Structure-Performance Relationships in Solid-Acid Aluminosilicates

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Summary

Zeolites and amorphous silica-aluminas (ASAs) are widely used as solid acid catalysts in the chemical industry. Their catalytic performance, notably the activity and selectivity, depends on their structures. This study focuses on the elucidation of the structure-performance relations in zeolites and ASAs.

Various zeolites of different structure type and with different Si/Al ratios and ASAs with different Si/Al ratios were synthesized. The intrinsic activity of the Brønsted acid sites was determined by the monomolecular conversion of propane, which was performed in a newly constructed reactor that contained six tubular quartz reactors. The catalyst samples are characterized by many different techniques, such as AAS, BET, FTIR, NMR, TPD-TGA, XRD, and TEM.

The relation between the catalytic activity of the Brønsted acid sites and zeolite framework topologies and Si/Al ratio is described in Chapter 3. In the monomolecular conversion of propane, there are two separately occurring reactions: protolytic cracking and dehydrogenation. The rates and apparent activation energies of each of these reactions were determined. The number of sites and the size and shape of the pores affected the catalytic activities. The influence of structure and Si/Al ratio on the activity and selectivity strongly depended on the rate-limiting step of the reaction. In the protolytic cracking, the protonation of the alkane by the Brønsted acid sites is the rate-limiting step. Different structure types all had the same intrinsic activation energies, which indicates that the ability to donate a proton to alkanes is independent of the zeolite structure type and of the Si/Al ratio larger than ~5. The sorption of the reactants in the pores dominates the differences in the observed activities. Alkanes are physisorbed in the pores of a zeolite and the dominant interactions are the dispersion forces, which are the van der Waals interactions. The strength of the adsorption depends on the fit of alkanes within the pore: the better the fit, the higher the heat of adsorption will be. Therefore, the size and shape of the pores are the dominant factors in determining the cracking activity of the Brønsted acid sites. The better the fit between the reactant and the pore size of the catalyst, the higher the observed activity will be. In the dehydrogenation reaction, the rate-limiting step is the desorption of the alkene from the alkoxide species that is formed after formation of a hydrogen molecule. The rate is determined by the stability of the alkoxide species. This stability depends on the local structure of the Brønsted acid site, which means that the region
of the surrounding of the sites, also participates in this reaction. Thus, the catalytic activity of the Brønsted acid sites in dehydrogenation is influenced by their local geometric and electronic structure and affected by zeolite structures and Si/Al ratio. Generally, larger pores and lower Si/Al ratios result in a higher activity.

The origin of the much lower activity of ASA compared to zeolites is described in Chapter 4. Three ASA samples with different Si/Al ratios were studied. The reaction rate increased with aluminum content, but the apparent activation energies were identical. Their rates per total aluminum content were almost a thousand-fold lower than that of zeolites. Nevertheless, their intrinsic activation energies were similar to that of zeolites. This implies that the acid strength of the Brønsted acid sites is independent of crystallinity of the structure. The much lower activity of ASA is due to a very low heat of propane adsorption on ASA and to a low number of the Brønsted acid sites that participated in the reaction. Therefore, only a small percentage of the aluminum atoms form Brønsted acid sites that are similar to those in zeolites and these dominate the activity of ASA in a demanding reaction like monomolecular cracking of alkanes.

Chapter 5 describe under what conditions zeolites are unstable and structural collapse occurs. The conditions, which resulted in a full recovery of the catalytic activity, were discussed. The Brønsted acid sites in zeolite Y were investigated by the combination of monomolecular cracking of propane and various physicochemical characterization methods. Exposure of a high-aluminum acidic zeolite Y to moisture leads to a loss of long-range and short-range structure observed by $^{27}$Al MAS NMR and XRD. Heating this partially collapsed zeolite caused a further structure collapse and an extra loss of catalytic activity. Adsorption of NH$_3$ before exposure to air of acidic zeolite prevented the structural collapse of the Brønsted acid sites and the loss of the catalytic activity. Water molecules are involved in the structural destruction, but also in the structural recovery with ammonia. The structures of acidic zeolites are very sensitive to temperature and presence of moisture. Different characterization methods probe different states of zeolite structures, because of structural changes that occur during sample preparations.

