carried out by means of a GC-Mass Spectrometer (QP-5000, Shimadzu). For the present studies, we used a fixed feed rate of 0.2 ml/min. The measurements were performed using 0.1 g of each catalyst at 453 K to determine the effect of temperature and catalyst loading on conversion and selectivity. There was no reaction in the absence of a catalyst.

Most of the samples used in this study were based on NH₄-BEA (Zeolyst International, #CP814E; Si:Al₂ = 24). The Brønsted-site density of the hydrogen form of the BEA zeolite, determined from the amount of 2-propylamine which reacted to propene and ammonia between 575 and 650 K in TPD-TGA [24], was found to be 650 μmol/g. Based on the ²⁷Al MAS NMR spectrum of the fully hydrated sample, obtained using a Bruker DSX-300 NMR spectrometer at a ²⁷Al frequency of 78.2 MHz with a 7 mm MAS probe, the non-framework Al was 15% of the total. The alkali forms of the BEA zeolite were prepared using the methods described in Chapter

2. 1 g of the NH_4^+ form of the BEA was exchanged with a 300 mL solution that was 0.1 M LiCl (NaCl, KCl) and 0.005 M LiOH (NaOH, KOH) for 4 h at room temperature. That this procedure resulted in complete exchange to the alkali forms of the zeolite was demonstrated by the fact that calcined forms of the alkali-exchanged samples showed no evidence for Brønsted sites by either FTIR of adsorbed pyridine or TPD-TGA of adsorbed 2-propanamine.

The siliceous BEA (designated here as SiBEA) was made by stirring a commercial BEA (Zeolyst, CP814C, $\text{Si}/\text{Al}_2=38$) in 7-M nitric acid for 8 h at 353 K. The sample was then filtered and dried overnight at 333 K. ICP-AES analysis of this sample showed that the bulk Si/Al_2 ratio was greater than 1500. In TPD-TGA measurements on this sample, the adsorption uptakes in the presence of 2-propylamine vapor were similar to that obtained on the unmodified H-BEA zeolite, indicating that the pore structure remained intact. In agreement with the high Si/Al_2 ratio, the Brønsted-site density was undetectable ($< 5 \mu\text{mol/g}$) and the loss of framework Al from the structure caused this material to have a high concentration of hydroxyl defects.

The SnBEA used for comparison in the reaction and adsorption studies had a Si/Sn ratio of 118 and was prepared by the procedure described by Corma et al [16]; characterization of this material has been described in detail elsewhere [51,57]. Because the SnBEA was made in a fluoride-containing medium, the defect site density was very low and the material was highly hydrophobic.

4.3 Results

4.3.1 Calorimetric Investigation of CO

To better understand the nature of the Lewis sites generated by alkali cations in BEA, we performed calorimetric experiments using CO adsorption at 195 K. CO is a weak Lewis base, with gas-phase affinities for Li^+ , Na^+ , and K^+ of 55, 33, and 19 kJ/mol, respectively [3]. Of critical importance for interpretation of the experimental results is that CO adsorption is

reversible at 195 K. Reversible adsorption is essential in microcalorimetry for ensuring that the molecules sample all sites in the catalyst, filling the strongest sites first, and that the molecules do not simply adsorb chromatographically at the first site with which they come in contact [82]. If adsorption is chromatographic and irreversible, the measured heats will appear to be constant up to the saturation coverage and there will be no possibility for measuring site distributions. Chromatographic adsorption is almost certainly a major problem with adsorption of strong bases, like pyridine and ammonia, on acidic zeolites [82].

In a previous study of CO adsorption on Li-exchanged MFI zeolites [83], the differential, isosteric heats of adsorption ($-\Delta H$) were found to be 36 kJ/mol at low coverages, decreasing to ~ 17 kJ/mol for coverages well in excess of one per cation. Because the heats of adsorption for CO on a siliceous MFI were ~ 17 kJ/mol and nearly independent of coverage, the heats in excess of this value can almost certainly be assigned to interactions with the Li cations. The zero-coverage heats were lower for Na-MFI (33 kJ/mol) and K-MFI (28 kJ/mol), and there was also evidence that more than one CO molecule could interact with these larger cations. Finally, it is worth noting that the heats of adsorption for O₂ on both siliceous MFI and Li-MFI were also ~ 17 kJ/mol. This fact is useful since it demonstrates that O₂ does not have significant interactions with the cations but interacts with the siliceous walls of the zeolite in a similar manner to that of CO. This implies that heats of adsorption for O₂ can be used to abstract that component of the CO adsorption heats due to interactions with the siliceous walls of the zeolite.

The heats of adsorption for CO on the alkali-exchanged BEA and SnBEA samples at 195 K are shown in Fig. 4.1, together with results for O₂ on Li-BEA. The results are very similar to what was observed on the MFI zeolites. Within experimental error, the zero-coverage heats for CO on the alkali-exchanged BEA were the same as what was observed on the MFI zeolites, with zero-coverage heats of 37 kJ/mol on Li-BEA, 34 kJ/mol on Na-BEA, and 26 kJ/mol on K-BEA.

The differential heats for O₂ on Li-BEA were ~15 kJ/mol, slightly lower than was observed on Li-MFI; but this is reasonable since BEA is a larger-pore zeolite and heats of adsorption for physically adsorbed molecules decrease with pore size [83]. For CO adsorption on Li-BEA at coverages above 800 $\mu\text{mol/g}$, the heats of adsorption approached the value observed for O₂, implying that molecules above one per Li are unable to approach the Li cations. The transition between the low- and high-energy states is gradual due to entropic effects [82]. On Na-BEA and K-BEA, the heats are initially lower than those found on Li-BEA but the heats remain elevated to much higher CO coverages. Based on molecular sizes [83], multiple CO molecules can interact with these cations simultaneously.

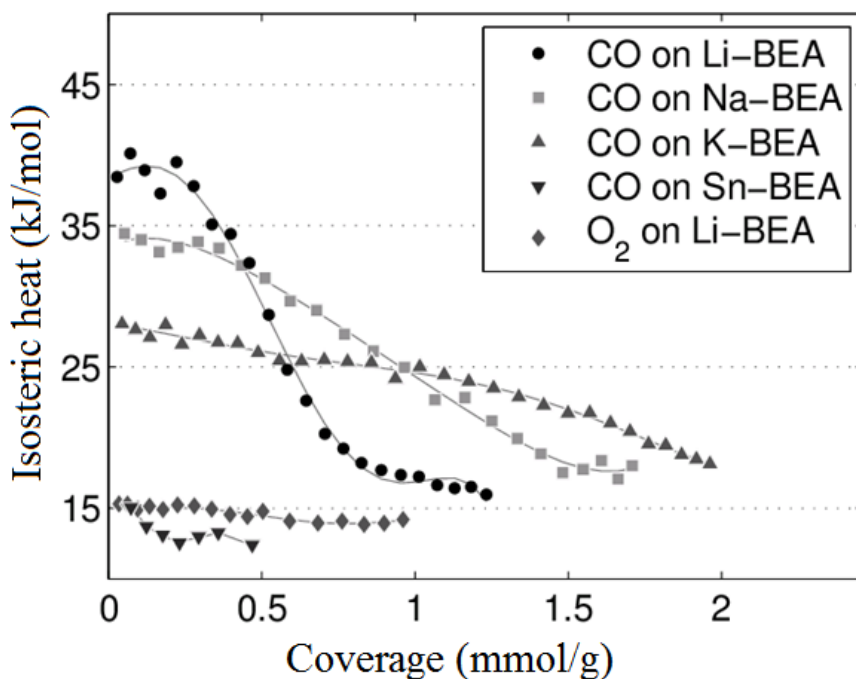


Figure 4.1: Calorimetric data for CO and O₂ adsorption on Li-BEA and for CO on Na-BEA, K-BEA and SnBEA. The measurements were performed at 195 K.

What is perhaps most surprising about the data in Fig. 4.1. is that the heats of adsorption for CO in SnBEA varied from 15 to 13 kJ/mol, essentially the same value one would expect for a

siliceous BEA. Although the Sn site density was lower than the site densities in the alkali-BEA samples, it should have been possible to observe some evidence for adsorption on the Sn sites if interactions existed. Even in the absence of an ion-dipole interaction, one would expect additional van der-Waals interactions because of the higher Sn molecular weight. The result here suggests that the Sn cations are not accessible to CO molecules.

To summarize, several important conclusions can be drawn from the data in Fig. 4.1. First, CO molecules clearly can interact with the cations in the alkali-exchanged BEA and the energetics of these interactions are significant. Second, the attractive interactions are strongest with Li and weakest with K, in good correspondence with the gas-phase affinities of these ions and their expected Lewis acidity. Third, more than one CO molecule can interact simultaneously with the larger cations. Finally, the interaction between CO and framework-substituted Sn sites is very weak.

4.3.2 Adsorption studies of 2-propylamine and pyridine

Among the most common methods for characterizing solid acidity are TPD and FTIR measurements of pyridine or propylamines. TPD-TGA results for 2-propylamine on SiBEA, SnBEA, and the alkali-exchanged BEA samples are shown in Fig. 4.2. The TGA data are reported as micromoles of 2-propylamine per gram of zeolite, referenced to the weight of the sample prior to exposure. All of the amine molecules on each of the samples desorbed as 2-propanamine ($m/e = 17, 41, 44$). If any of the samples had contained Brønsted sites, there would have been a reaction to propene ($m/e = 41$) and ammonia ($m/e = 17$) between 575 and 650 K [20].

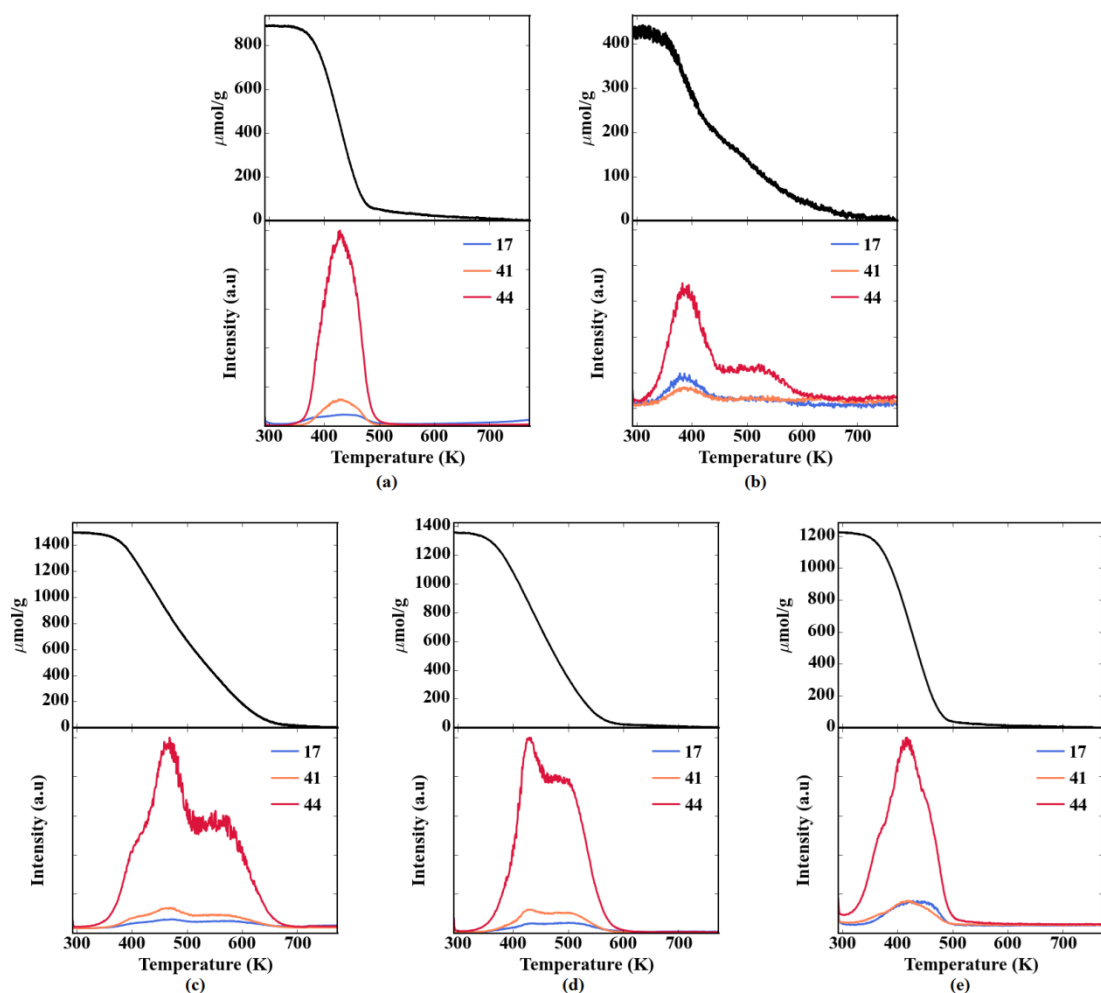


Figure 4.2: TPD-TGA results for 2-propylamine on (a) SiBEA, (b) SnBEA (c) Li-BEA, (d) Na-BEA, and (e) K-BEA. For 2-propylamine TPD, the peaks correspond to 2-propylamine ($m/z=44$), propene ($m/z=41$) and amine ($m/z=17$). Deamination reaction is not observed on any of these samples

Although none of the samples contained Brønsted sites, it is still interesting to consider the desorption curves in more detail. For SiBEA, the initial coverage after exposure to the amine and 2-h evacuation at room temperature was 850 $\mu\text{mol/g}$. This adsorption is likely associated with amine molecules on silanol defect sites. The silanols are not strongly acidic, as demonstrated by the fact that all of the amine desorbed below 500 K. On SnBEA, the initial amine coverage

following adsorption and evacuation was slightly greater than 400 $\mu\text{mol/g}$ and the TPD results showed two desorption features, centered at ~ 390 K and ~ 520 K. The amount of 2-propanamine desorbing from the 520-K feature appears to be ~ 150 $\mu\text{mol/g}$, which is close to expected Sn site density, 140 $\mu\text{mol/g}$ based on a Si/Sn ratio of 118. Therefore, the high-temperature feature is likely associated with framework Sn sites. Because the concentration of silanol defects in this sample is expected to be very low, the 390-K feature is likely due to amine molecules that are hydrogen-bonded to the molecules adsorbed at the Sn sites [32].

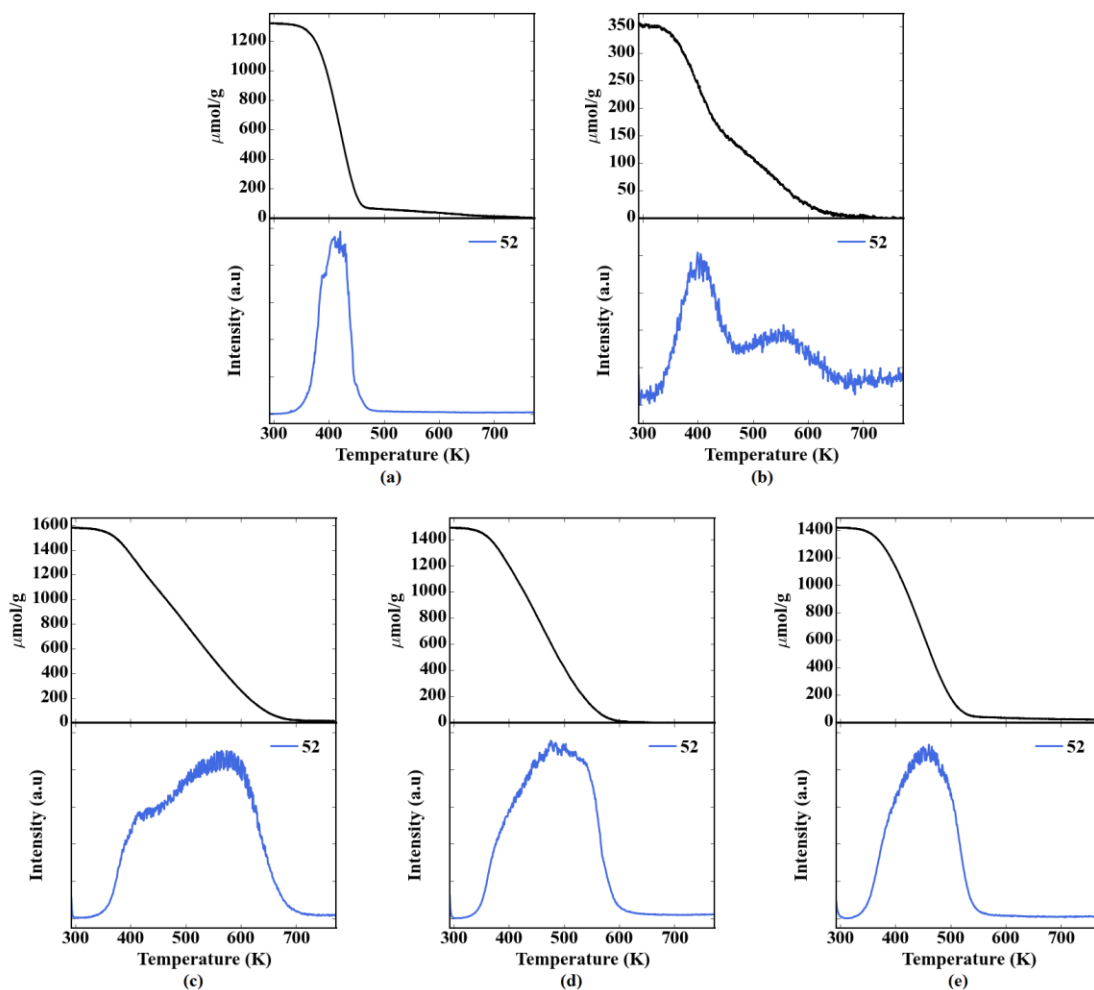


Figure 4.3: TPD-TGA results for pyridine on (a) SiBEA, (b) SnBEA (c) Li-BEA, (d) Na-BEA, and (e) K-BEA. For pyridine TPD, the peak correspond to pyridine ($m/z=52$).

TPD-TGA results for each of the alkali-exchanged BEA samples also showed high initial coverages following evacuation and there were at least two peaks in desorption, at least from Li-BEA and Na-BEA. The high-temperature peaks on Li-BEA (centered at ~ 580 K) and Na-BEA (centered at 500 K) corresponded to coverages that were close to the expected alkali site density of $650 \mu\text{mol/g}$. Additional features in the TPD below 500 K could be due to molecules that were hydrogen-bonded to the first molecule at the site or to the adsorption of multiple molecules at each site. With K-BEA, all of the 2-propanamine molecules desorbed below 500 K, implying that there is weaker adsorption on the larger cations.

The TPD-TGA results for pyridine ($m/e = 52$) in Fig. 4.3 lead to similar conclusions as those reached from 2-propanamine. Again, the initial coverage of pyridine on SiBEA following exposure to the vapor and evacuation was high, $\sim 1300 \mu\text{mol/g}$, but all of this desorbed below 450 K. TPD-TGA on SnBEA again showed two peaks, centered at 400 and 550 K, with the 550-K feature corresponding to a coverage similar to that of the Sn site density. TPD-TGA on the alkali-exchanged BEA samples showed high initial coverages, between 1300 and $1500 \mu\text{mol/g}$. Although the desorption peaks were broad, there is a progressive decrease in the peak temperatures of the highest-temperature peaks, from nearly 600 K on Li-BEA to ~ 520 K on Na-BEA and ~ 475 K on K-BEA. Clearly, there is an interaction between pyridine and the alkali cations and strength of this interaction decreases with increasing cation size.