Chapter 6 provided clues into the origin of the enhanced catalytic activity of steamed zeolite HUSY through comparison to zeolite Y that had high Si/Al ratios from synthesis. The effect of framework Si/Al ratio on the intrinsic activity of Brønsted acid sites in zeolite Y was investigated by monomolecular cracking of
propane and various physicochemical characterization methods. High-silica zeolite Y showed similar characteristic features as the high aluminum one, although they were more stable. Treatments of ammonia and ethylenediaminetetraacetic acid were performed on an ultrastable Y (HUSY) to remove its extra-framework aluminum. In all cases, the rates per gram increased with the framework Si/Al ratio. However, the apparent activation energies were identical and independent of the Si/Al ratio and the presence of extra-framework aluminum. This implies that the structure and acid strength of Brønsted acid sites that participate in the reaction are identical in all these samples. The enhanced activity of the samples with higher Si/Al ratio (up to 5) is attributed to the creation of more isolated Brønsted acid sites, which are active in this demanding reaction. Extra-framework aluminum did not affect the intrinsic catalytic activity.
Zusammenfassung


Eine Vielzahl von Zeolithen mit unterschiedlichen Strukturtypen und unterschiedlichen Si/Al-Verhältnissen, sowie ASAs mit unterschiedlichem Si/Al-Verhältnis wurden im Rahmen dieser Arbeit synthetisiert. Die intrinsische Aktivität der Brönsted-Säurezentren wurde durch monomolekulare Reaktionen von Propan in einem neuen Reaktor getestet, der sechs Quarzrohrreaktoren enthielt. Die einzelnen Katalysatorproben wurden durch eine Vielzahl von instrumentellen Techniken charakterisiert, wie z.B. AAS, BET, NMR, TPD-TGA, XRD und TEM.

Der Zusammenhang zwischen der katalytischen Aktivität der Brönstedzentren, den Gerüststrukturen der Zeolithe und dem Si/Al-Verhältnis wird im Kapitel 3 beschrieben. Bei der monomolekularen Umsetzung von Propan laufen zwei verschiedene, parallele Reaktionen ab: Cracking und Dehydrogenierung. Die Reaktionsraten und beobachteten Aktivierungsentnergien aller dieser Reaktionen wurden bestimmt, wobei sich herausstellte, dass die Anzahl der Säurezentren, sowie die Grösse und Form der Poren die katalytische Aktivität beeinflusste. Der Einfluss von Struktur und Si/Al-Verhältnis auf die Aktivität und Selektivität hing dabei vor allem von dem Reaktionsschritt ab, der die Reaktionsgeschwindigkeit limitiert.

Im Falle des protolytischen Crackens ist dies die Protonierung des Alkans am Brönstedzentrum. Verschiedene Strukturtypen zeigten dabei identische, intrinsische Aktivierungsentnergien, was darauf schliessen lässt, dass die Abgabe eines Protons an ein Alkan unabhängig vom Strukturtyp des Zeolithen und dem Si/Al-Verhältnis ist, falls letzteres grösser als ~5 ist. Die unterschiedliche Aktivität der Katalysatoren entzieht sich dabei der direkten Beobachtung, da sie durch die unterschiedliche Adsorption der Reaktanden in den jeweiligen Zeolithporen überdeckt wird. Alkane werden in den Poren der Zeolithe durch Physisorption gebunden, wobei vor allem Dispersionskräfte wirken, die so genannten van der Waals Kräfte. Dabei beruht die Adsorptionsstärke darauf, wie gut die Alkane in die Poren passen: je besser sie passen, desto höher ist die Adsorptionswärme. Daher sind die Grösse und Form der Poren der entscheidende Faktor um die Cracking-Aktivität von Brönstedzentren zu bestimmen. Je besser die Reaktanden in die Poren passen, desto höher ist die beobachtete
katatalytische Aktivität. In Dehydrierungsreaktionen ist der limitierende Reaktionsschritt die Desorption des Alkens von den Alkoxy-Spezies, die nach der Bildung des Wasserstoffmoleküls erfolgt. Die Reaktionsrate wird dabei durch die Stabilität der Alkoxy-Spezies bestimmt. Diese Stabilität beruht auf der lokalen Umgebung durch das Brönsted-Zentrum, das heißt, auch die umgebende Region ist an der Reaktion beteiligt. Zusammenfassend kann gesagt werden, dass die katalytische Aktivität der Brönstedzentren in Dehydrogenierungsreaktionen durch die lokale, geometrische und elektronische Struktur der Zentren und das Si/Al-Verhältnis des Zeolithen beeinflusst wird, wobei generell gilt, dass größere Poren sowie niedrigere Si/Al-Verhältnisse eine höhere Aktivität bewirken.


Chapter 1

Introduction

In the oil refining, petrochemicals, and fine chemicals industry, acids are widely used as catalysts. Liquid acids, such as HF, H₂SO₄, and H₃PO₄, have traditionally been most. Since 1940, solid acid catalysts replace the liquid acids because of their green advantages [1], which include decreasing the problem of reactor corrosion, simplifying the process, regenerating the catalysts, and disposing in environmentally safe manners. In addition, solid acid catalysts, in particular zeolites, may tune a reaction based on size of the reactant, intermediate, or product (vide infra). Among the different solid acids, amorphous silica-aluminas (ASAs) and zeolites are the most generally applied. Their success is based on their strong acidity and stability, which is inherent to their structures. Therefore, studying the structure and nature of the acid sites is relevant to determine structure-performance relations. Understanding these relations enables a rational design of better catalysts, which is the ultimate aim of our research. The structure and activity of Brønsted acid sites in ASAs and zeolites will be described in this thesis.

1.1 Zeolites

1.1.1. Introduction

Zeolites are crystalline aluminosilicates, whose structures are based on an infinitely extending three-dimensional network of “AlO₄” and “SiO₄” tetrahedrons that are connected to each other by shared oxygen atoms. Because each oxygen is part of a bridge between two tetrahedrally coordinated atoms, the “SiO₄” unit is neutral. Each framework “AlO₄” unit bears one net negative charge, which is balanced by an extra-framework cation. These cations are mobile and can be exchanged. When they are exchanged by protons, they form the Brønsted acid sites and the zeolite shows Brønsted acidity. The structural formula of a zeolite can be written as:

\[
M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot mH_2O \tag{1.1}
\]

where \(n\) is the valence of cation \(M\), \(x\) and \(y\) are the number of tetrahedral silicon- and aluminumoxide units, respectively, and \(m\) is the number of water molecules per unit cell. Aluminum and silicon occupy the crystallographic T-sites. According to Löwenstein rule [2], Al-O-Al links are forbidden and, thus, the Si/Al ratios of zeolites
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vary from 1 to infinity. The “AlO₄” and “SiO₄” tetrahedral units are interconnected to form secondary building units, which consist of cubes, hexagonal prisms, and cubo-octahedra. The final framework structure is formed by combining the secondary units. A zeolite framework structure is relatively open and is characterized by the presence of channels and cavities. The sizes of the pores and cages are defined by the number of T-sites that encompass the pores and cages. For example, when eight T atoms form a pore, this pore consists of eight member rings (MR). Typically, the pore sizes are between 0.3 and 1.0 nm and can be divided into small pores with 8 MR, medium pores with 10 MR, and large pores with 12 MR.