The nature of the adsorbed pyridine on each of the samples was examined by FTIR, with the results shown in Fig. 4.4. In each case, the spectra were obtained after exposure to pyridine vapor at room temperature, followed by flushing with dry He at 353 K to remove at least some of the physisorbed molecules. The spectrum for pyridine adsorbed on H-BEA is shown in spectrum i) for comparison. The peaks at 1546 cm^{-1} and 1489 cm^{-1} are due to pyridinium ions, showing that the pyridine has been protonated by Brønsted sites. The peak at 1450 cm^{-1} , along with part of the

intensity at 1489 cm^{-1} , is likely due to additional physisorbed pyridine, perhaps bonded to the pyridinium ions. Spectrum ii), which was obtained on the dealuminated BEA sample with no Al, shows there is one major peak 1446 cm^{-1} , with possibly a small band near 1490 cm^{-1} , similar to a spectrum reported previously for pyridine on silica [84]. The SnBEA sample shows peaks at 1439 and 1484 cm^{-1} , Spectrum iii), while spectra for the three alkali-exchanged BEA samples are reported in Spectra iv) through vi) and are virtually identical exhibiting bands between 1439 and 1442 cm^{-1} and between 1487 and 1492 cm^{-1} .

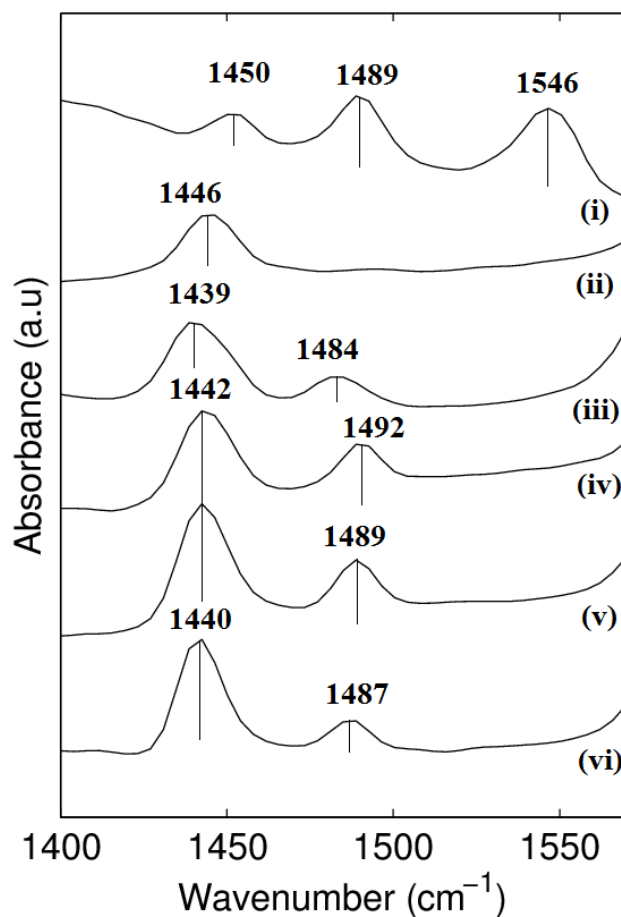


Figure 4.4: FTIR spectra of pyridine adsorbed on (i) H-BEA, (ii) SiBEA (iii) SnBEA (iv) Li-BEA, (v) Na-BEA, and (vi) K-BEA.

There are certainly no major differences between the spectrum obtained on SnBEA and those spectra for the alkali-exchanged BEA samples. The peak positions are also very similar to what is observed on alumina, a known Lewis acid [85]. Whether the small changes one observes in the region between 1484 and 1492 cm^{-1} are significant is uncertain. There may be a systematic shift with increasing binding strength that correlates with binding strength on the alkali-exchanged materials, since the peak shifts from 1487 cm^{-1} on K-BEA to 1492 cm^{-1} on Li-BEA; however, pyridine also binds strongly on Sn sites in SnBEA and the peak position in that case is to 1484 cm^{-1} . One obvious conclusion is that there is no clear correlation between acid strength and peak positions for Lewis acids in general or alkali-exchanged zeolites in particular.

4.3.3 Adsorption studies of acetonitrile

Acetonitrile has previously been found to be a useful molecule for probing Lewis acid sites in SnBEA [9,57]. TPD-TGA results for acetonitrile on SiBEA, SnBEA and alkali-exchanged BEA samples are shown in Fig. 4.5. For SiBEA, the initial coverage after room-temperature adsorption and evacuation was below 100 $\mu\text{mol/g}$, much lower than the initial coverages in the case of 2-propylamine and pyridine. Meanwhile the TPD result shows no obvious desorption features. Results here suggest that adsorption of acetonitrile on silanols was extremely weak, making acetonitrile a good probe molecule to discriminate between Lewis acid sites and silanols. On SnBEA, initial coverage was between 80~100 $\mu\text{mol/g}$ and desorption occurs in a peak centered at 400 K. Because the coverage is less than the framework Sn concentration and desorption occurs at such low temperatures, the attraction between acetonitrile and framework Sn sites must be weak; some of the molecules adsorbed at Sn sites must have been removed during evacuation at room temperature.

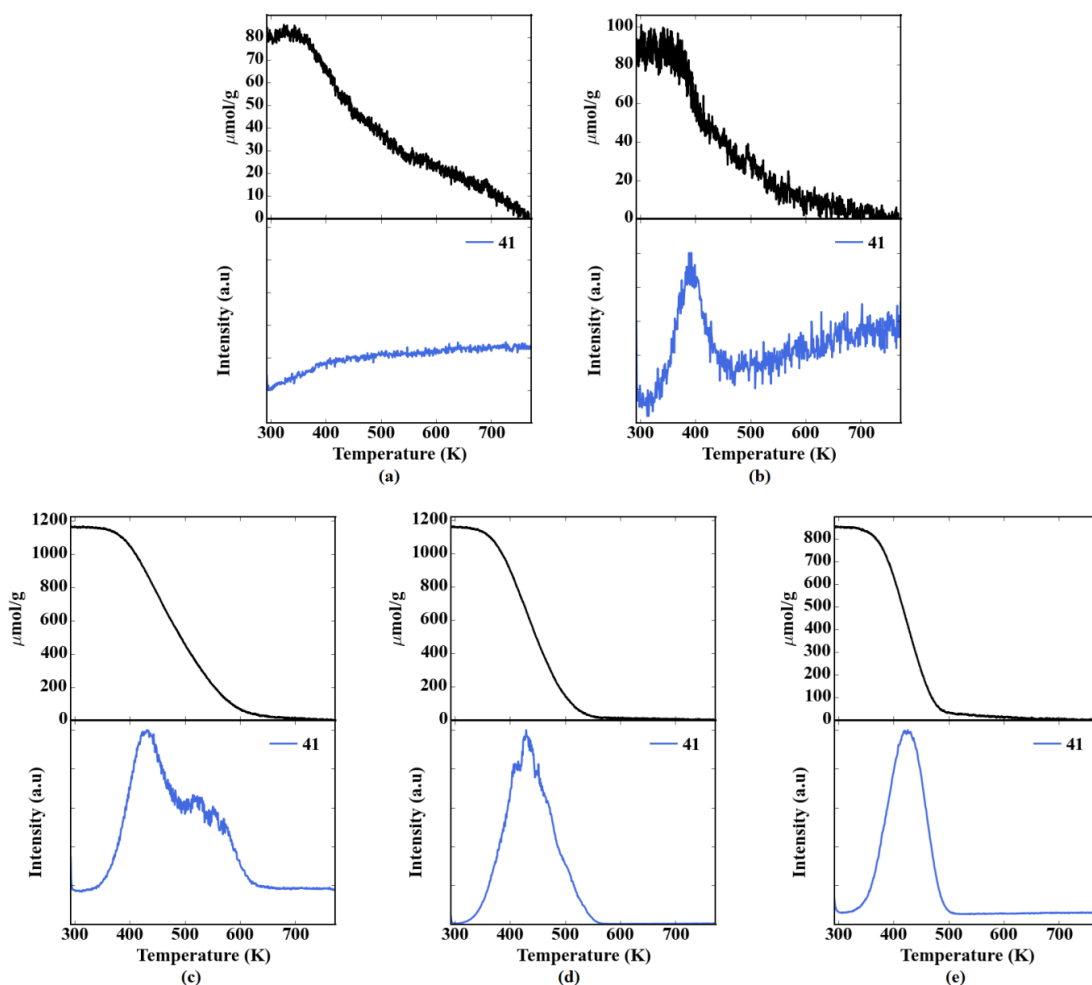


Figure 4.5: TPD-TGA results for acetonitrile on (a) SiBEA zeolite, (b) SnBEA (c) Li-BEA, (d) Na-BEA, and (e) K-BEA. For acetonitrile TPD, the peak correspond to acetonitrile ($m/z=41$).

On the alkali-exchanged BEA samples, the initial coverages after evacuation were between $850 \mu\text{mol/g}$ and $1200 \mu\text{mol/g}$, higher than the alkali site densities, implying either that more than one molecule can be adsorbed on the same alkali cation site or that there is clustering of molecules at the site. Based on TPD results on Li-BEA, there is clear evidence for two desorption states, at ~ 450 and 550 K, with the second corresponding to a coverage close to that of the Li site density, $650 \mu\text{mol/g}$. Desorption appears to occur in a single broad peak from Na- and

K-BEA but the peak temperature is higher on Na-BEA (~440 K) compared to K-BEA (~410 K), implying that the strength of the interactions again decreases with cation size.

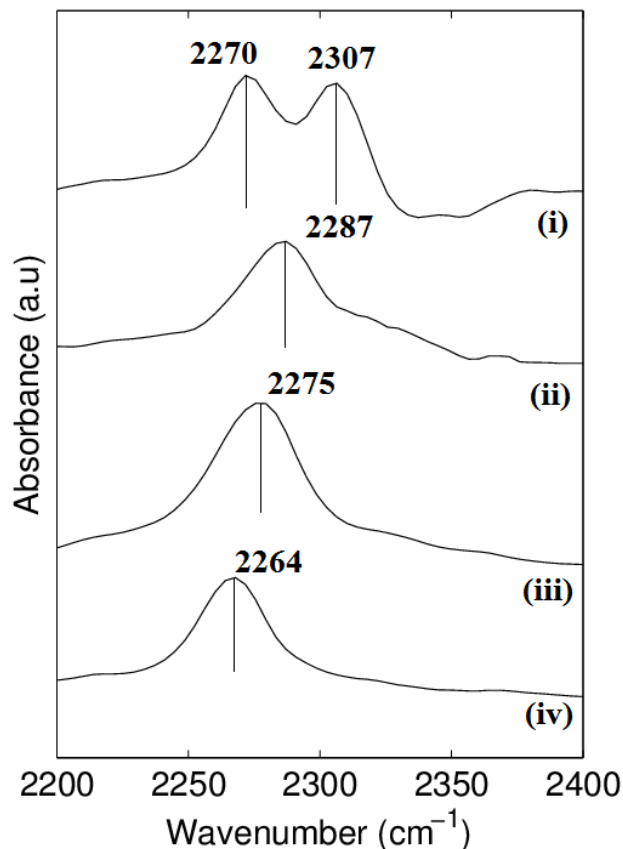


Figure 4.6: FTIR spectra of CD_3CN adsorbed on (i) SnBEA, (ii) Li-BEA, (iii) Na-BEA, and (iv) K-BEA.

FTIR spectra of adsorbed CD_3CN adsorbed on SnBEA and the three alkali-exchanged BEA samples are given in Fig. 4.6. Again, spectra were acquired after exposure to CD_3CN vapor at room temperature, followed by flushing with dry He at 353 K. Previous reports demonstrated that CD_3CN adsorbed on framework Sn sites exhibits a $\nu(\text{CN})$ stretch centered near 2310 cm^{-1} [9,57]. When CD_3CN was present at higher coverages on Sn-BEA, additional vibration bands were observed at 2268 and 2276 cm^{-1} , which were assigned to physisorbed acetonitrile and

acetonitrile on silanols [9]. However, since IR spectra of acetonitrile on a BEA zeolite with only extraframework SnO_2 showed only bands at 2263 and 2270 cm^{-1} [57], the band at 2276 cm^{-1} may be associated with the framework Sn sites, perhaps as a second molecule hydrogen-bonded to the first. It is noteworthy that acetonitrile binds to Brønsted-acid sites with a similar energy as it does to framework Sn sites based on the fact that desorption peak temperatures in TPD are almost the same [32,57]; however, the $\nu(\text{CN})$ vibrational stretch for CD_3CN adsorbed at Brønsted-acid sites occurs at a significantly lower frequency, 2298 cm^{-1} [86]. Therefore, there is no simple relationship between the $\nu(\text{CN})$ stretching frequency and binding strength.

Spectrum i) in Fig. 4.6 was obtained on SnBEA. In basic agreement with past work, there were two bands at 2270 and 2307 cm^{-1} . The band at 2307 cm^{-1} can confidently be assigned to adsorption at framework Sn sites. The spectra for Li-BEA, Na-BEA and K-BEA, reported in ii) through iv), show only one peak. The peak positions for the $\nu(\text{CN})$ stretch vary with cation size, decreasing from 2287 cm^{-1} for Li-BEA, to 2275 cm^{-1} for Na-BEA, and 2264 cm^{-1} for K-BEA. Although the peak position for the adsorbed CD_3CN shifts with cation size and the apparent strength of interaction with those cations, there is no evidence for new peaks that can be clearly identified with adsorption on the cations. For the alkali cations, the shift in the $\nu(\text{CN})$ stretch is likely due to the strength of the ion-dipole interactions and not any well-defined adsorption at a Lewis site.

4.3.4 Adsorption of 2-Methyl-2-Propanol and Diethyl Ether

In previous work characterizing Lewis acid sites in SnBEA, adsorption stoichiometries of one molecule per framework Sn site were observed in TPD-TGA measurements of diethyl ether and 2-methyl-2-propanol [57]. The framework Sn sites were also able to catalyze the dehydration of 2-methyl-2-propanol, making this an interesting probe molecule for understanding the nature of the acid sites.

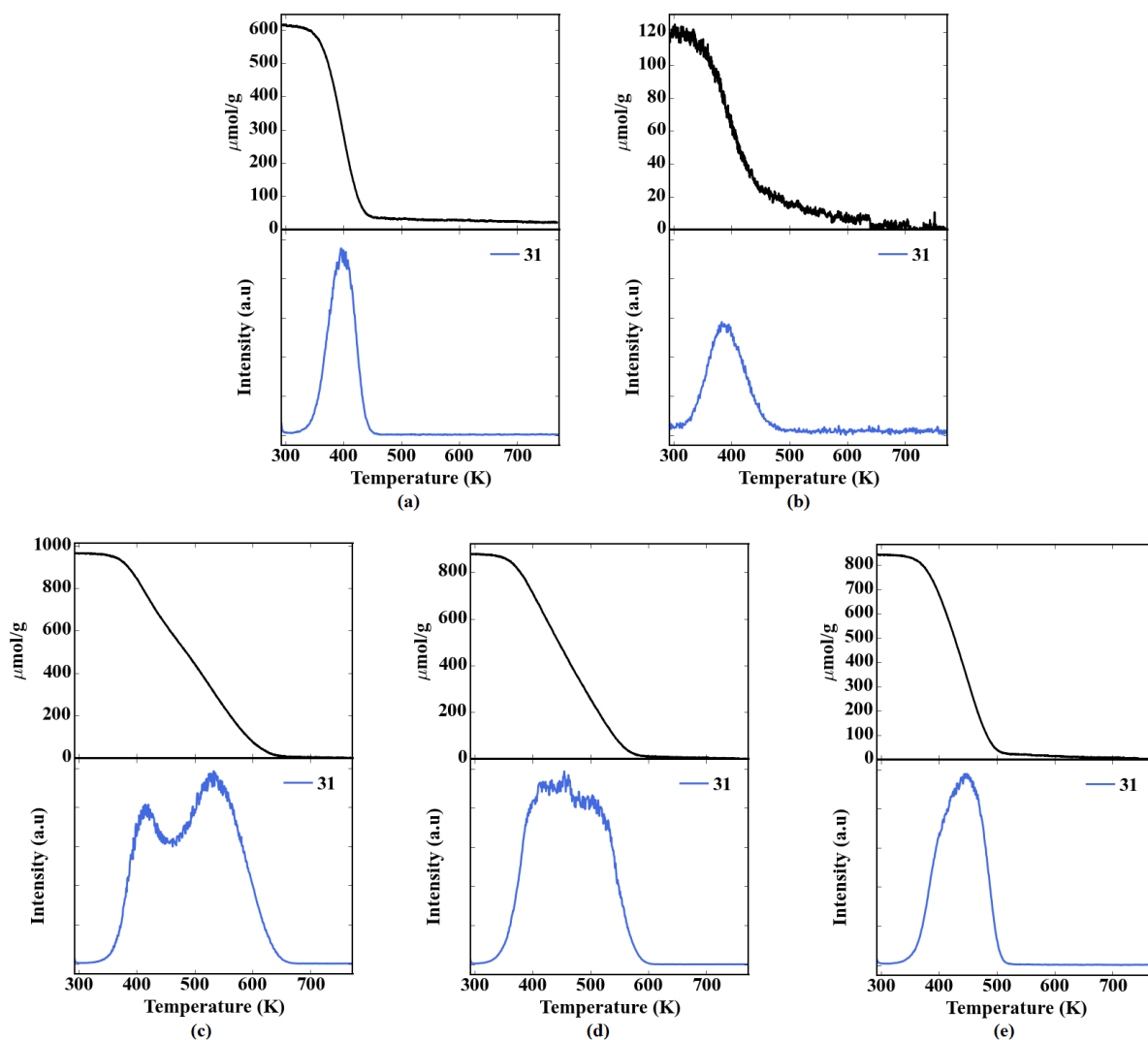


Figure 4.7: TPD-TGA results for diethyl ether on (a) SiBEA, (b) SnBEA (c) Li-BEA, (d) Na-BEA, and (e) K-BEA. For diethyl ether TPD, the peak correspond to diethyl ether ($m/z=31$).

TPD-TGA results for diethyl ether on the five samples are shown in Fig. 4.7 and exhibit some similarities to the results for acetonitrile. Unlike previously published data for H-ZSM-5 [32], there is no evidence for reaction of the diethyl ether during TPD on any of the samples. For SiBEA, the initial coverage after adsorption and room-temperature evacuation was 500 $\mu\text{mol/g}$, implying that there must be some interaction between the ether molecules and the silanol defects,

but all of the molecules desorbed by 425 K. On SnBEA, initial coverage after evacuation was 120 $\mu\text{mol/g}$, slightly less than the framework Sn concentration. Again, because the coverage is less than the framework Sn concentration and desorption occurs at below 450 K, the diethyl ether molecules must bind weakly to the framework Sn sites. Adsorption on the alkali-exchanged BEA samples was much stronger than that on the SiBEA and SnBEA samples. The initial coverages were between 800 and 1000 $\mu\text{mol/g}$; and there was evidence for two adsorption states, at least for Li-BEA and Na-BEA. On Li-BEA, the two ether-desorption ($m/e=31$) peaks were centered at ~ 420 and 540 K. Since the ether coverage at 500 K was ~ 650 $\mu\text{mol/g}$, molecules desorbing from the 540-K peak must be associated with the Li-exchange sites. The results on Na-BEA were similar but the two desorption states were not clearly resolved, due to the fact that the second peak occurs at lower temperatures. On K-BEA, desorption is complete by 500 K.