Zeolites are applied in catalysis because of their particular properties. Often zeolites, especially the high silica materials, show a high (hydro)thermal stability, which enables their use in reactions and regenerations that are run at high temperature in the presence of aggressive gases. With the uniform pore systems that have sizes similar to molecules, zeolites show unique and high selectivities in many reactions. Three main types of shape selectivity have been identified [3]: reactant, product, and reaction intermediate or transition state selectivity. Reactant and product selectivity are due to the relative rates of diffusion of reactants and products, i.e., mass transfer affects the rate of reaction. This diffusion controlled selectivity is affected by the crystal size and by making the zeolite crystals mesoporous [4]. Intermediate or transition state selectivity occurs when large intermediates or transition states are prevented from forming because of space constraints. Reactions that are affected by this selectivity can be optimised by choosing between zeolites with different pore structures [4]. In many cases, the combination of these shape selectivities is used for a particular reaction. Zeolites have ion-exchange capacities, which is the reason for their use as detergents. For catalytic applications, ion-exchange is not only used to introduce different catalytically active metals but also to produce the acidity via ammonia ion-exchange followed by calcination.

1.1.2. Zeolites types

There are 133 distinct framework structures of zeolites that have been accepted [5] and new zeolite structures are still demonstrated [6–8]. Some of the important zeolite types have been used in commercial applications, include MFI, MOR, BEA, and FAU, which are described in this chapter and are investigated in this study.
The MFI (Mobile five) structure contains two intersecting ten MR channels that are formed from the interconnected five MR units (Fig. 1.1). The straight channels along [010] have a size of 5.3 × 5.6 Å; while the sinusoidal channels along [100] have a size of 5.1 × 5.5 Å. MFI can be synthesized with Si/Al ratios from ~10 to infinity. ZSM5 (Zeolite Secony Mobil-five) belongs to this structure family.

Fig. 1.1. Framework of MFI viewed along [010] and unit cell (b) [5].

In the mordenite (MOR) framework type (Fig. 1.2), four units of five MR and one four MR are joined to form parallel 12 MR that are connected via the eight MR side pockets. The size of the 12 MR is 6.5 × 7.2 Å along [001] and that of the eight MR side pockets is 3.4 × 4.8 Å along [010].

Fig. 1.2. Framework of MOR viewed along [001] and unit cell (b) [5].

The Beta framework structure (Fig. 1.3) is built by interconnected four and five MR, which results in layers that contain saddle-shaped 12 MR. Adjacent layers are related to one another by a rotation of 90° and these well-defined layers are stacked in a more or less random fashion. Independent of the stacking sequence, a pore system with
three-dimensional 12 MR channels is formed. The diameter of the channels in the [100] direction is $6.6 \times 6.7$ Å and along [001] it is $5.6 \times 5.6$ Å. BEA belongs to this structure type.

![Fig. 1.3. Framework of Beta viewed along [010] and unit cell (b) [5].]

The faujasite (FAU) type framework structure is shown in Fig. 1.4. Sodalite cages are joined to one another via hexagonal prisms to form the so-called supercages, which have 12 MR pore openings and build a three-dimensional pore system. The diameter of the supercage is about 13 Å and that of the windows is 7.4 Å [9]. Zeolite Y belongs to this class.

![Fig. 1.4. Framework of FAU viewed along [001] [5].]

1.2. Amorphous silica alumina (ASA)

In contrast to zeolites, ASAs have no long-range order and are amorphous. They consist of tetrahedral “SiO$_4$” units that, as in zeolites, build a three-dimensional framework, however, without long-range order. The aluminum substitution into the silica framework forms the tetrahedral “AlO$_4$” unit even though ASAs contain often Al$_2$O$_3$ domains. As in zeolite, a negative charge balance is required for a framework
with “SiO₄” and “AlO₄”. ASA contains no micropores, but has a relative high external surface area and a large volume of mesopores.