TPD-TGA data for 2-methyl-2-propanol on SiBEA, SnBEA, and three alkali-exchanged materials are given in Fig. 4.8. After exposure to the vapor and evacuation on SiBEA, the coverage of 2-methyl-2-propanol remained above 600 $\mu\text{mol/g}$, probably due to hydrogen-bonding of the alcohol to silanol defects in the structure. All of this desorbs unreacted (2-Methyl-2-propanol has a major peak at $m/e = 59$ in its mass spectrum, with minor peaks at 18 and 56.) in a peak centered at 400 K. It is interesting to note that, if the 2-methyl-2-propanol had been adsorbed on Brønsted sites, the dehydration reaction would have occurred at room temperature [24]. On SnBEA, the initial coverage was much lower, 250 $\mu\text{mol/g}$, because of the lower defect concentration on this material. While some of the alcohol desorbs unreacted at 350 K, an amount close to the site concentration of framework Sn reacts to butene ($m/e = 56$) and water ($m/e = 18$) in a peak at 400 K, in close agreement with results reported previously [57]. Interestingly, 2-methyl-2-propanol adsorbed on another Lewis acid, $\gamma\text{-Al}_2\text{O}_3$, reacts to butene and adsorbed water

between 425 and 475 K, implying that the Sn sites are more catalytically active than the Lewis sites on $\gamma\text{-Al}_2\text{O}_3$ [87] for reaction of this tertiary alcohol.

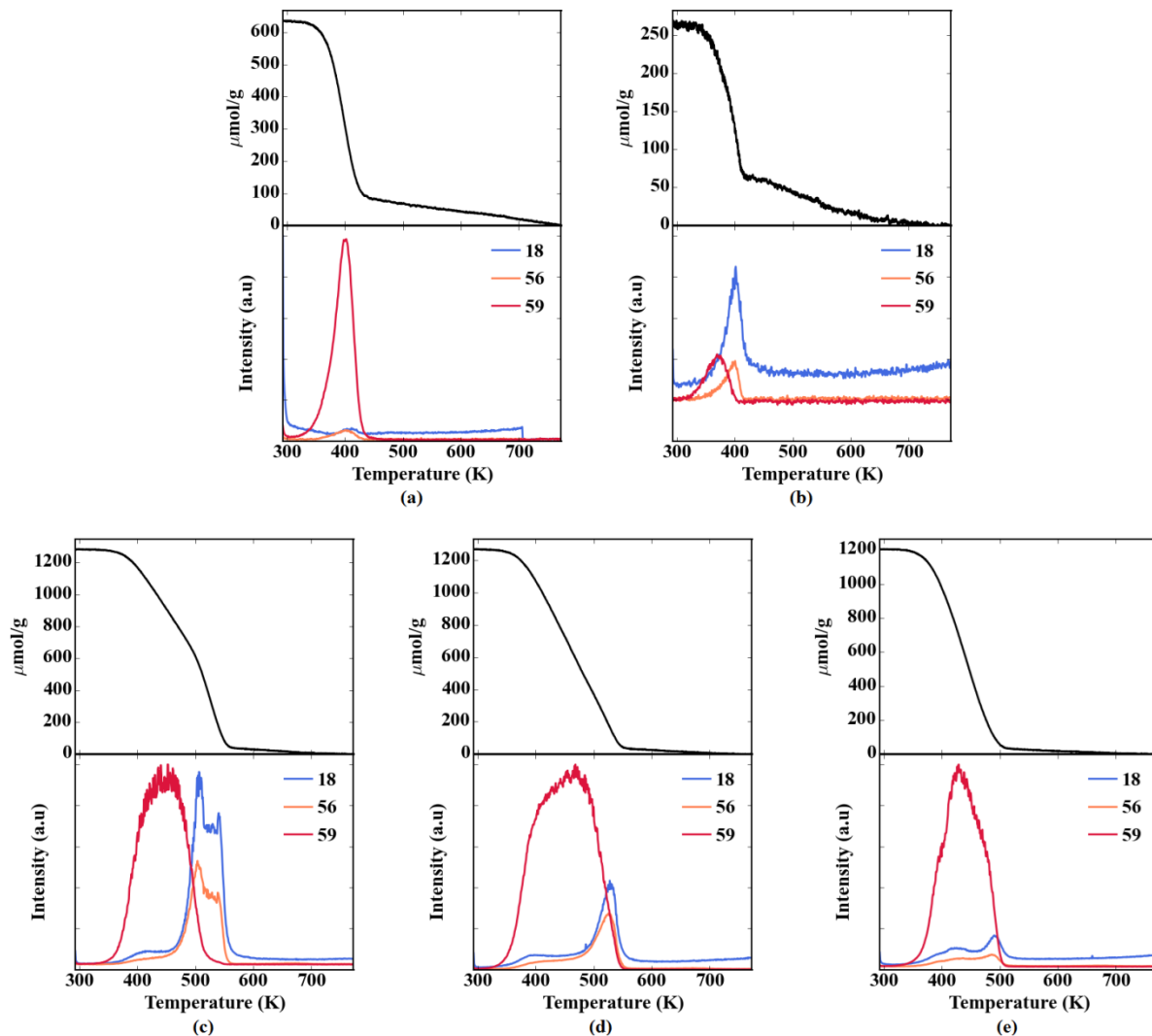


Figure 4.8: TPD-TGA results for 2-methyl-2-propanol on (a) SiBEA, (b) SnBEA (c) Li-BEA, (d) Na-BEA, and (e) K-BEA. For 2-methyl-2-propanol TPD, the peaks correspond to 2-methyl-2-propanol ($m/z=59$), 2-methyl-2-propene ($m/z=56$) and water ($m/z=18$)

The initial coverages 2-methyl-2-propanol following adsorption and evacuation on alkali-exchanged BEA samples were all approximately 1200 $\mu\text{mol/g}$, which is nearly two molecules per

exchange site. This implies that there must be clustering of the alcohol molecules at those sites. On Li-BEA, unreacted 2-methyl-2-propanol desorbs in a broad peak centered at 450 K, leaving approximately 650 $\mu\text{mol/g}$ of the alcohol to react to butene and water between 500 and 550 K. Because the tert-butyl cation is so stable and 2-methyl-2-propanol so reactive, it is unclear whether the reaction at higher temperatures is catalyzed by the site or simply an indication of the thermal stability of the alcohol. In either case, the Li sites are much less reactive than the framework Sn sites in SnBEA or the Lewis sites in $\gamma\text{-Al}_2\text{O}_3$, as indicated by the higher temperature required to initiate reaction. TPD-TGA results on Na-BEA and K-BEA are similar to that found on Li-BEA except that progressively less of the 2-methyl-2-propanol is held on the sample at 500 K, so that less of the alcohol reacts.

4.3.5 Liquid-Phase Reductive Etherification of HMF

It has previously been shown that a wide range of solid Lewis acids are able to catalyze the reductive etherification of 5-hydroxymethylfurfural (HMF) in 2-propanol to first produce 2,5-bis(hydroxymethyl)furan (BHMF) by the oxidation of 2-propanol to acetone, followed by subsequent reactions of the BHMF to the mono-ether (5-[(1-methylethoxy)methyl]-2-furanmethanol, MEFA) or di-ether (2,5-bis[(1-methylethoxy)methyl]furan, BEF) [51] at high yields [88]. To determine whether the ion-exchanged BEA zeolites were able to catalyze this reaction, the liquid-phase reaction was performed on Li-BEA, K-BEA, SiBEA and SnBEA, with results shown in Table 1. These experiments were carried out at 453 K and 62 bar using the same amount of catalyst and the same liquid flow rates. A complete description of the results for SnBEA is given elsewhere; for the present, it is simply worth noting that the HMF conversion was 35.8% for the conditions that were used. On SiBEA, the conversion was 4.5%, perhaps due to a small residual concentration of Al sites or to reaction on the nested-silanol defects. However,

there was no observable reaction on either Li-BEA or K-BEA. For this reaction, the alkali-exchanged zeolites are not catalytically active.

4.4 Discussion

There are a number of interesting conclusions that can be drawn from this study. First, the alkali-exchanged zeolites are not good catalysts for either alcohol dehydration reactions or reductive etherification reactions. In retrospect, this is perhaps not surprising. The bonding in alkali-exchanged materials is ion-dipole in nature, as is clearly shown by the fact that adsorption was strongest on Li sites, followed by Na and K. Ion-dipole interactions are expected to decrease with increasing ion size [3]. Since there is no possibility for coordination chemistry on the alkali cations, there is no possibility of accepting electrons and catalyzing reactions. The fact that framework Sn sites are catalytically active implies that these more complex interactions must be possible in that material, as has been shown in recent spectroscopic studies [57].

However, the results also clearly demonstrate that typical basic probe molecules, like pyridine, which are often used to characterize Brønsted and Lewis acidity, do indeed interact very strongly with alkali cations, especially Li. Strong adsorption is also observed with ethers and alcohols, which desorbed at much higher temperatures on the alkali-exchanged BEA samples than are observed on SnBEA. Adsorption strength in this case clearly does not correlate with catalytic activity. Using standard probe molecules, like ammonia and pyridine, to quantify site strengths should only be used on a set of similar materials because there is no clear relationship between adsorption strength and site activity. Even in this case, reactive probe molecules should probably be preferred, since there is a clearer relationship with catalytic chemistry.

An important implication of all this is that measurement of Lewis acidity is intrinsically difficult. This should not be surprising, given the fact that bonding between a Lewis acid and a Lewis base tends to be specific to the particular acid and base being considered. Even in the much

simpler case of Brønsted acids, there is no simple relationship between adsorption energetics and catalytic activity [89]. For example, the heats of adsorption for ammonia and pyridine are the same at Brønsted sites formed by framework Al and by framework Fe in the MFI structure, even though the reactivity of these sites for alkane cracking and olefin oligomerization are very different [90]. While the idea of quantifying acidity by means of measuring heats of adsorption for a standard probe molecule is appealing, the situation is clearly more complex.

Obviously, we have not examined all possible reactions or reactive molecules and alkali-exchanged zeolites may be active catalysts for some specific cases. For example, alkali-exchanged zeolites have been reported to catalyze the dehydration of lactic acid to acrylic acid [91,92]. It is also possible that alkali cations may promote reactions at neighboring Brønsted sites. These kinds of interactions still need to be explored.

4.5 Summary

Alkali-exchanged BEA zeolites interact strongly with alcohols, amines, pyridine, and acetonitrile and can be considered Lewis acids on that basis. However, the adsorption bonding in these materials is due to ion-dipole interactions, as demonstrated by the fact that interactions are strongest with Li, followed by Na and K. Unfortunately, these materials were not catalytically active for reactions like alcohol dehydration or the reductive etherification of HMF.

Chapter 5. Adsorption Study of CH₄ on ZSM-5, MOR, and ZSM-12 Zeolites

5.1 Introduction

Methane, the main component of natural gas, would be an attractive fuel for vehicles if it could be stored at high densities, without requiring high pressures or cryogenic temperatures. One method for achieving high storage densities at reasonable temperatures and pressures involves adsorbing methane on a porous solid and a great deal of effort has gone into developing both materials and theoretical understanding for this application [93,94]. 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 [95] 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 [96].

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 [97]. 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 [98], 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 [99]. With non-polar molecules, the situation is less clear. Interactions between molecular O₂ and Brønsted sites are reported to be negligible [99], but there is both experimental [100,101] and theoretical [102,103] 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 [32,104] and because methane has a much lower proton affinity compared to even ethane (543.5 kJ/mol versus 596.3 kJ/mol [105]), 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 [106–108], 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 [82]. If the measurement temperature is too low so that adsorption is not reversible, the adsorbate will not be able to sample all possible sites. In this case, if adsorption is irreversible, 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 [36]. On the other hand, for weakly bound molecules like methane, adsorption should be performed at temperatures that are low enough for adsorption to occur preferentially at the strongest sites. For example, if a material

has two types of sites (e.g. in MOR, these might be pocket sites and main-channel sites), separated in energy by values similar to kT (where k is the Boltzmann constant and $kT \sim 2.5$ kJ/mol at room temperature), a significant fraction of molecules added to a fresh sample will occupy the weaker sites at equilibrium, especially if the weaker sites are present in higher concentrations and if adsorption on those sites is entropically preferred. 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 [82].

Past work from one of our laboratories demonstrated that site heterogeneity in physisorption can be measured using differential calorimetry at 195 K [99]. In siliceous, defect-free ZSM-5 (a zeolite with the MFI structure), the differential heats of adsorption for CO were found to be 16 ± 1 kJ/mol, independent of coverage. 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 O₂, which do not interact with Brønsted sites, showed the same heats of adsorption on both samples [83]. Therefore, the coverage-dependent differential heats provide a measure of the site energetics for these materials.

In the present work, 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 and experimental measurements, we will show that methane adsorption at 195 K appears to be an excellent probe for determining structural differences. By studying CH₄ 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 CH₄.

5.2 Methods

5.2.1 Experimental

The Tian-Calvet calorimeter used in this study was home-built and has been described in detail in Chapter 2. The instrument was constructed from five, 2.54-cm square, thermal-flux meters (International Thermal Instrument Company, Del Mar, CA) placed between a cubic, pyrex sample cell and a large Al block. The 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 losses due to radiation out the top. The sample was evacuated using a mechanical pump and exposed to gases from a calibrated GC sample loop. All experiments were performed at 195 K, maintained by placing the Al-block heat sink in a styrofoam container with dry ice. The thermopiles had previously been calibrated by passing current through a Pt wire placed between the sample cell and the thermopiles. The uncertainty in our measurement of each point was $\sim 2\%$, 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 ~ 1 kJ/mol.

Table 5.1: Zeolite samples used in this study.

Zeolite	Si/Al₂	Brønsted-acid site densities (μmol/g)	Pore volume with n-hexane (cm³/g)
Zeolyst, H-ZSM-5(50)	50	470	0.1856
Zeolyst, H-ZSM-5(280)	280	80	0.1875
Defect free, H-ZSM-5(F,Al)	-	240	0.1744
Defect free, ZSM-5(F,Si)	-	10	0.1696
H-MOR	20	-	0.1026
ZSM-12	-	20	0.0939

The zeolites in this study, along with some of their properties, are listed in Table 5.1. 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 [109]. A typical synthesis was as follows: distilled water was mixed with Ludox AS-40 silica sol, tetrapropylammonium bromide (TPABr), NH_4F , and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. (A purely siliceous ZSM-5 was prepared using the same procedure, but without the addition of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.) The mixture was heated at 450 K for seven 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. The H-ZSM-12 sample was used in a previous study and has been described there in more detail [97]. Brønsted-site concentrations were determined using simultaneous temperature-programmed desorption and thermogravimetric analysis of 2-propanamine [20]. 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.

5.2.2 Calculations

All electronic structure calculations were carried out using Vienna ab initio simulation package (VASP) [110,111]- a plane wave density functional theory (DFT) code. PAW [112] potentials with generalized gradient approximation (GGA) using the PBE exchange correlation functional [113] with Grimme-D2 [114] 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 [115] in parenthesis) lattice parameters for the three zeolites in their siliceous forms are: (a) 20.2 x 19.9 x 13.3 Å (20.1 x 19.7 x 13.1 Å) for the orthorhombic phase of ZSM-5, (b) 18.4 x 20.7 x 7.6 Å (18.3 x 20.5 x 7.5 Å) for the orthorhombic mordenite (MOR) structure, and (c) 25.8 x 5.3 x 12.2 Å (25.6 x 5.3 x 12.1 Å with $\beta=109.3^\circ$ 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 website [116]. 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 x 20.5 x 21 Å allowing for more than 10 Å of vacuum between periodic images. Figures of zeolite structures and adsorbate configurations were generated using VESTA [117].

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

$$BE = E_{molecule+Zeolite} - E_{molecule, gas} - E_{Zeolite} \quad 5.1)$$

where $E_{molecule+Zeolite}$ is the total energy of the zeolite with the adsorbed molecule, $E_{molecule, gas}$ is the total energy of the gaseous molecule, and $E_{Zeolite}$ 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 $E_{molecule+Zeolite}$ and $E_{Zeolite}$ 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 ν_i of the adsorbate (and the Brønsted proton, if present) were computed using harmonic approximation and ZPE was calculated using the following formula:

$$ZPE = \frac{1}{2} \sum_{i=1}^{\# \text{ modes}} h \nu_i \quad 5.2)$$

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.

5.2.2.1 Calculating models: 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:

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

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

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

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

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 $H = E + \text{ZPE}$ 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: $S = S_{trans} + S_{rot} + S_{vib}$.

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 [118]. For the adsorbed species, a 2D translational freedom is assumed (see Equation (5.3) below). 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. [103]; 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.

5.3 Results and Discussion

5.3.1 H-ZSM-5

5.3.1.1 Experimental

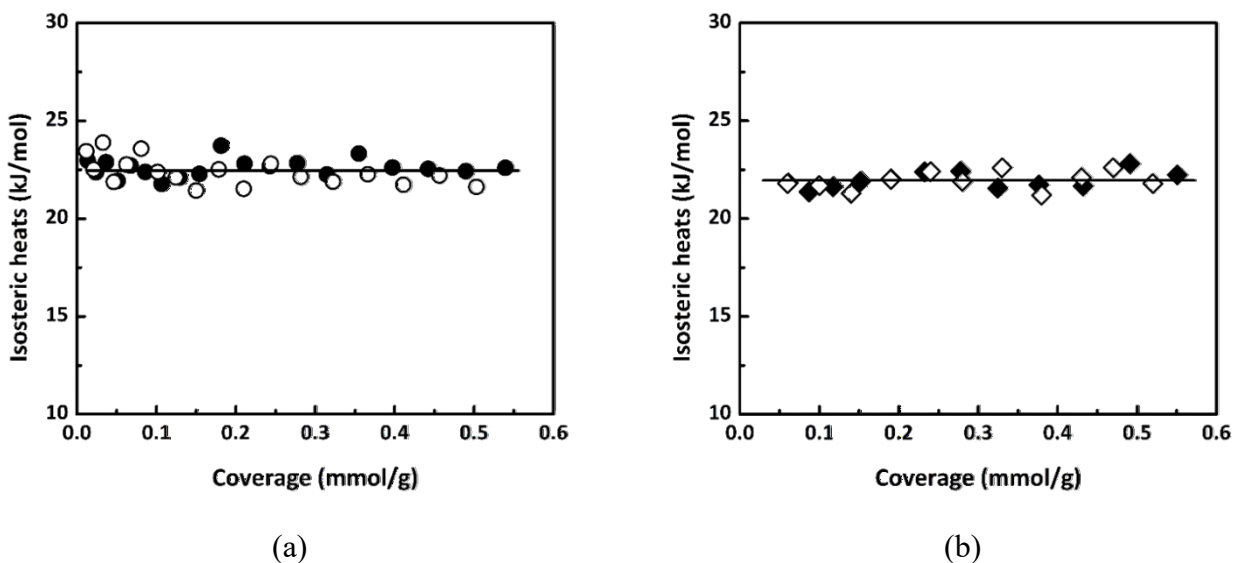


Figure 5.1: Differential heats for CH₄ adsorption on the different H-ZSM-5 samples at 195 K. (a) (●)H-ZSM-5(50) and (○)H-ZSM-5(280). (b) (◆) ZSM-5(F,Si) and (◇)H-ZSM-5(F,Al).

In order to understand the possible effects of Brønsted sites and silanol defects on CH₄ adsorption, calorimetric measurements were performed at 195 K on the four H-ZSM-5 samples listed in Table 5.1. The differential heats are reported as a function of coverage in Fig. 5.1, with results for the two Zeolyst samples in Fig. 5.1a) and for the two defect-free samples in Fig. 5.1b). 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 5.2, were not identical on the four samples. 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.

Table 5.2: 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.

Zeolite	Slope at zero coverage 10^{-7} (mol/(g · Pa))
H-ZSM-5(50)	6.47
H-ZSM-5(280)	4.15
H-ZSM-5(F,Al)	4.80
ZSM-5(F,Si)	1.54

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 Equations 5.3) and 5.4):

$$S_{trans,2D} = R \left[\ln \left(\frac{2\pi mkT}{h^2} \right) + \ln \left(\frac{SA}{N} \right) + 2 \right] \quad 5.3)$$

$$S_{trans,1D} = R \left(\log \left(\frac{\sqrt{2\pi mkT}}{h} \right) + \log(L_0) + 1.5 \right) \quad 5.4)$$

where **m** is the mass of the molecule, **k** is the Boltzmann constant, and **h** Planck's constant. $\frac{SA}{N}$ is the average surface area available for a molecule at the reference state of a monolayer coverage, equal to 200 pm x 600 pm for ZSM-5 [103], and **L₀** can be taken to be a lattice parameter, on the order of 600 pm in this case. For CH₄ at 195 K, the difference between these values is nearly 20 J/mol·K.

5.3.1.2 Calculations

Since previous theoretical studies have indicated hydrocarbons should interact with Brønsted sites [107,119], 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 CH₄, 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 Fig 5.2) [99].

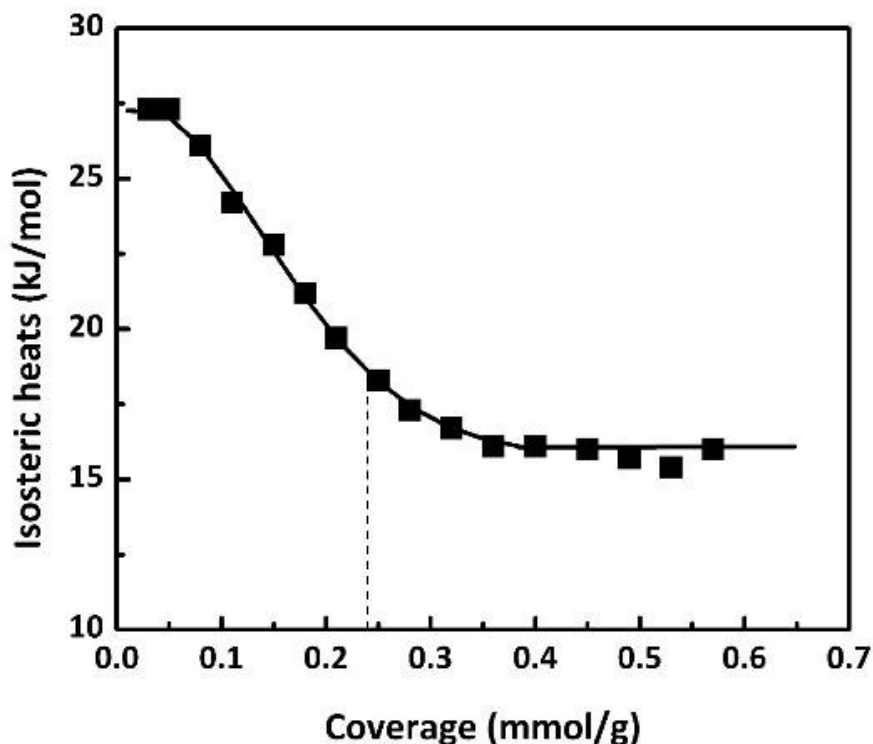


Figure 5.2: CO adsorption on the defect free H-ZSM-5(F,Al) at 195 K. The dashed line is shown at the Brønsted-site concentration.

Two locations for the acid sites were considered. The most stable acid site (Al7-O17-Si8 defined per the scheme adopted by IZA) is shown in Fig 5.3, where the Brønsted proton (bonded to O17) is hydrogen bonded to another oxygen atom (O-H distance of 1.85 Å). A less stable site (Si12-O26-Al12) (by 0.23 eV or ~22 kJ/mol) was also considered at the entrance of the sinusoidal channel and pointing into the straight channel is shown in Fig. 5.4. These two sites have been considered in the literature as the likely positions for the Brønsted sites in HZSM-5 [120–123]. The enthalpy of adsorption at the DFT-D2 level of theory for CO and CH₄ on these two locations, with and without the Brønsted site, are reported in Table 5.3 and discussed below. The

corresponding binding energy values (ZPE corrected) are in Table 5.4. Figs. 5.5-5.8 show the adsorption structures for CH₄ and CO on the Brønsted and non-Brønsted forms of the two sites considered.

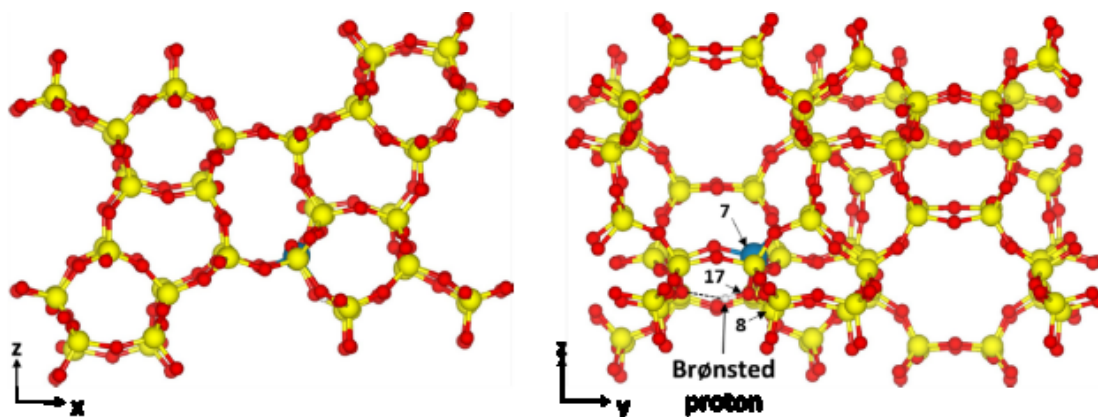


Figure 5.3: Zeolite ZSM-5 with the most stable location of Brønsted site (Al17-O17-Si8). The left hand side shows the view perpendicular to the axis of the straight channel. The right hand side explicitly shows the structure along the axis of the straight channel. The dashed line indicates a hydrogen bond between the Brønsted proton and a nearby oxygen atom. Key: Oxygen (●), silicon (○), aluminum (●), and hydrogen (○).

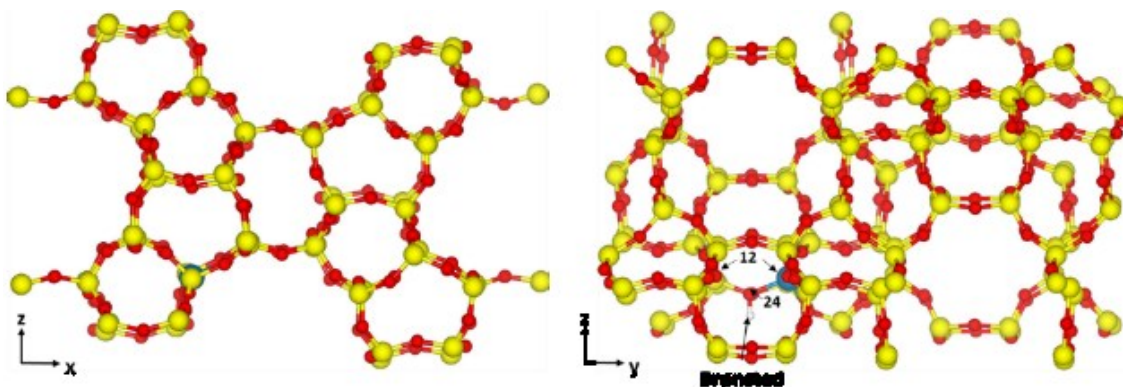


Figure 5.4: Zeolite ZSM-5 with a Brønsted site (Al12-O26-Si12) at the intersection of straight and sinusoidal channels. The left hand side shows the view perpendicular to the axis of the straight channel. The right hand side explicitly shows the structure along the axis of the straight channel. Key: Oxygen (●), silicon (○), aluminum (●), and hydrogen (○).

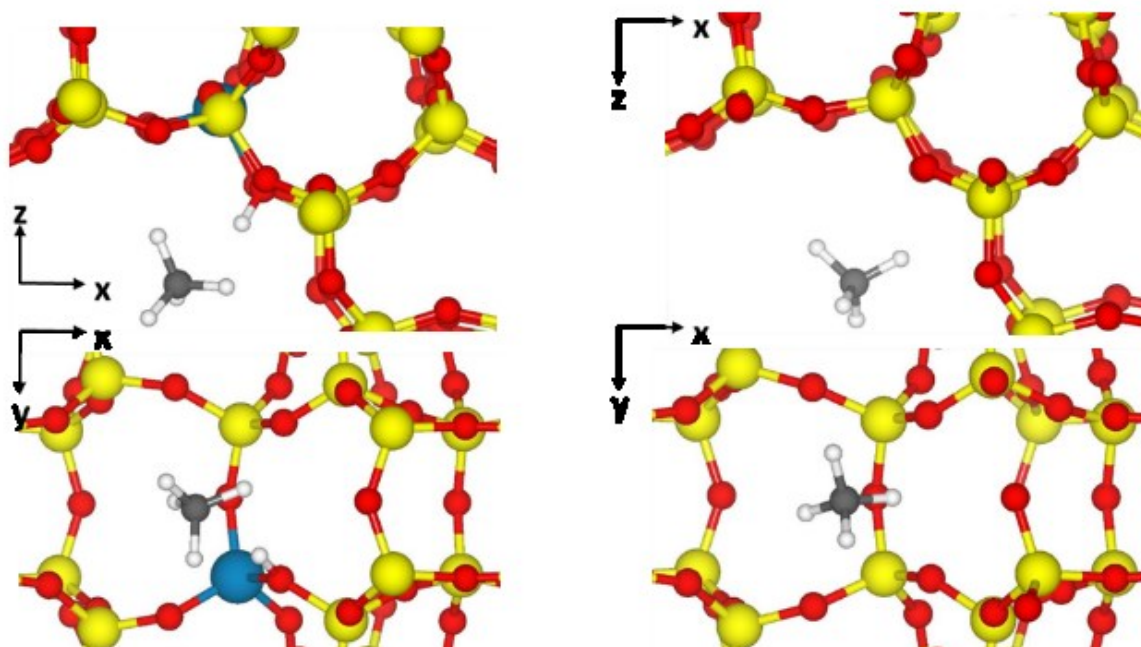


Figure 5.5: Preferred CH₄ adsorbed state on T7-O17-T8 location with a Brønsted site (left) and in purely siliceous form (right) in zeolite ZSM-5. Two views (top and bottom) are shown for comparison on the CH₄ location in the presence and absence of Brønsted proton. Key: Oxygen (●), silicon (●), aluminum (●), carbon (●), and hydrogen (○).

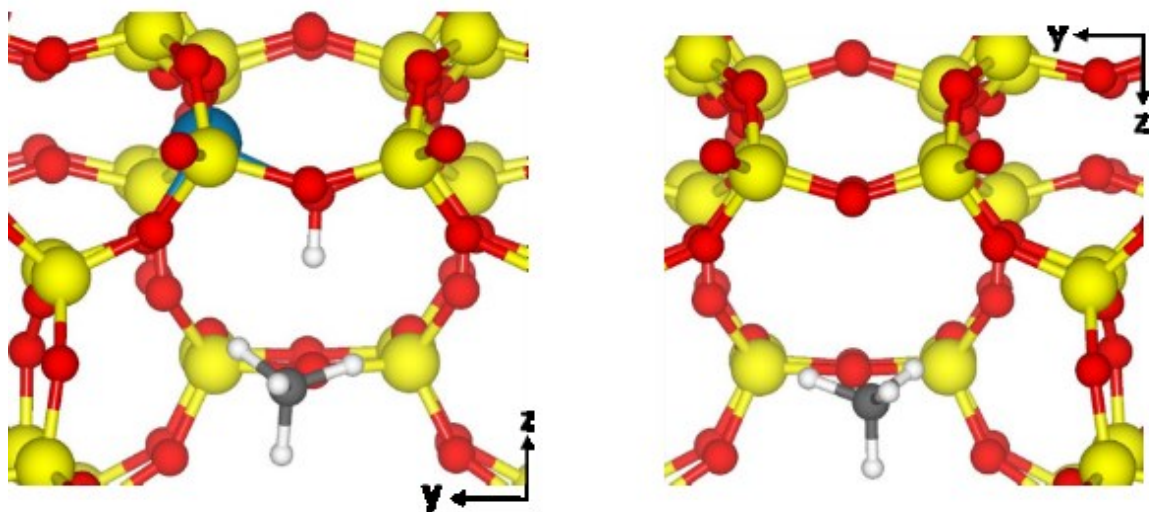


Figure 5.6: Preferred CH₄ adsorbed state on T12-O26-T12 location with a Brønsted site (left) and in purely siliceous form (right) in zeolite ZSM-5. Key: Oxygen (●), silicon (●), aluminum (●), carbon (●), and hydrogen (○).

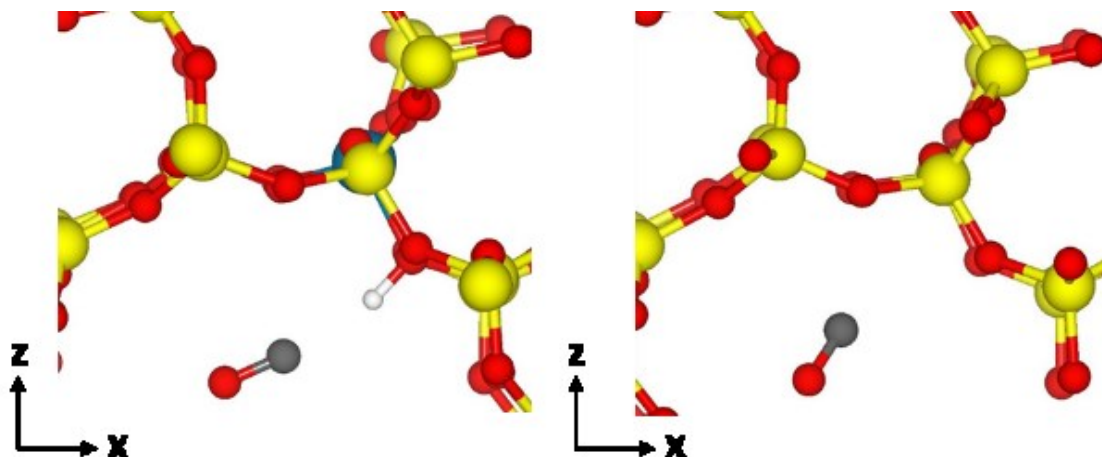


Figure 5.7: Preferred CO adsorbed state on T7-O17-T8 location with a Brønsted site (left) and in purely siliceous form (right) in zeolite ZSM-5. Key: Oxygen (●), silicon (●), aluminum (●), carbon (●), and hydrogen (○).

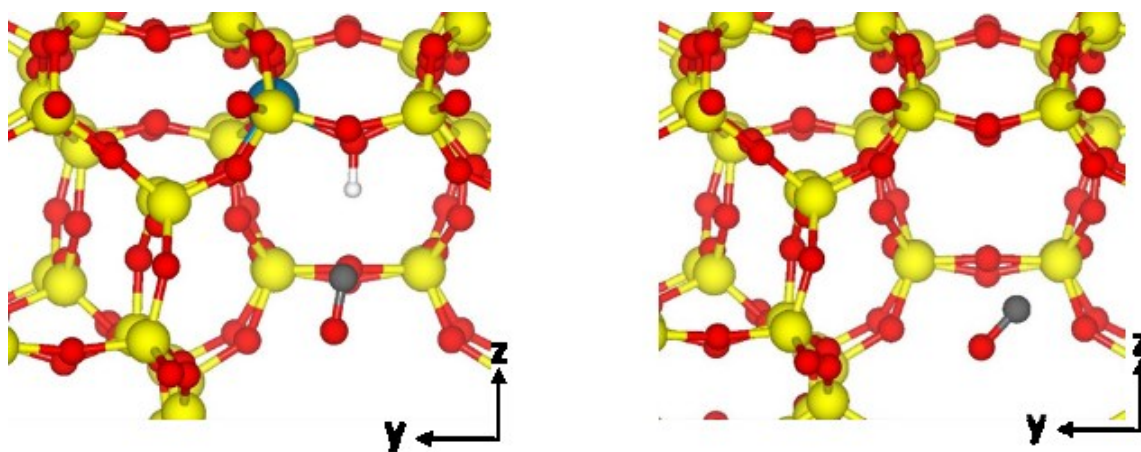


Figure 5.8: Preferred CO adsorbed state on T12-O26-T12 location a with Brønsted site (left) and in purely siliceous (right) form of zeolite ZSM-5. Key: Oxygen (●), silicon (●), aluminum (●), carbon (●), and hydrogen (○).

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 [124,125]; in the

presence of a Brønsted site, the molecule points towards the Brønsted proton, leading to an additional stabilization of about 7 kJ/mol for T7-O17-T8 and 22 kJ/mol eV 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 (26.5 kJ/mol) for carbon monoxide on ZSM-5 [83]. 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.

Table 5.3: 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.

Adsorbate	T7-O17-T8 ^a		T12-O26-T12 ^a	
	Brønsted ^b	Non-Brønsted ^b	Brønsted ^b	Non-Brønsted ^b
CO	-26.7	-19.1	-41.7	-19.6
Methane	-23.2	-21.2	-35.0	-20.1

^a “T” refers to the tetrahedral atom that is either Si or Al atom; ^b “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 5.4: Calculated binding energy (ZPE corrected) values for CO and CH₄ (in eV) on Brønsted and non-Brønsted forms of two sites in ZSM-5 (1 eV ~ 96.5 kJ/mol).

Adsorbate	T7-O17-T8 ^a		T12-O26-T12 ^a	
	Brønsted ^b	Non-Brønsted ^b	Brønsted ^b	Non-Brønsted ^b
CO	-0.27	-0.17	-0.39	-0.19
Methane	-0.27	-0.24	-0.38	-0.23

^a “T” refers to the tetrahedral atom that is either Si or Al atom; ^b “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-O24-T12 Al replaces Si atom in the tetrahedral position 12.

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 (Fig. 5.9).

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 [126]. 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 5.3). 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 5.5). The effect of Brønsted site for methane adsorption on the T12-O8 site is about 3.5 kJ/mol.

Table 5.5: Calculated enthalpy of adsorption for CH₄ (in kJ/mol) on the T12-O8-T3 Brønsted and non-Brønsted forms of ZSM-5

Adsorbate	T12-O8-T3	
	Brønsted	Non-Brønsted
Methane	-24.8	-21.2

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.