1.3. The active site

In a SiO₂ matrix, the replacement of a silicon atom by a tetrahedrally-coordinated aluminum atom creates a negative framework charge. Compensation by a proton [10] leads to a bridging hydroxyl group that is a strong Brønsted acid site (Fig. 1.5). A non-classic three-fold coordinated bridging oxygen is formed and the bridging Si-O and Al-O bonds are lengthened. The Al-O bond length is longer than the Si-O bond.

![Fig. 1.5. Active site in hydrogen aluminosilicates.](image)

Generally, it is accepted that the zeolitic acid strength is like conventional strong acids rather than superacids [11]. Fig.1.5 shows that one tetrahedrally-coordinated aluminum atom corresponds to one Brønsted acid site. Thus, the number of acid sites is directly related to the framework aluminum content, through which the concentration of the acid sites can be adjusted. The acid strength of the Brønsted acid site and their corresponding activity in aluminosilicates are complicated issues. The strength of the Brønsted acid sites is affected by the acid site density, i.e. the Si/Al ratio [12], the T–O–T bond angles [13,14], the presence of nonframework aluminum [15-19], and of charge-balancing cations [19,20]. Lewis acid centers are proposed to withdraw electron density, enhancing the Brønsted acid strength [20,21]. Theoretical and experimental evidence suggest that the acid strength per aluminum is a maximum when the framework aluminum ions have no second nearest neighbor aluminum [22,23]. These issues are described in more detail in later chapters.

As for the structure and activity of Lewis acid sites, their structure and location are presently a matter of debate [24-26], but they are not investigated in this study.

1.4 Synthesis of zeolites and ASAs

Zeolite synthesis proceeds in basic solutions, because tetrahedrally-coordinated aluminate ions are only stable at high pH. Zeolites are made by hydrothermal
synthesis using, in principle, six chemical sources: SiO₂, AlO₂⁻, OH⁻, alkali cations, a template, and water. Generally, the first step is the preparation of the reaction mixture at low temperature (< 335 K). The different chemicals are mixed in this step to result in the so-called gel, in which silicate and aluminate monomers and oligomers are in equilibrium [27]. The gel is then transferred into a reaction vessel, which is an autoclave, and a temperature between 373 and 573 K is chosen. The zeolite crystallizes and the crystallisation aging time depends on the structure type of zeolite. The final step is to separate the crystals, which are dried and often calcined. Organic templates, or structure-directing agents, are regularly used. They can be divided in charged and neutral molecules containing functional atoms or groups. The structure-directing agents stabilize a particular type of zeolite framework. Some charged templates are also required for charge compensation. One type of template can be applied to synthesize various zeolites whereas the same type of zeolites may be obtained by using different templates.

Conventionally there are two methods for preparing ASA [28]. One is to start from a silica hydrogel with an aluminum sulfate solution and hydrolysing the mixture by the addition of aqueous ammonia and the ASA precipitates; the other involves reaction between sodium silicate and sodium aluminate. In both cases the complete preparation process involves drying, ion-exchange with ammonia, and calcination. Alkylammonium cations have been used to control the distribution of the pore size [29,30]. Recently, sol-gel and coprecipitation methods were developed in the synthesis of ASA [31,32].

1.5 Zeolite activation

Post-synthesis treatments are required to generate active zeolites. If a zeolite contains template molecules, they are removed by calcination. Because these molecules are strongly sorbed in the zeolite lattice, a high temperature and an oxidizing atmosphere are required for their complete removal. Following the template removal step, ion exchange in aqueous solution is performed to obtain the desired charge-compensating cations. Acidic zeolites are obtained by ion-exchanging NH₄⁺ cations into the pores of the zeolites and removing the ammonia by calcinations. To completely remove sodium cations, repeated ion exchanges are usually required. Zeolites with a Si/Al ratio 10 or higher are stable enough to allow direct exchange of sodium by protons in an acid solution [33].
Introduction

For many desired catalytic properties of zeolites, further post-synthesis treatments are utilized. Steam activation is generally applied to activate zeolites [34,35]. For example, the acidic form of zeolite Y is quite useful as a cracking catalyst. However, its thermal and hydrothermal stability is limited. It was discovered that even at room temperature the structure of acidic zeolite Y partially collapsed when exposed to moisture [36,37]. Therefore, a thermally stable Y, so called ultra-stable zeolite Y (USY), was developed by dealumination via the controlled addition of steam [38]. Mesopores often form during this process [39-42]. Except for its higher thermal stability, HUSY exhibits a much higher catalytic activity than the non-activated samples [35-46].