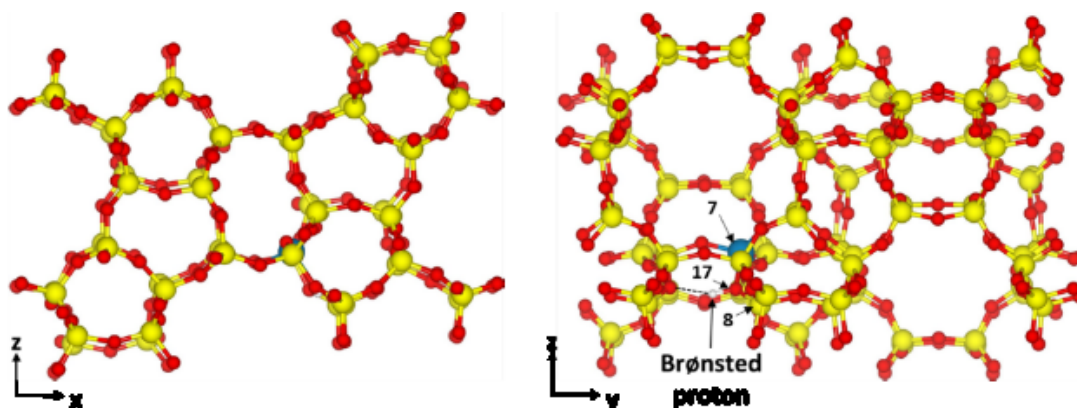


Figure 5.9: Zeolite ZSM-5 with the most stable location of Brønsted site (Al7-O17-Si8). The left hand side shows the view perpendicular to the axis of the straight channel. The right hand side explicitly shows the structure along the axis of the straight channel. The dashed line indicates a hydrogen bond between the Brønsted proton and a nearby oxygen atom. Key: Oxygen (●), silicon (●), aluminum (●), and hydrogen (○).

Table 5.6: Difference in CH₄ binding energies between Brønsted and non-Brønsted T7-O17-T8 site of ZSM-5 using different functionals and dispersion treatments

Method	Dispersion-corrected	Difference [eV (kJ/mol)] ^{a,b}
Reference (PBE+D2) ²⁶⁻²⁷	Yes	0.05 (4.7)
PBE ²⁶	No	0.05 (4.7)
PW91 ³⁹⁻⁴⁰	No	0.05 (4.9)
RPBE ⁴¹	No	0.01 (1.3)
PBE ²⁶ + D3 ⁴²	Yes	0.07 (6.6)
PBEsol ⁴³	No	0.07 (6.5)
BEEF-vdW ⁴⁴	Yes	0.06 +/- 0.03 ^c (6.0 +/- 2.9)

^apositive value of the difference indicates CH₄ binds more strongly on the Brønsted site. ^benergy values are non-ZPE corrected. ^cestimated Bayesian statistical error calculated from a distribution of total energies estimated using an ensemble of parameter values representing the functional.

Table 5.7: Difference in methane binding energies between Brønsted and non-Brønsted T12-O26-T12 site of ZSM-5 using different functionals and dispersion treatments.

Method	Dispersion-corrected	Difference [eV (kJ/mol)]
Reference (PBE+D2)	Yes	0.17 (16.3)
PBE	No	0.16 (15.1)
PW9	No	0.16 (15.3)
RPBE	No	0.13 (11.8)
PBE + D3	Yes	0.16 (15.1)
PBEsol	No	0.20 (19.2)

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 5.6 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 5.7). These results are consistent with other theoretical studies [107,119] 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 [127–132]. Various benchmarking studies on the accuracy of DFT functionals to treat hydrogen bonding have been reported [133–136]. While the specific conclusions of these studies vary (some report under-prediction while others observed over-prediction 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.

5.3.2 MOR and MTW

5.3.2.1 Experimental Data

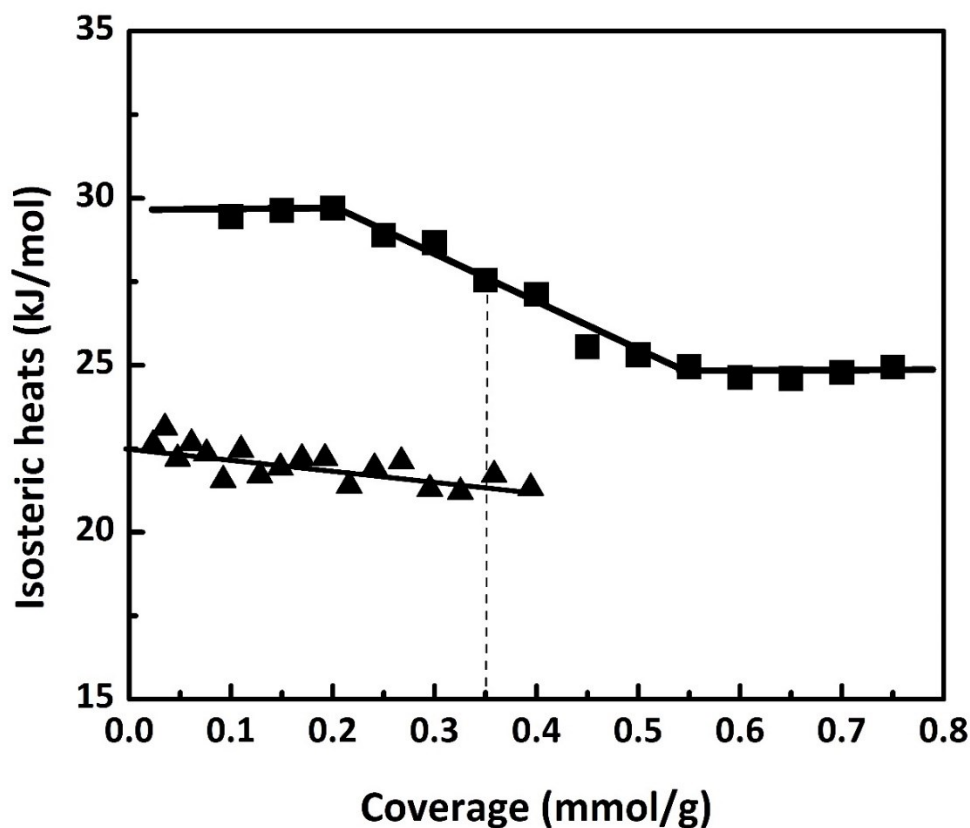


Figure 5.10: Differential heats of adsorption for CH₄ at 195 K on (■) H-MOR and (▲)H-ZSM-12.

In order to determine the effect of zeolite structure on adsorption properties, we performed calorimetric measurements of CH₄, O₂, and 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 CH₄, O₂ and 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 [83].

Fig. 5.10 shows the differential heats for CH₄ 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 [97]. 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 CH₄ loses its translational degrees of freedom in going to the adsorbed phase, so that the heat capacities of gas-phase and adsorbed-phase CH₄ 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 [82].

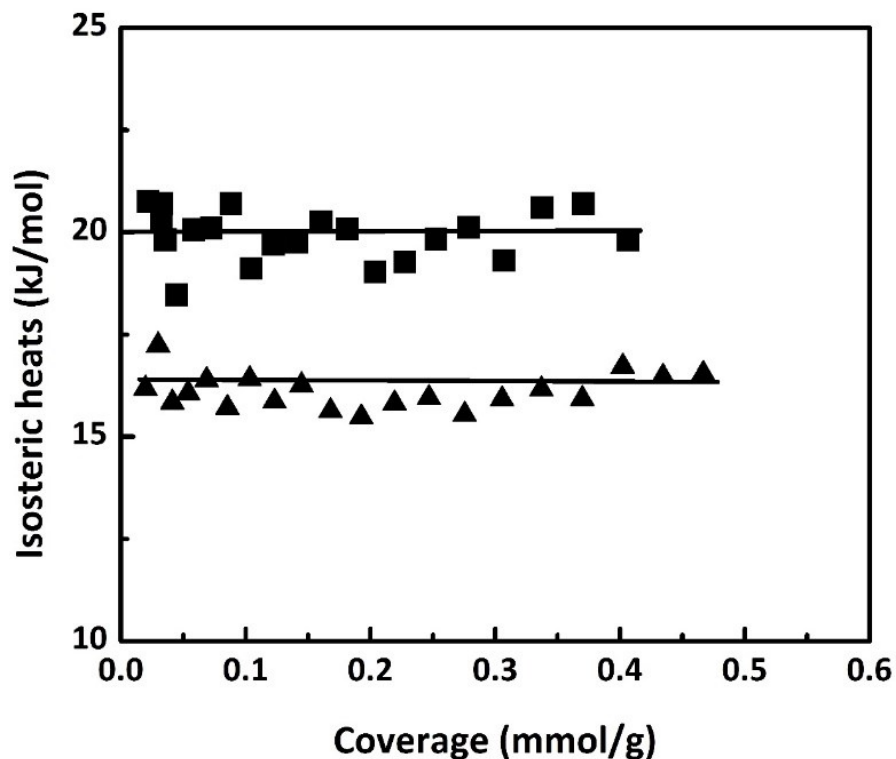


Figure 5.11: Differential heats of adsorption for O₂ at 195 K on (■) H-MOR and (▲) H-ZSM-12.

Fig. 5.11 shows the corresponding differential heats for O₂ in the ZSM-12 and MOR samples. Heats of adsorption for O₂ in ZSM-12 were 16 kJ/mol, independent of coverage. As with CH₄, this value is again similar to the heat of adsorption reported for O₂ in siliceous ZSM-5 [83]. The differential heats for O₂ on MOR, 20 kJ/mol, were higher than those found on ZSM-12; however, unlike the case for CH₄, the differential heats for O₂ were independent of coverage. Because O₂ 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 Fig. 5.12, are nearly the same as those for O₂.

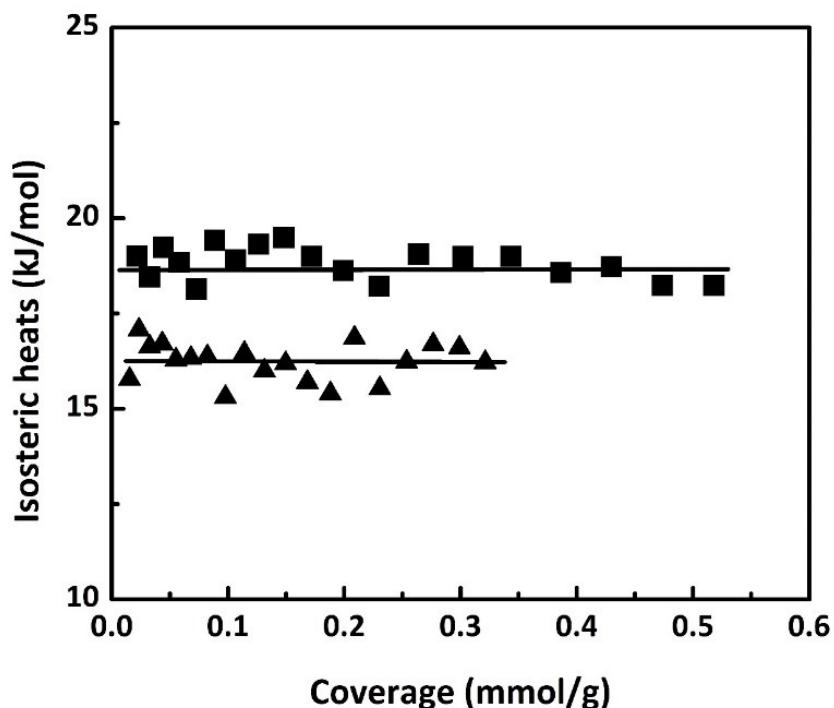


Figure 5.12: Differential heats of adsorption for Ar at 195 K on (■) H-MOR and (▲) H-ZSM-12.

5.3.2.2 Calculations

The adsorption of CH₄, O₂, and Ar in siliceous MOR and ZSM-12 was studied using DFT-D2. Fig. 5.13 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 Fig. 5.13, 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 II) and the region of 8 MR side pockets (marked region II) are potential locations for adsorption.

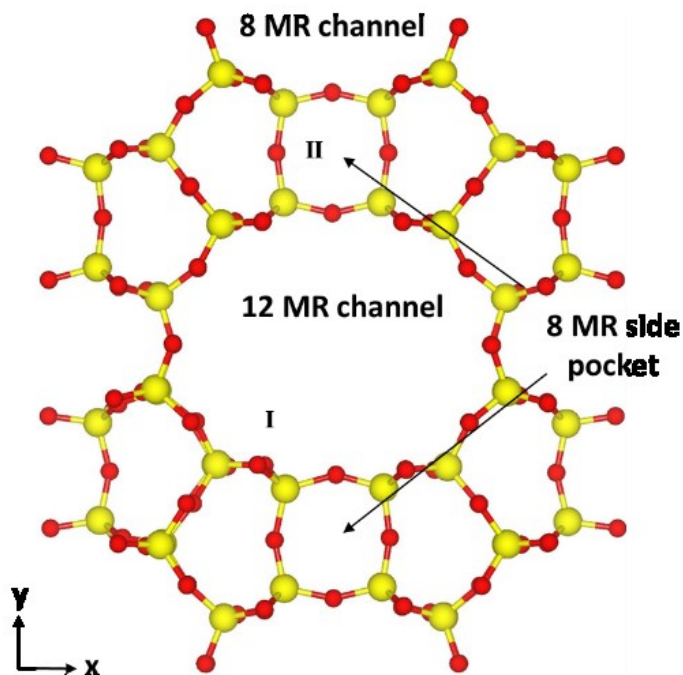


Figure 5.13: Siliceous mordenite (MOR) showing the channels along z axis. Two channels with eight (8 MR) and twelve (12 MR) membered-ring openings and a side pocket with eight membered ring opening (8 MR side pocket). Two regions of adsorption have been marked – 12 MR channel near the walls (I) and 8 MR side pocket (II). Key: Oxygen (●) and silicon (●).

Table 5.8: Enthalpy of adsorption of CH₄, O₂, and Ar in the two adsorption regions of MOR at 195 K. All values are in kJ/mol.

Adsorbate	12 MR channel	8 MR side pocket
CH ₄	-17.0	-27.5
O ₂	-14.7	-19.9
Ar	-14.0	-20.6

Table 5.9: ZPE corrected binding energy of CH₄, O₂, and Ar in the two adsorption regions of MOR. All binding energy values are in eV (1eV ~ 96.5 kJ/mol).

Adsorbate	12 MR channel	8 MR side pocket
CH ₄	-0.20	-0.31
O ₂	-0.13	-0.19
Ar	-0.14	-0.21

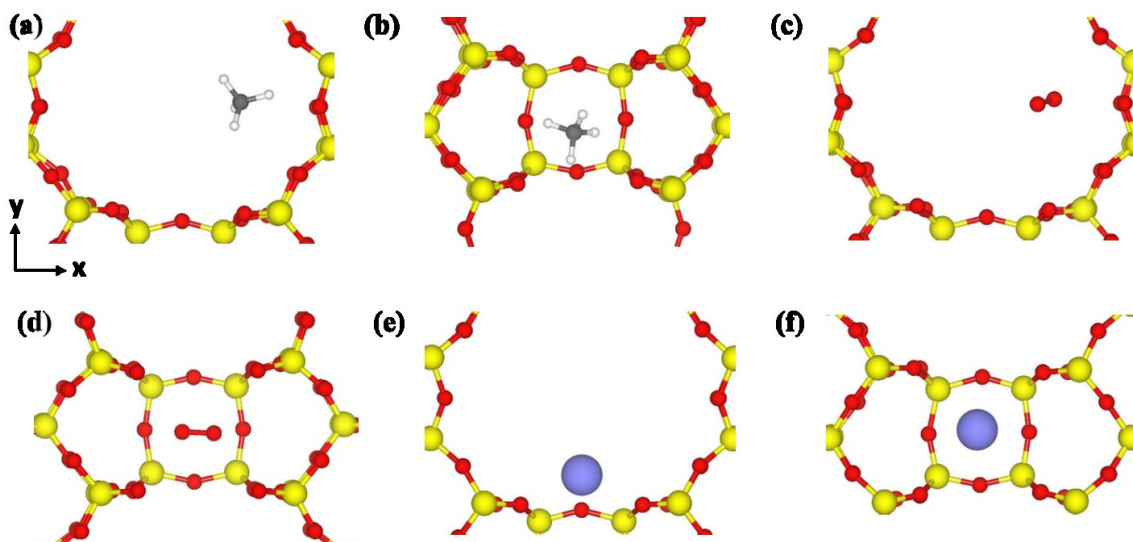


Figure 5.14: Most stable adsorption structure of: (a) methane in 12 MR channel, (b) methane in 8MR side pockets, (c) oxygen in 12 MR channel, (d) oxygen in 8 MR side pockets, (e) argon in 12 MR channel, and (f) argon in 8 MR side pockets of MOR. Key: Oxygen (●), silicon (●), carbon (●), hydrogen (○), and argon (●).

The calculated adsorption enthalpy of CH₄, O₂, and Ar in the two regions of MOR are given in Table 5.8 (ZPE corrected binding energies are in Table 5.9) and their adsorption structures are shown in Fig. 5.14. CH₄ binding energies vary from ~ -28 kJ/mol to -17 kJ/mol while O₂ 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 CH₄ in the 12 MR channel by 5 kJ/mol (compared to experimental heats at high coverage). This

under-prediction 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 O₂ 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 O₂ 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 .

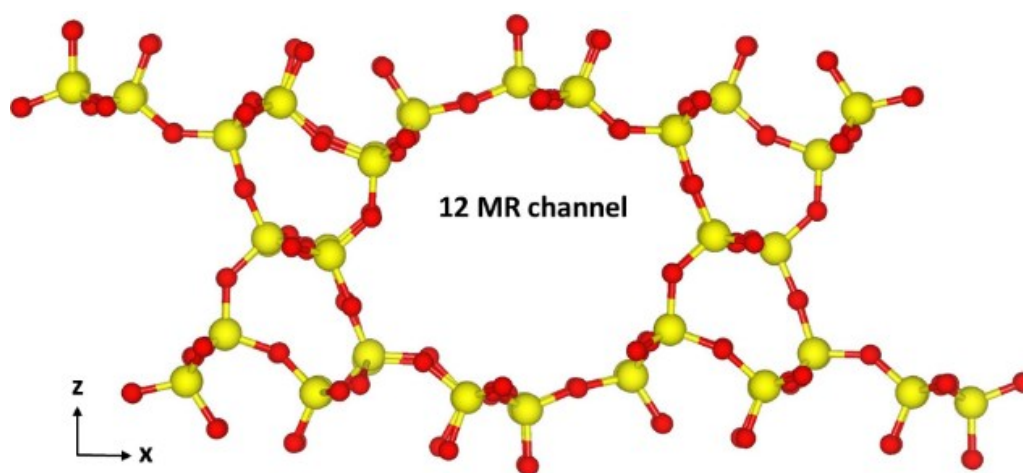


Figure 5.15: Siliceous ZSM-12 showing the channel along z axis. Adsorption is in the channel with 12 membered ring opening (12 MR channel). Key: Oxygen (●) and silicon (●).

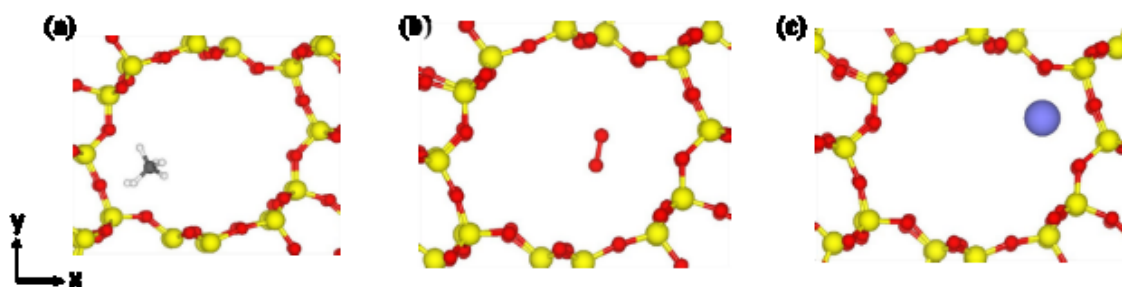


Figure 5.16: Most stable adsorption structure of (a) methane, (b) oxygen, and (c) argon in the 12 MR channels of ZSM-12. Key: Oxygen (●), silicon (●), carbon (●), argon (●), and hydrogen (○).

A schematic of ZSM-12 showing the 12-MR channels is given in Fig. 5.15. The DFT-D2 adsorption enthalpy of CH₄, O₂, and Ar in ZSM-12 is given in Table 5.10 (ZPE corrected binding energy values are in Table 5.11) and the adsorption structures are shown in Fig. 5.16. 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.

Table 5.10: Enthalpy of adsorption of CH₄, O₂, and Ar in ZSM-12 at 195 K. All energy values are in kJ/mol.

Adsorbate	Binding energy
CH ₄	-20.3
O ₂	-13.8
Ar	-16.6

Table 5.11: ZPE corrected binding energy of CH₄, O₂, and Ar in ZSM-12. All binding energy values are in eV (1eV ~ 96.5 kJ/mol).

Adsorbate	Binding energy (eV)
CH ₄	-0.23
O ₂	-0.13
Ar	-0.17

5.4 Summary

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 over-predict the effect of Brønsted sites.

Chapter 6. Adsorption and Reaction Properties of SnBEA, ZrBEA, and H-BEA for Formation of p-Xylene from DMF and Ethylene

6.1 Introduction

The reaction of 2,5-dimethylfuran (DMF) and ethylene to p-xylene is of significant interest, because it offers the possibility of producing an important commodity chemical from lignocellulosic biomass [137]. Yields above 90% have been achieved for this reaction, which proceeds via two separate steps, a Diels-Alder addition and subsequent dehydration. The reaction requires a catalyst and most work has been performed with zeolites that have Brønsted acidity [138]. Rates with these zeolites have been shown to depend on acid-site concentrations. For example, in a study using H-Y zeolites, two kinetic regimes were observed [139]. At low site concentrations, rates increased linearly with the number of sites and the activation energy was 45 ± 8.8 kJ/mol. Theoretical calculations indicated that the reaction under these conditions was limited by the catalyzed dehydration of the Diels-Alder cycloadduct. At high site concentrations, the overall rates were proposed to be limited by homogeneous Diels-Alder reaction. The rates in this regime were independent of site concentration and showed an activation energy of 84 kJ/mol.

Most recently, it was demonstrated that BEA zeolites that have only Lewis-acid sites, formed by either framework Zr, Sn, or Ti, are also active catalysts for this reaction [140–143]. Interestingly, the specific rates and product selectivities were similar for materials that had Brønsted acids formed by framework Al and for materials that had only Lewis sites. Given that past adsorption studies on zeolites with framework Sn showed very different characteristics from what is observed on Brønsted-acid sites [57], this similarity in rates is surprising. For example, Temperature-Programmed Desorption (TPD) studies clearly show alcohol dehydration, a reaction similar to the dehydration of the Diels-Alder cycloadduct, is much more facile on Brønsted sites compared to Sn sites. Furthermore, in the formation of p-xylene, competition for the acid sites by

other reactant and product molecules will affect the observed chemistry. Therefore, one goal of the present study was to compare the adsorption properties of Lewis-acid (SnBEA and ZrBEA) and Brønsted-acid (H-BEA) zeolites for DMF, p-xylene, and other molecules similar to those that could form during reaction in order to gain additional insights into the reaction mechanism.

The second part of the present study involved rate measurements on SnBEA, ZrBEA, and H-BEA for the formation of p-xylene from DMF and ethene using a continuous-flow, tubular reactor similar to that used in studies of hydrodeoxygenation of 5-hydroxymethylfurfural (HMF) [144,145]. Because the reaction of DMF with ethylene must be carried out at high pressures and with long residence times, most of the previously published work has been performed in semi-batch reactors [137–140,146–149]. However, continuous-flow reactors more closely simulate industrial performance. Furthermore, because continuous-flow reactors can operate at steady state, it is easier to monitor catalyst deactivation.

The present work shows that even though the Lewis-acid and Brønsted-acid BEA zeolites exhibit different adsorption properties, rates for the formation of p-xylene on SnBEA, ZrBEA, and H-BEA are similar and can be described by a simple rate over a wide range of pressures and temperatures. One major difference between the zeolites is that deactivation due strong adsorption and oligomerization of reactants is a problem on H-BEA, while the Lewis-acid zeolites appear to be stable.

6.2 Experimental Methods

Four BEA zeolites were used in this study. The H-BEA sample was prepared from NH_4 -BEA, obtained from Zeolyst (CP814C ($\text{Si}/\text{Al}_2 = 38$)), by calcination at 823 K in flowing air for four hours. SiBEA (siliceous form of zeolite BEA) was synthesized according to the method of Cambor et al. [150]. First, 8.47 g of tetraethylorthosilicate (TEOS, Sigma Aldrich, 98%) was added into the mixture of 8.08 g of tetraethylammonium hydroxide (TEAOH, 40 wt% Sigma

Aldrich) and 1.44 g of DI water. After stirring the solution at room temperature for 6.5 h, 0.915 g of HF (48 wt%, Sigma Aldrich, fresh) was added. This solution with a final composition of 0.54 TEAOH: 0.54 HF: 1 SiO₂: 7.5 H₂O, was then transferred into a Teflon-lined, stainless steel autoclave (Parr) and heated in a convection oven at 413 K for 14 days, with rotation (~ 40 rpm). The solid that was produced in this process was filtered, washed with DI water, and calcined in dry flowing air at 830 K for eight hours using a temperature ramp of 1 K min⁻¹. X-Ray Diffraction (XRD) indicated that this material had the BEA structure. The Si/Al ratio was determined to be greater than 80,000 by atomic absorption and solid-state ²⁹Si MAS NMR spectroscopy indicated a low concentration of defects [150].

SnBEA and ZrBEA with Si/Sn and Si/Zr ratios of 126 and 168 (determined by ICP-MS) were synthesized by a seeded-growth method [140]. Using the synthesis of SnBEA to demonstrate the preparation procedures, 20.94 g of tetraethylorthosilicate (TEOS, Sigma Aldrich, 99%) were added to tetraethylammonium hydroxide (TEAOH, 35% SACHEM) and stirred in a plastic beaker for 1 h. A solution containing 0.3 g of tin chloride hydrate (SnCl₄•xH₂O, 34.4 wt% of tin) in 1.96 g of water was then added dropwise into the silicate solution. After removing some of the water and ethanol by evaporation, 1.541 mL of a seed suspension (corresponding to 4.0 wt% dealuminated BEA seed with respect to silica) was added into this solution. Next, 1.941 mL of HF (49%, Alfa Aesar) was added to the solution, which caused formation of a hard gel with a composition of 1 SiO₂: 0.08 SnO₂: 0.54 TEAOH: 0.54 HF: 7.5 H₂O. The hard gel was then transferred to a stainless steel autoclave and heated to 310 K for four days with rotation (~ 2.0 rpm). The resulting solids were washed with DI water, filtered, dried overnight at 350 K, and calcined at 830 K for overnight using a ramping rate of 1 K min⁻¹ under flowing dry air. More details on the properties of the SnBEA and ZrBEA prepared in this way are given elsewhere [140].

Temperature Programmed Desorption (TPD) and Thermogravimetric Analysis (TGA) experiments was described in Chapter 2 [87]. The reaction of DMF with ethene was examined in a continuous-flow reactor which was also described in Chapter 2 [144]. Approximately 0.1 g of catalyst was packed in the middle of a 4.6-mm ID, stainless-steel tube, 20-cm long. The catalyst was held in place using glass wool, and a 4.5-mm stainless-steel rod was inserted downstream from the catalyst to reduce the empty volume of the reactor. Liquid reactants, typically 2.0 g DMF in 100 mL of n-heptane (99%, Acros Organic), were fed into the reactor using an HPLC pump (Series III, Scientific System), which could be used to control the liquids flow rate and measure the pressure in the reactor. The pressure was controlled using a back-pressure regulator (KPB series, Swagelok) placed downstream from the reactor. Ethene (C_2H_4 , UHP grade, Praxair Inc) was introduced into the reactor from a high-pressure regulator, through 7 ft of 0.002 in. ID capillary tubing (Valco Instruments), and the gas flow rate was controlled using the pressure drop across the capillary tubing.

In the reaction studies, it was not possible for us to completely duplicate the reaction conditions used in previous semi-batch reaction studies [138,139]. First, the HPLC pump would not reliably operate with DMF concentrations higher than 0.2 M, because higher concentrations led to phase separation. Second, because the lowest rate that we could reliably measure in our system in its present configuration was $0.1 \text{ mmol} \cdot \text{gcat}^{-1} \text{ h}^{-1}$, it was necessary for us to work at higher temperatures than used in earlier studies. Using the rate expressions reported by Patet, et al [139] for the high acid-site regime, the minimum temperature at which we expect to see conversion of DMF on H-BEA is approximately 573 K. Because this is above the critical temperature of n-heptane, 540 K, there may be differences in the rate expressions derived in our studies compared to those obtained previously.

6.3 Results

A summary of some key properties for the catalysts used in this study is shown in Table 6.1. For H-BEA, the acid-site density is the Brønsted-site density determined by TPD-TGA of 2-propanamine. Because alkyl-ammonium ions formed by adsorption of the amine on Brønsted sites undergo Hoffman elimination to propene and ammonia between 575 and 650 K, the Brønsted site density can be obtained by measuring the amount of 2-propanamine which reacts in this temperature range [20]. The Brønsted site density on the H-BEA sample, 500 $\mu\text{mol/g}$, is somewhat lower than the bulk Al density, 1140 $\mu\text{mol/g}$, possibly in part due 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 [22]. Because there were no Brønsted sites on the SnBEA and ZrBEA samples, there was no reaction of 2-propanamine in TPD-TGA measurements. The Lewis-site densities for SnBEA and ZrBEA, 140 and 100 $\mu\text{mol/g}$ respectively, were assumed to be that of the bulk Sn and Zr compositions. Pore volumes were determined by gravimetric uptakes for n-hexane on H-BEA and 1-hexene on SnBEA and ZrBEA at 0.01 bar at room temperature, assuming that the n-hexane or 1-hexene molecules pack the pores with its liquid density.

Table 6.1: Brønsted- and Lewis-acid site densities for the three acidic zeolite catalysts used in this study. The Pore volumes were determined by gravimetric uptakes of n-hexane on H-BEA, SnBEA and ZrBEA at 0.01 bar and room temperature.

Catalyst	H-BEA	SnBEA	ZrBEA
Site density	500 $\mu\text{mol/g}$	140 $\mu\text{mol/g}$	100 $\mu\text{mol/g}$
Pore Volume	0.22 cm^3/g	0.20 cm^3/g	0.21 cm^3/g

6.3.1 Adsorption Studies

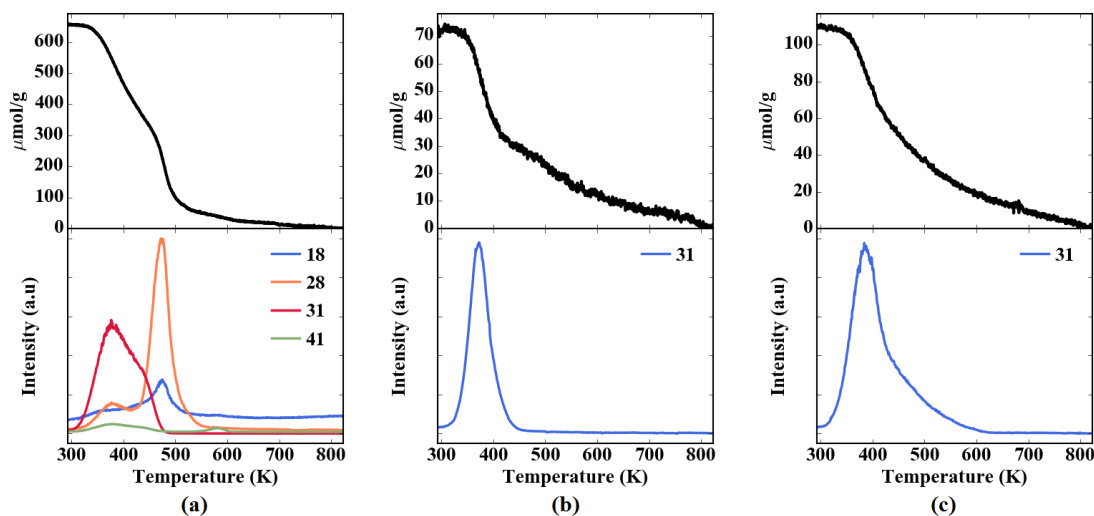


Figure 6.1: TPD-TGA of diethylether on (a) H-BEA, (b) SnBEA, and (c) ZrBEA. The peaks corresponds to diethylether ($m/e=28, 31$), ethene ($m/e=28$), and water ($m/e=18$).

The adsorption of diethyl ether was chosen to be a surrogate for the Diels-Alder cycloaddition product, 1,4-dimethyl-7-oxabicyclo[2.2.1]hept-2-ene. Fig 6.1 shows the TPD-TGA results for diethylether on H-BEA, SnBEA, and ZrBEA following a saturation exposure and one hour evacuation; as discussed elsewhere, diethyl ether was completely removed from the SiBEA following 1-h evacuation. On H-BEA (Fig 6.1a), the initial coverage of diethylether after evacuation corresponded to 620 $\mu\text{mol/g}$, a value slightly above the Brønsted-site density of this sample. Because diethyl ether desorbs completely from siliceous BEA, some of the diethyl ether may be adsorbed on Lewis sites associated with the Al in the H-BEA that is in excess of the Brønsted sites. During TPD, roughly half of the ether molecules desorbed unreacted ($m/e = 31, 28$) below 450 K, with the remaining molecules desorbing as ethene ($m/e = 28$) and water ($m/e = 18$) in a sharp feature centered at 490 K. The presence of two desorption features does not indicate the presence of two types of sites since reaction and desorption are likely parallel

processes. Rather, we suggest that those molecules remaining at Brønsted sites to 450 K in a normal desorption profile simply decompose when the reaction temperature is reached. Water and ethene desorb simultaneously, because they are formed above their normal desorption temperatures. The TPD-TGA data for SnBEA and ZrBEA, reported in Figs. 6.1b and 6.1c respectively, demonstrate that diethyl ether desorbs intact from the framework Sn and Zr sites, with most desorption occurring below 450 K. The fact that the initial coverages are slightly lower than the metal site densities indicates that molecules adsorbed at the Lewis sites can be removed by evacuation over time.

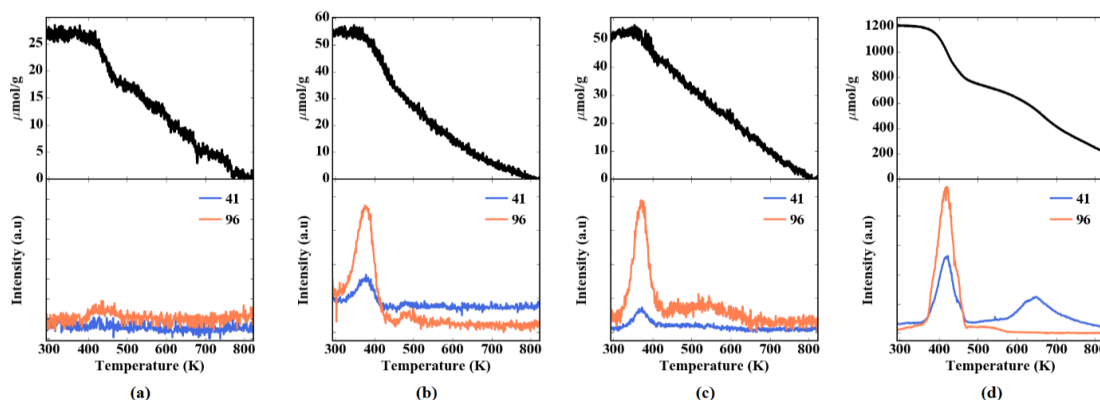


Figure 6.2: TPD-TGA of 2,5-dimethylfuran on (a) SiBEA, (b) SnBEA, (c) ZrBEA, and (d) H-BEA. Peaks correspond to 2,5-dimethylfuran ($m/e=41, 96$) and oligomers ($m/e=41$).

TPD-TGA results obtained on each of the four zeolites following a brief, saturation exposure of DMF, followed by 1-h of evacuation, are shown in Fig. 6.2. The data in Fig. 6.2a indicate that 1-h evacuation is sufficient to remove essentially all of the DMF from SiBEA. Most of the very small apparent weight change observed in TGA could be due to the physical effects of heating a siliceous sample in vacuum, as demonstrated by the fact that little DMF is observed leaving the sample by mass spectrometry. The initial DMF coverages on SnBEA and ZrBEA, shown in Figs. 6.2b and 6.2c, were only slightly higher, about 50 $\mu\text{mol/g}$, but well-defined DMF

peaks ($m/e = 41, 96$) were observed between 300 and 400 K. That the initial DMF coverages were below the Sn and Zr site densities shows that DMF is so weakly held that even molecules present at the Lewis sites can be removed by evacuation at room temperature. These results on the Lewis acids are in sharp contrast to what is observed with H-BEA, Fig. 6.2d. The weight change on H-BEA following exposure to DMF corresponded to more than two molecules per Brønsted site. Some DMF desorbed in a peak centered at 420 K but coverage at 500 K remains above one per Brønsted site. Some of the remaining molecules desorb as olefin products (propene and most olefins exhibit a peak at $m/e = 41$) [151] ; but the sample weight did not return to its initial value, even after heating to 800 K, implying that some of the DMF was converted to coke.

Previous mechanistic studies have shown that 2,5-hexanedione is a side product in the reaction of DMF to p-xylene and likely at least partially responsible for inhibiting isomerization of p-xylene [146]. TPD-TGA results on SiBEA and H-BEA following a saturation exposure to 2,5-hexanedione and 1-h evacuation are reported in Fig. 6.3. Even on SiBEA, Fig. 6.3a, the initial coverage was high, more than 1100 $\mu\text{mol/g}$; but all of the 2,5-hexanedione ($m/e = 99$) desorbed intact below 500 K. The adsorption should probably be classified as physical but fairly strong. The initial coverage on H-BEA, Fig. 6.3b, was similar but the products in TPD very different. Hexanedione was not observed in the desorbing products. Nearly 600 $\mu\text{mol/g}$ of the 2,5-hexanedione was converted to DMF ($m/e = 96, 41$) and water in a peak centered at about 375 K. Additional water was formed between 370 and 550 K, leaving unidentified products at the acid sites, some of which desorbed as olefins near 600 K and some of which remained on the sample. Because the TPD-TGA data in Fig. 6.3b are so similar to those in Fig. 6.2d, the results suggest that 2,5-hexanedione was rapidly converted to DMF and water at low temperatures, consistent with reports that 2,5-hexanedione and DMF are essentially in equilibrium with each other under reaction conditions.