1.6 Akane activation over Brønsted acid sites

It is generally accepted that the reactions of alkanes on Brønsted acid sites occur via two major mechanistic routes. One is the monomolecular reaction route, which proceeds via carbocations as the transition states [47,48], even though the carbocations are seldom observed in zeolites [49]. Carbocations are involved in cracking and dehydrogenation. The second mechanism is the bimolecular reaction route, in which an alkane is activated via a hydride transfer step from an alkoxide [50]. The transition state resembles a carbocation [51].

The monomolecular mechanism involves the formation of carbocations via the protonation of an alkane and the cleavage of the C-C or C-H bond to yield the cracking products: an alkane and an alkene, or hydrogen and an alkoxide species [52-54], which can desorb as an alkene. An alkoxide species is reactive in bimolecular reactions. Quantum chemical calculations suggested the existence of different carbocation transition states for cracking and dehydrogenation [48, 55 - 57]. Experimental studies showed that the rate-limiting step of cracking is the protonation by the Brønsted acid sites [58] and of dehydrogenation it is the olefin desorption [59]. The monomolecular pathway is governed by the reaction conditions and is favoured at high temperature, low surface concentration of the reactant, and low conversion [47]. The monomolecular cracking of an alkane is a first order reaction and physical adsorption of alkane reactants contributes to the apparent kinetics [54,58]. The sorption of alkanes in zeolites can be adequately described by a Langmuir isotherm [60], which is a rapid and completely reversible equilibrium sorption and with the loading-independent heat of sorption. Henry's Law constant K represents the
proportionality factor of the linear part of the isotherm. Therefore, the concentration of the alkane adsorbed on the zeolite surface can be expressed as:

\[ C_{\text{sw}} = \frac{K[A]}{1 + K[A]} \]  

(1.2)

where \([A]\) the gas phase concentration. Because the surface coverage of alkanes is low, equation 1.2 can be written as:

\[ C_{\text{sw}} = K[A] \]  

(1.3)

For the monomolecular cracking of an alkane, which is a first order reaction, the apparent reaction rate, \(r_{\text{app}}\), is expressed with \(k\), the intrinsic rate constant:

\[ r_{\text{app}} = kC_{\text{sw}} \]  

(1.4)

Combining equations 1.3 and 1.4 yields:

\[ r_{\text{app}} = kC_{\text{sw}} = kK[A] = k'[A] \]  

(1.5)

where \(k'\) is the apparent rate constant and equals:

\[ k' = kK \]  

(1.6)

Therefore, the apparent rate constant \(k'\) contains the sorption properties (\(K\)) and only the intrinsic rate constant \(k\) reflects the reaction on the acid sites. With

\[ k' = A \exp(-E_{\text{app}}/RT) = A \exp(-E_{\text{sw}}/RT) \exp(-\Delta H/RT) \]  

(1.7)

the relation is obtained that the intrinsic activation energy (\(E_{\text{int}}\)) is the difference between the apparent activation energy (\(E_{\text{app}}\)) and the heat of reactant adsorption (\(\Delta H_{\text{ads}}\)) [61]. As in monomolecular cracking the rate-limiting step is the transfer of the proton to the alkane, which is an acid-base reaction, the intrinsic activity is a measure of the ability of the acid site to donate a proton, which represents the acid strength of the site.