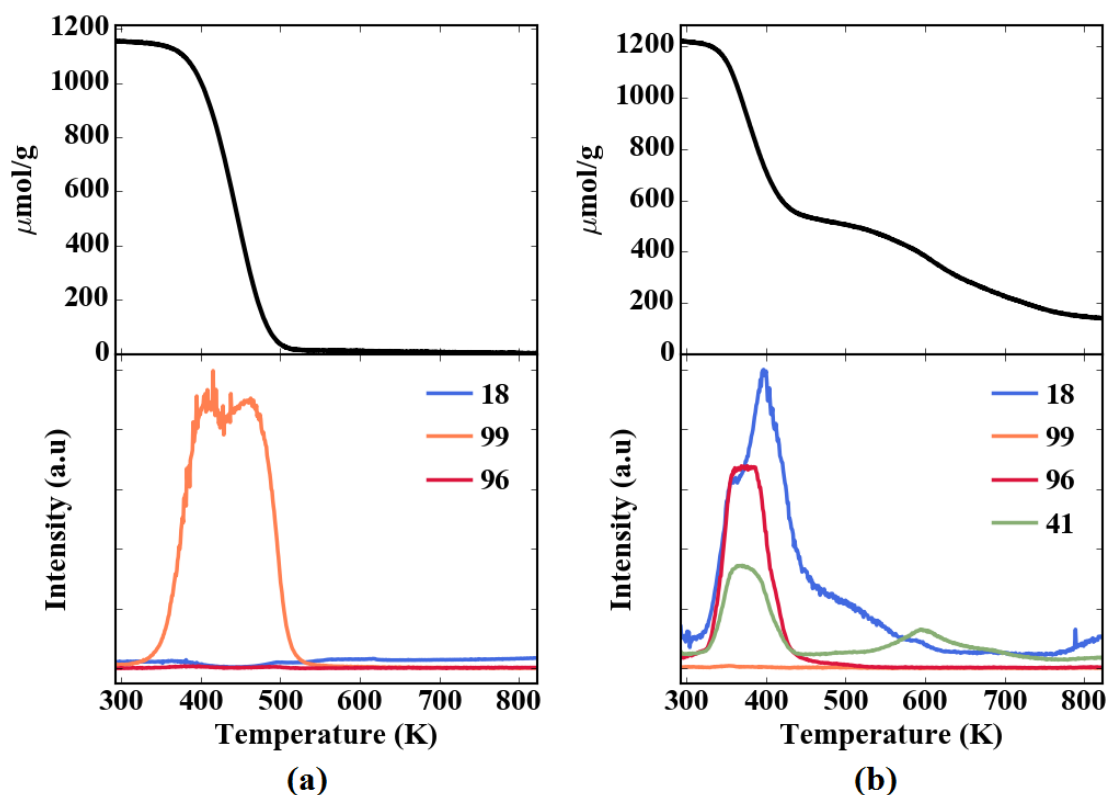


Figure 6.3: TPD-TGA of 2,5-hexanedione at high coverage on (a) SiBEA and (b) H-BEA. Peaks correspond to 2,5-hexanedione ($m/e=99$), 2,5-dimethylfuran ($m/z=96$), water ($m/e=18$) and oligomers ($m/e=41$).

The high initial coverages observed in the results from both zeolites in Fig. 6.3 make it difficult to follow the initial chemistry that occurs on the acid sites. Therefore, additional experiments were performed in which the three acidic zeolites were exposed to controlled doses of 2,5-hexanedione corresponding to initial coverages of approximately 200 $\mu\text{mol/g}$. TPD-TGA following the controlled exposures are shown in Fig. 6.4. The results on H-BEA, Fig. 6.4a, were qualitatively similar to those obtained following saturation exposures. Again, DMF and water were observed leaving the sample below 450 K, olefin products were observed above 550 K, and some of the products remained in the sample. The data is consistent with conversion of 2,5-

hexanedione to DMF and water at low temperatures, followed by oligomerization during the desorption process. That oligomerization would occur, even with the low initial coverage and desorption into high vacuum, implies that 2,5-hexanedione is very reactive at Brønsted sites. The TPD-TGA data on SnBEA and ZrBEA, Figs. 6.4b and 6.4c, were similar to each other but different from that on H-BEA. Some 2,5-hexanedione was observed in the TPD in peaks centered near 430 K; however, there was also reaction to DMF and water near 480 K. All of the adsorbates were removed after heating to high temperatures. What the data indicate is that the Lewis sites formed by framework Sn and Zr were able to catalyze the dehydration of 2,5-hexanedione to DMF and water at moderate temperatures but that the Lewis sites do not further oligomerize and further react the DMF.

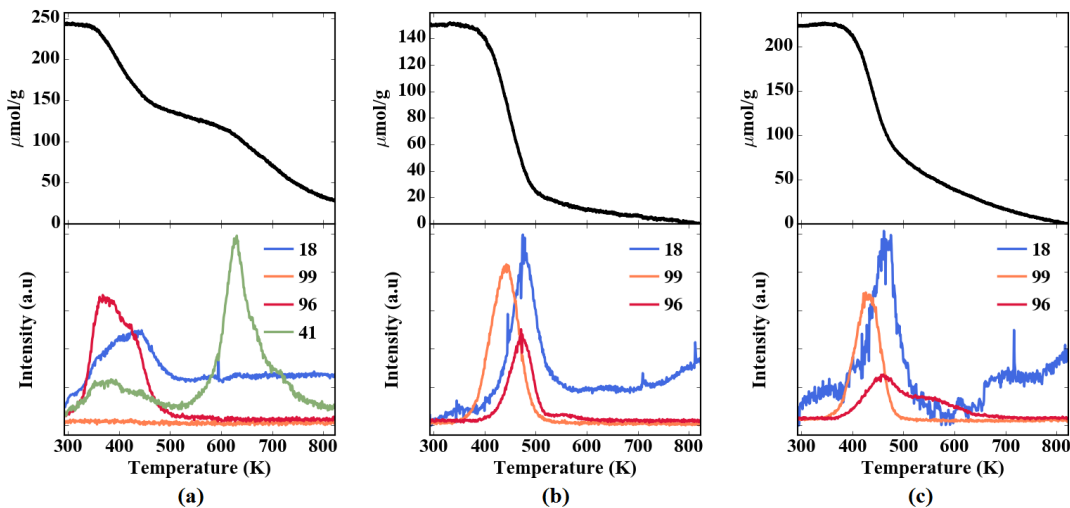


Figure 6.4: TPD-TGA of 2,5-hexanedione at low coverage on (a) H-BEA, (b) SnBEA, and (c) ZrBEA. Peaks correspond to 2,5-hexanedione ($m/e=99$), 2,5-dimethylfuran ($m/e=96$), water ($m/e=18$), and oligomers ($m/e=41$).

Finally, TPD-TGA data for all four zeolites samples following a saturation exposure to p-xylene and 1-h evacuation are shown in Fig. 6.5. A small amount (220 $\mu\text{mol/g}$, Fig. 6.5a) of p-xylene remained in the SiBEA sample, but all of this desorbed by 470 K. The initial coverages on

the three acidic zeolites, shown in Figs. 6.5b-d, were higher, between 600 and 800 $\mu\text{mol/g}$. The TPD on the acidic zeolites also seemed to show two peaks, suggesting that there may be an additional interaction between p-xylene and the Brønsted sites in H-BEA and the Lewis sites in SnBEA and ZrBEA. This interaction must be weak, however, since all of the p-xylene could be removed from each of the samples by 500 K.

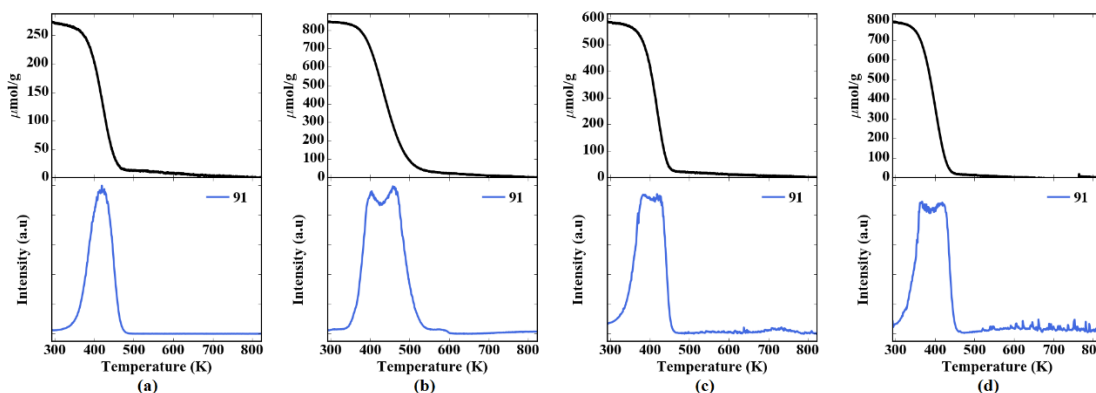


Figure 6.5: TPD-TGA of p-xylene on (a) SiBEA, (b) H-BEA, (c) SnBEA, and (d) ZrBEA.

6.3.2 Reaction Measurements

In order to better understand the relationship between adsorption and catalytic properties, the reaction between DMF and ethene was examined on all four zeolites used in the adsorption studies. Initial reaction experiments were performed using a total pressure of 55 bar and an ethene:DMF mole ratio of 50 in the feed stream. In a demonstration that reliable rates could be obtained in our system, we first examined the reaction over the SnBEA catalyst as a function of space time at 700 K, with the results shown in Table 6.2. The conversions were found to increase almost linearly with space time for conversions ranging from 7.5% to 35%, resulting in Turnover Frequencies (TOF) in the range of 11.7 to 12.5 h^{-1} . The selectivity to p-xylene decreased with conversion, from 94% at 7.5% conversion to 74% at 35% conversion. By contrast, the conversion

of DMF was negligible on SiBEA for all conditions studied, including for temperatures as high as 723 K.

Table 6.2: Rates for 2-wt% 2,5-dimethylfuran in heptane with ethylene as a function of space time at 700 K.

Catalyst loading (g)	Total mol flow rate (*10 ⁻³ mol/min)	Space time W/F (*10 ⁻³ g.min/g)	Temperature (K)	Conversion	Selectivity	Turn Over Frequency (h ⁻¹)
0.1	3.4	1.7	700	7.5%	94%	12.5
0.1	1.7	3.4	700	16%	85%	12.2
0.1	0.9	6.8	700	35%	74%	11.7

The reaction kinetics on SnBEA were investigated more carefully by varying the catalyst loading in the reactor, the total feed flow rate, the ethene:DMF ratio in the feed, the total pressure, the temperature, and DMF concentration, all under conditions of differential conversions. Because the conversions were low, the selectivities to p-xylene, were typically above 90%. The raw data from experiments conducted at 650 K are shown in the Supplemental Information section, Table S1. What the data show is that the rates can be described by a single rate expression of the form given in Eqn 6.1).

$$r = kc(\text{DMF}) \cdot c(\text{C}_2\text{H}_4) \quad (6.1)$$

This is demonstrated by plotting the data from Table 6.3 in Fig. 6.6. The line in this plot, which extends from the origin, shows that there is an excellent fit to this rate expression for a wide range of compositions. Similar results were observed at other temperatures.

Table 6.3: results on Sn-BEA at 650 K with different partial pressure of C₂H₄ and 2,5-dimethylfuran

	Loadi ng (g)	Total mol flow rate (*10 ⁻³ mol/min)	Heptane mol concentration	C ₂ H ₄ mol concentration	DMF mol concentration	Press ure (bar)	Conve rsion	Selecti vity	Turn Over Frequency (h ⁻¹)
1	0.1	2.3	29%	70%	1%	55	3.9%	95%	3.3
2	0.1	1.7	39%	60%	1%	55	6.9%	93%	5.7
3	0.1	1.1	61%	37%	2%	55	7.9%	92%	6.5
4	0.1	1.4	24%	75%	1%	55	8.5%	92%	3.9
5	0.1	1.7	39%	60%	1%	55	6.9%	93%	5.7
6	0.1	2.4	55%	43%	2%	55	3.7%	94%	6.1
7	0.1	1.7	39%	60%	1%	69	9.0%	87%	7.0
8	0.1	1.7	39%	60%	1%	55	6.9%	93%	5.7
9	0.1	1.7	39%	60%	1%	41	4.9%	94%	4.1
10	0.1	1.7	39%	60%	1%	28	2.8%	97%	2.4
11	0.1	1.7	39%	60%	1%	10	1.2%	99.5%	3.1
12	0.1	1.7	39%	60%	1%	55	6.9%	93%	5.7
13	0.1	1.7	37%	60%	3%	55	6.1%	85%	11.6
14	0.1	1.7	35%	59%	6%	55	5.7%	74%	18.8
15	0.05	1.7	39%	60%	1%	55	14%	85%	5.9
16	0.1	1.7	39%	60%	1%	55	6.9%	93%	5.7
17	0.2	1.7	39%	60%	1%	55	3.4%	98.5%	5.3

Reaction rates over SnBEA and ZrBEA were stable and did not change with time over days of testing; however, this was not observed with H-BEA. Initial rates on H-BEA were high and the selectivities were typically above 50%, but there was rapid deactivation under all conditions. The change of TOF over H-BEA at 625 K with time and the comparison with SnBEA and ZrBEA at 650 K is shown in Fig. 6.7, using an ethene:DMF ratio of 50 and a total pressure of 55 bar. The first data point for H-BEA in this experiment was taken 1 h after the catalyst was exposed to the feed stream, and the initial rates may have been even higher than those shown here. After four hours, the catalyst had almost completely deactivated. Because of the rapid deactivation, all of the rates for H-BEA reported in this paper were taken within one hour of

introducing the feed and fresh catalyst was used for each rate measurement. On the other hand, activities of SnBEA or ZrBEA did not change over the same period of time at all.

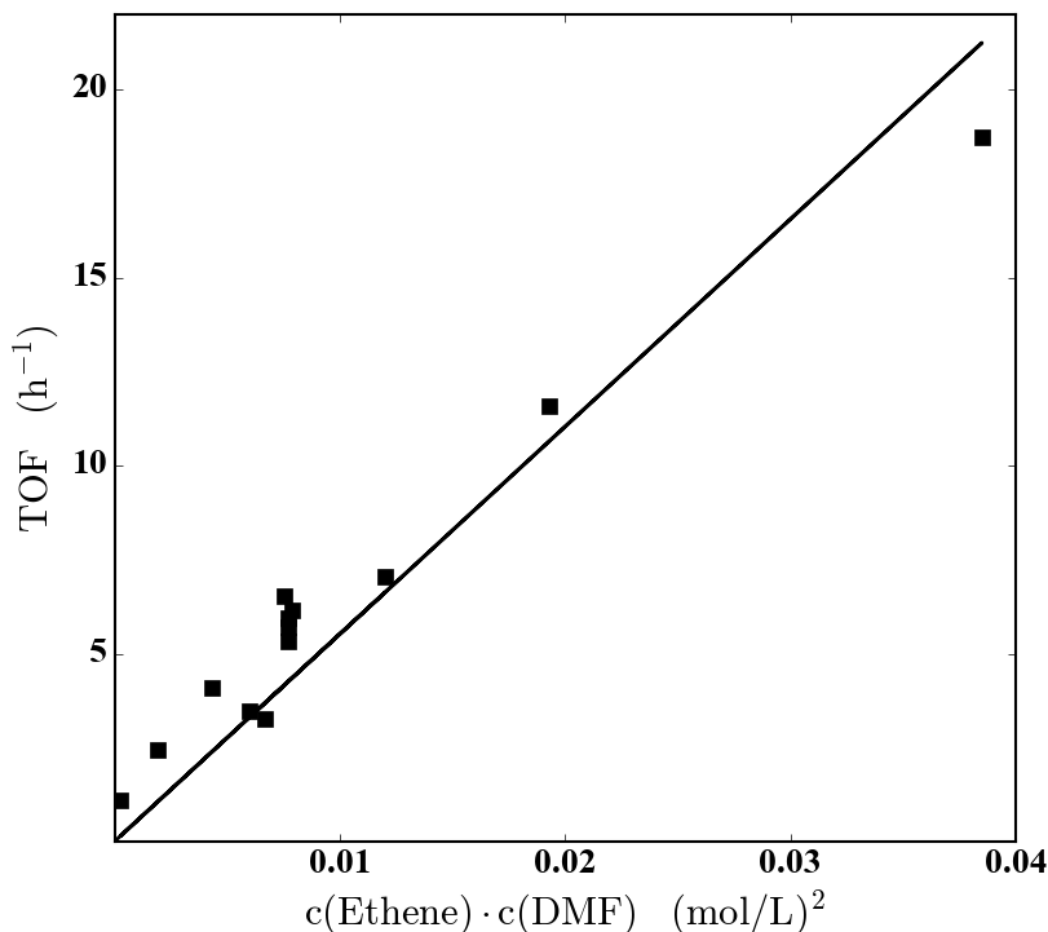


Figure 6.6: Turn over frequency versus the product of $c(\text{C}_2\text{H}_4)$ and $c(\text{DMF})$ on Sn-BEA at 650 K

It is interesting to compare our measured rates to those reported in previous studies. At the reaction conditions of Fig. 6.7, the rate expression reported by Patet, et al. [139] for the linear acid-site regime where the reaction is limited by dehydration reaction would give a TOF of 1.15 h^{-1} using an activation energy of 45 kJ/mol, compared to our initial rate of 1.5 h^{-1} . Because the extrapolation from low temperature would not take the deactivation of catalysts into

consideration, these results suggest that the mechanism in batch reactor or flow reactor were similar.