The bimolecular mechanism is a classical chain process, which involves hydride transfer between an alkane and an alkoxide species [53, 62-64], followed by isomerization and/or \(\beta\)-scission. The hydride transfer does not involve the interaction between the Brønsted acid site and an alkane. The rate-limiting step of the bimolecular mechanism is the hydride transfer after the initial generation of the alkoxide species [54]. These can be formed in the monomolecular dehydrogenation or by adsorption of alkenes that are present in the feed or that had been formed earlier in the reactor. The bimolecular pathway is dominant at low temperature, high surface concentration of the reactant, high olefin content, and high conversion.
1.7 Aim and scope of this work

Zeolite-based catalysts have been developed for alkane transformations. The mechanism of these reactions has been discussed for years and is seemingly established. However, many open questions remain, such as, why these catalysts have their unique catalytic behaviour, how the structures influence activity, and how acid strength depends on structure and affects activity. This work addresses these questions.

The aim of this work is to relate the structure of aluminosilicates to their activity for the high-temperature activation of alkanes.

For this purpose, selected samples of different zeolites and ASAs were synthesized. A new reactor that contains six tubular quartz reactors was built. The catalyst samples were characterized by many different techniques, such as AAS, BET, FTIR, NMR, TPD-TGA, XRD, and TEM. The intrinsic activity of the Brønsted acid sites was determined by the monomolecular conversion of propane.

Chapter 2 describes the experimental methods that have been used in this thesis. The relation between the rate of reaction and intrinsic activity (cracking/dehydrogenation) on the one hand and zeolite pore size and framework Si/Al ratio one the other is established in Chapter 3. Chapter 4 elucidates the origin of the much lower activity of ASA compared to zeolites. The intrinsic activation energy is determined and the number of sites that participate in the reaction is estimated. Chapter 5 describes the structural changes that acidic zeolite Y undergoes when exposed to moisture. The reversibility of the structural change will be shown and the role of water in both collapse and restoration of the structure will be described. Chapter 6 provides insight into the origin of the enhanced catalytic activity of steamed zeolite HUSY through physicochemical characterization and comparison to zeolites Y that contain low framework aluminum contents. This thesis will end with conclusions and an outlook.

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Chapter 2

Experimental

2.1 Reactor setup

The catalytic setup that is used in this thesis is shown in Fig. 2.1. The setup contained six parallel-flow tubular quartz reactors, which are plug flow reactors. They were positioned inside a temperature-controlled environment. The flow rate was controlled by mass-flow controllers (MFC) that were obtained from Brooks Instrument. A multivalve enabled the selection of one of the gas streams to be analyzed with an online gas chromatograph (MicroGC, Fig. 2.1). The other streams were then connected to the exhaust. The MicroGC was a Agilent 3000 and comprised three self-contained modules, each consisting of an injector, column, a flow-control valve, and a thermal conductivity detector. The columns that were used are MolSieve 5A, PLOT U, and Alumina PLOT, which enabled detection of hydrogen, natural gas, and refinery gases. The setup also had three pressure controllers to assure a constant pressure. All parts were computer controlled.

Fig. 2.1. Reactor setup for the monomolecular conversion of propane over solid acid catalysts. MFC = mass flow controller and P = Pressure controller.
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The six reactors were tested and calibrated for isothermicity, flow rates, and it was confirmed that identical conversions were obtained over identical catalysts in all reactors.

2.2 Catalytic conditions

The catalytic reaction was performed with 10% propane (10 kPa) in argon at 675 to 875 K and 100 kPa total pressure. Propene was not detected in the feed. The flow rates varied from 5 to 50 mL/min, and the catalyst weight from 50 to 200 mg. Before the reaction, the catalysts were activated in the reactor in 10% oxygen in argon at 878 K for 1 h using a heating ramp of 2 K/min, unless mentioned otherwise. The reaction rate was calculated as [1]:

\[ r_i = \frac{X_i V}{m_{\text{cat}}} \]  

(2.1)

\( X_i \) is the individual reaction conversion, \( V \) the volumetric flow rate of the feed, and \( m_{\text{cat}} \) the weight of the catalyst. The apparent activation energy \( (E_{\text{app}}) \) and preexponential \( (A_{\text{app}}) \) term are defined as:

\[ \ln r = \frac{-E_{\text{app}}}{RT} + \ln A_{\text{app}} \]  

(2.2)

The apparent activation energies were determined from the slopes of the Arrhenius plots, \( \ln(r) \) vs \( 1/T \).