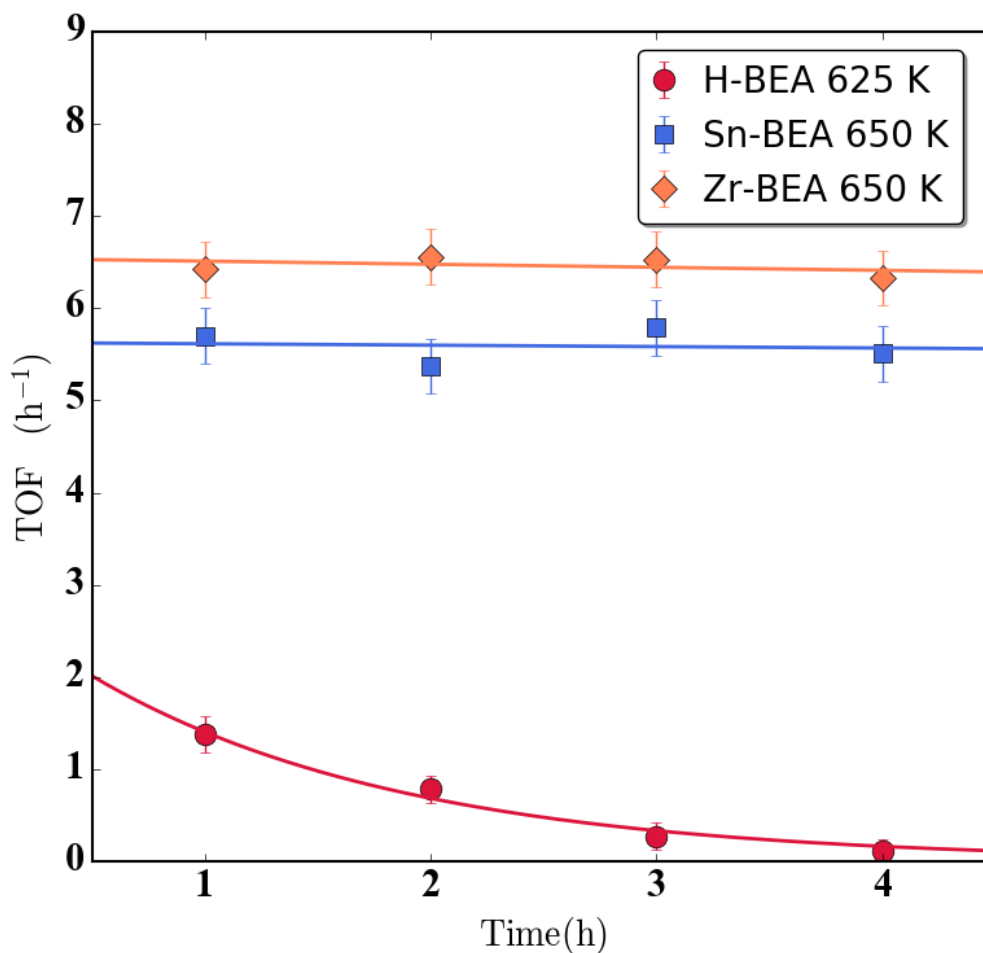


Figure 6.7: Turn over frequency vs time on 0.1 g H-BEA at 625 K, on 0.1g ZrBEA at 650 K, and on SnBEA at 650 K. The total pressure was 55 bar.

Using data obtained 1 h after introducing the feed, rates on both H-BEA and ZrBEA were found to again fit the rate expression in Eqn 6.1. This is shown in Fig. 6.8, using raw data from Table 6.4, where we have again plotted the TOF versus the product of ethene and DMF concentrations. For ZrBEA, data is plotted for measurements at 650 and 700 K. For H-BEA, the

measurements were performed at 625 K in an attempt to minimize the deactivation rate. Again, fits of the data by lines that extend through the origin were excellent.

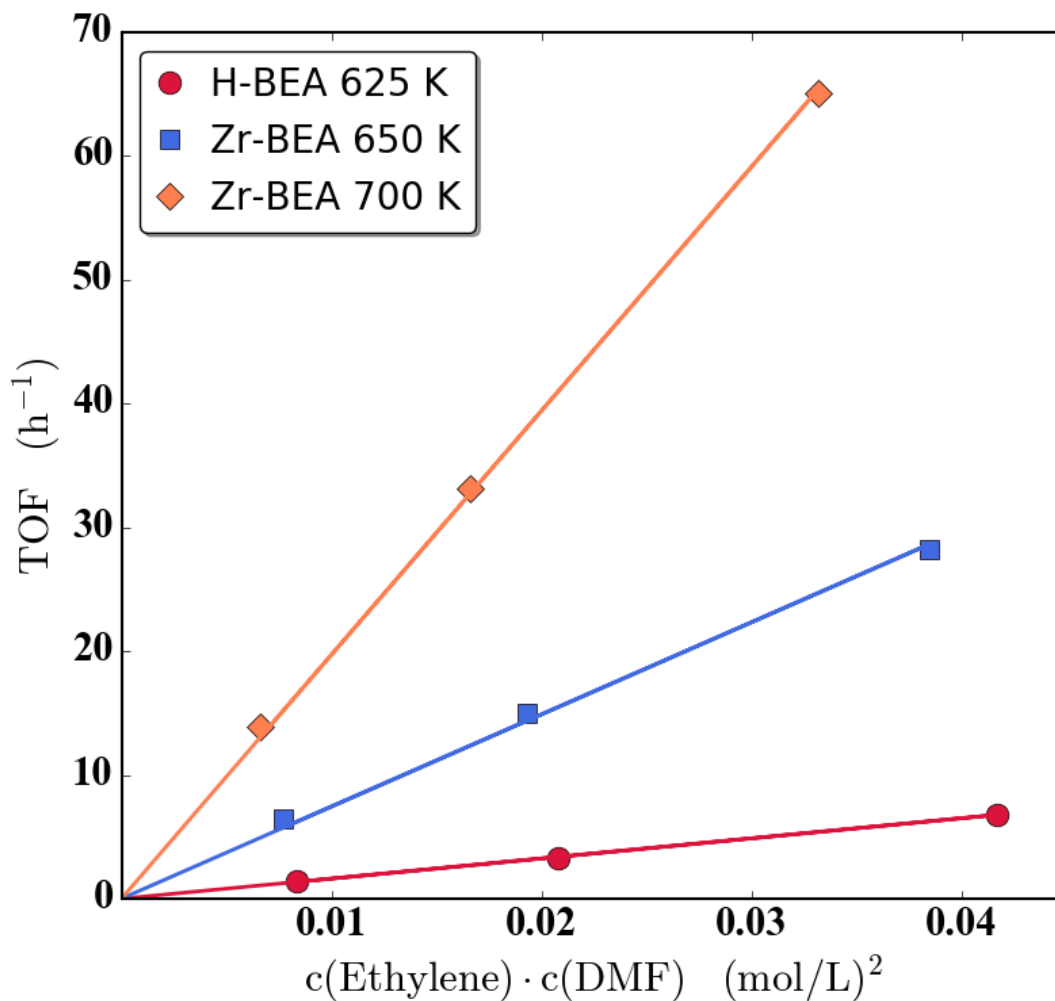


Figure 6.8: Turn over frequency vs the product of $c(\text{C}_2\text{H}_4)$ and $c(\text{DMF})$, for 0.1 g H-BEA and ZrBEA at 55 bar

The rate constants determined for the three acidic zeolites were plotted as a function of inverse temperature in Fig 6.9, from data shown in Table 6.5. First, it is apparent that the rate constants decreased in the order of ZrBEA $\sim$ SnBEA $>$ H-BEA. Because the site densities varied in the opposite direction, the overall volumetric rates on the three zeolites were similar. The

activation energy on H-BEA was 50 kJ/mol, which is close to 45 kJ/mol, the activation energy reported by Patet, et al [139] for the regime in which reaction is limited by dehydration of the Diels-Alder cycloadduct. However, because deactivation may be worse at high temperatures, it is possible that our apparent activation energy on H-BEA was affected by this. The activation energies on SnBEA and ZrBEA, ~68 kJ/mol, should be considered more reliable, but data does not exist for comparison. Based on the lower reactivity of Lewis sites for performing the dehydration reaction, it is reasonable that the activation energy would be higher.

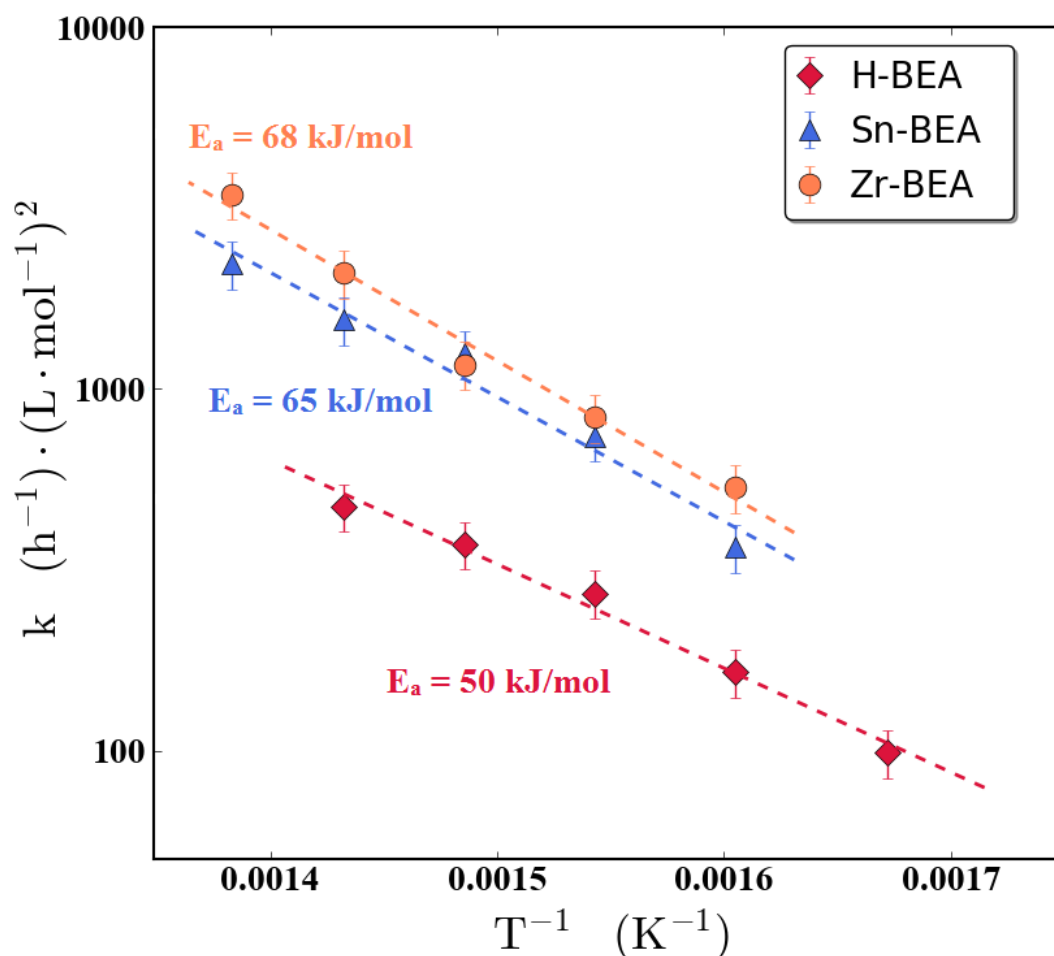


Figure 6.9: Reaction rate coefficient (k) versus inverse temperature ($1/T$) for H-BEA, Sn-BEA and ZrBEA

Table 6.4: Reaction rates for 0.1g H-BEA and Zr-BEA under 55 bar at different temperature with different partial pressure of C₂H₄ and 2,5-dimethylfuran

Catalyst	Total mol flow rate (*10 ⁻³ mol/min)	Heptane mol concentration	C ₂ H ₄ mol concentration	DMF mol concentration	Temperature (°C)	Conversion	Selectivity	Reaction rate (1/(site.h))
H-BEA	1.7	38.9%	59.9%	1.2%	350	11.4%	48%	1.3
H-BEA	1.7	37.4%	59.6%	3.0%	350	11.8%	45%	3.3
H-BEA	1.7	34.9%	59.1%	6.0%	350	12.5%	43.5%	6.8
Zr-BEA	1.7	38.9%	59.9%	1.2%	375	5.8%	88%	9.7
Zr-BEA	1.7	37.4%	59.6%	3.0%	375	5.5%	87%	17.2
Zr-BEA	1.7	34.9%	59.1%	6.0%	375	5.2%	86.5%	19.7
Zr-BEA	1.7	38.9%	59.9%	1.2%	425	12.8%	87%	13.9
Zr-BEA	1.7	37.4%	59.6%	3.0%	425	12.4%	85%	33.2
Zr-BEA	1.7	34.9%	59.1%	6.0%	425	12.8%	81%	65.0

Table 6.5: Reaction results for different temperature at 55 bar, gas flow rate 25ml/min, liquid flow rate 0.1ml/min, 0.1g catalysts (H-BEA, Sn-BEA, Zr-BEA), 2% 2,5-dimethylfuran concentration in heptane

Catalyst	Temperature(°C)	Conversion	Selectivity	Reaction rate (1/(site.h))	log(k) ($k = \frac{r}{c(C_2H_4)c(DMF)}$)
H-BEA	325	8.4%	42%	0.9	4.6
H-BEA	350	11.4%	48%	1.4	5.1
H-BEA	375	16.3%	51%	2.1	5.6
H-BEA	400	18.7%	57%	2.7	5.9
H-BEA	425	25.8%	49%	3.1	6.2
Sn-BEA	350	3.7%	93%	3.03	6.9
Sn-BEA	375	6.9%	92%	5.7	7.6
Sn-BEA	400	11.6%	86%	8.9	8.2
Sn-BEA	425	13.6%	85%	10.3	8.4
Sn-BEA	450	18.2%	85%	13.8	8.7
Zr-BEA	350	4.1%	87%	4.5	6.3
Zr-BEA	375	5.9%	88%	6.4	6.7
Zr-BEA	400	7.6%	88%	8.3	7.1
Zr-BEA	425	12.8%	87%	13.9	7.6
Zr-BEA	450	19.8%	86%	21.4	8.1

6.4. Discussion

The comparison of adsorption and reaction properties on SnBEA, ZrBEA, and H-BEA reveal important information about the reaction of ethene and DMF to form p-xylene. At first glance, it is surprising that materials with such dramatically different adsorption properties for the reactants would give similar reaction rates. However, this is consistent with the mechanism presented by Patet, et al. [139], where it was proposed that the reaction occurs in two steps, an uncatalyzed Diels-Alder reaction to form the oxanorbornene intermediate, followed by its acid-catalyzed dehydration to p-xylene. Since both Brønsted- and Lewis-acid sites are able to carry out dehydration reactions at the reaction temperatures [57], both are effective in catalyzing the reaction. Indeed, similarities found in the conversion of 2,5-hexanedione to DMF in the TPD results on all three acidic zeolites tends to confirm this.

It is important to notice that the Diels-Alder adduct was not observed on SiBEA, even though catalytic sites are not required for this part of the reaction. The fact that the oxanorbornene intermediate was not observed implies either that its formation is reversible upon cooling or that it is present in low concentrations within the zeolite cavities.

The rapid deactivation observed on H-BEA is almost certainly related to the strong adsorption and oligomerization observed following adsorption of DMF and 2,5-hexanedione. The fact that Lewis sites are not able to catalyze this oligomerization is critically important. Practical implementation of this technology will require stable catalysts and the Lewis-acidic materials appear to be better suited for this than Brønsted-acidic materials. The Lewis-acid zeolites have an additional advantage in that they are not expected to catalyze the isomerization of p-xylene to the ortho- and meta-isomers. High selectivities are achieved in H-BEA because strong adsorption of DMF and 2,5-hexanedione on the Brønsted sites limits access of the p-xylene to those sites, but SnBEA and ZrBEA should be intrinsically more selective.

There is still much to learn about the reaction of DMF with ethene and the use of zeolites to catalyze it. We believe that the combination of adsorption and reaction studies advances those goals.

6.5. Summary

SnBEA, ZrBEA, and H-BEA all catalyze the formation of p-xylene from DMF and ethene effectively, even though their adsorption properties for the reactants are significantly different. The key property required of the Lewis- and Brønsted-acid sites for this reaction is the ability of the sites to catalyze the dehydration of the oxanorbornene intermediate. Because the Brønsted sites in H-BEA tend to oligomerize DMF and 2-5 hexanedione, H-BEA is found to be less stable than the Lewis-acid zeolites, SnBEA and ZrBEA.

Chapter 7. Conclusion

The focus of this thesis was the characterization of solid Lewis acids by various types of adsorption studies, including TPD-TGA and calorimeter measurements and reactivity measurements for several solid Lewis acids in biomass conversions. Bulk metal oxides, framework substituted Lewis acid zeolites, and ion-exchanged zeolites were compared and studied. The results presented in this thesis make a significant contribution towards a better understanding of the nature of Lewis acidity in solid Lewis acids and the function of Lewis sites in biomass conversions.

In Chapter 3, the acidity and reactivity of bulk oxides including γ -Al₂O₃, ZrO₂, TiO₂ and bulk oxides over SBA-15 support materials were discussed. Acidity of oxides were determined to be pure Lewis acidity by TPD-TGA of 2-propylamine; however, metal oxides supported on SBA-15 were found to have Brønsted acid sites. TPD-TGA results show that Al₂O₃/SBA-15 contains strong Brønsted acid sites, while ZrO₂/SBA-15 and TiO₂/SBA-15 have weak Brønsted sites. Alcohol dehydration and HMF etherification with 2-propanol were studied over these materials. In alcohol dehydration, the formation of Brønsted sites for oxides on SBA-15 led to a temperature shift for dehydration in TPD. The dehydration temperature for 1-propanol TPD in Al₂O₃/SBA-15 was 50 K lower than was found on bulk Al₂O₃. In HMF etherification, materials with Lewis acid sites or weak Brønsted acid sites were active for hydride transfer from 2-propanol to HMF, with subsequent reactions to mono- or di-ethers, while materials with strong Brønsted acidity were only able to catalyze the formation of mono-ethers, with the carbonyl group on HMF unreacted. This work explains differences in reactivity and adsorption properties between Lewis acids and Brønsted acids.

In Chapter 4, the possibility of using alkali-exchanged BEA zeolites as Lewis-acid catalysts was examined using TPD-TGA measurements of adsorbed pyridine, 2-propanamine, diethyl ether, 2-methyl-2-propanol, and acetonitrile, FTIR of pyridine and CD_3CN , calorimetry of CO, and reaction rates for reductive etherification of 5-hydroxymethyl furfural (HMF) with 2-propanol. Adsorption on the alkali cations occurs through ion-dipole interactions, as evidenced by the fact that adsorption is strongest on Li, followed by Na and K. Adsorption of all the probe molecules were much stronger on Li-BEA than on acid sites formed by framework Sn in SnBEA; however, the alkali-exchanged BEA samples were not catalytically active for alcohol dehydration or reductive etherification of HMF. The important implication here is that the measuring of Lewis acidity is intrinsically difficult in that catalytic activities are not related in any simple way to heats of adsorption for standard probe molecules.

In Chapter 5, CH_4 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 CH_4 should bind to this site by an additional 1 to 7 kJ/mol, a discrepancy that is due to the inability of standard DFT methods to capture hydrogen-bonding effects accurately with CH_4 . Differential heats for CH_4 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 CH_4 is an excellent probe molecule for characterizing the pore structure of zeolites.

In Chapter 6, the adsorption and reaction properties of H-BEA, SnBEA, ZrBEA, and siliceous BEA were examined to understand the reaction of 2,5-dimethylfuran (DMF) with ethene to produce p-xylene. Temperature-programmed desorption (TPD) of diethyl ether, DMF, 2,5-hexanedione, and p-xylene on each of the zeolites demonstrated that the Brønsted sites in H-BEA are more reactive than the Lewis sites in SnBEA and ZrBEA and tend to promote oligomerization of DMF and 2,5-hexanedione, even at 295 K; however, adsorbed 2,5-hexanedione is converted to DMF at both Lewis- and Brønsted-acid sites. H-BEA, SnBEA, and ZrBEA all catalyzed the reaction to p-xylene with high selectivity in a continuous flow reactor, with all three catalysts showing rates that were first-order in both DMF and ethene. H-BEA was found to deactivate rapidly due to coking, while ZrBEA and SnBEA were both stable. These results suggest that the Lewis-acidic materials appear to be better suited for than Brønsted-acidic materials for practical implementation of this reaction because of stability.

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