The reaction conditions were chosen so that the molar ratios of \( C_1 \) and \( C_2 \) as well as of \( H_2 \) and \( C_3 \) were unity; no hydrocarbons with more than three atoms were detected. The conversions were kept below 5%.

2.3 Characterization methods

2.3.1. Atomic absorption spectroscopy (AAS)

AAS was mainly applied to determine the Si/Al ratios and sodium contents of the materials after synthesis and modification. This method is based on the energy that is absorbed during the transition between the electronic energy levels of an atom, which corresponds to a specific wavelength of light [2]. After atomising the sample, it is irradiated in a suitable source of light, such as a hollow cathode lamp, and the degree of radiation absorption is measured at the wavelength of the considered element. The amount of light that is absorbed is proportional to the number of atoms in the light
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path. Therefore, quantitatively measuring the amount of light absorbed yields the content of the element. Usually, the sample is prepared in a solution and sprayed into a flame that atomizes the sample. Two different types of flame were used: the air-acetylene flame (2523 K) for analyzing the sodium content and the nitrous oxide-acetylene flame (2973 K) for determining the concentrations of the elements silicon and aluminum concentrations in the samples.

The amount of light absorbed is determined by comparing the intensity of the incident beam ($I_0$) with that of the transmitted one ($I$). The Lambert-Beer law describes the linear relationship between adsorption ($A$) and the concentration of the absorbing species ($c$):

$$ A = \log \left( \frac{I}{I_0} \right) = \varepsilon \cdot l \cdot c $$

(2.3)

where $\varepsilon$ is the absorption coefficient, characteristic of the absorbing species, and $l$ is the length of the light path.

Around 25 mg of catalyst was dissolved in 1 mL 40% hydrofluoric acid and the solution was kept overnight. After adding 1.5 mL of 2.5 M nitric acid, the solution was filled to 25 mL with double deionized water. For the determination of sodium and aluminum, 2000 ppm potassium was added to suppress their ionization. All the analyses were performed on a Varian SpectrAA-220FS instrument.

2.3.2. Nitrogen physisorption

Nitrogen physisorption is a common method to study the porosity of porous materials. According to the IUPAC classification, pores with diameters between 0.3 and 2 nm are classified as micropores, between 2 and 50 nm as mesopores, and larger than 50 nm as macropores [3]. Using small inert gases, such as nitrogen, the pore volume and the distribution of the different pore sizes can be determined. The sorption isotherms of nitrogen, whose shapes reflect the size and shape of the pores, are typically measured at its condensation temperature of 77 K.

The surface area of the materials can be determined by using the BET equation [4], which assumes that all the adsorption sites for multilayer adsorption are energetically identical and that all the layers after the first have liquid-like properties:

$$ \frac{p}{(p_0 - p)V} = \frac{1}{cV_{m0}} + \frac{(c - 1)p}{cV_{m0} + p_0} $$

(2.4)
where \( V \) is the volume of gas adsorbed, \( V_{\text{mon}} \) the volume of gas adsorbed in the monolayer, \( p/p_0 \) the relative vapour pressure of the gas, \( c \) is proportional to \( \exp[(Q-L)/RT] \), and \( Q \) is the heat of adsorption in the first adsorbed layer and \( L \) the heat of adsorption in all following layers. The BET equation (2.4) is normally able to describe a physical adsorption isotherm in the relative pressure range between 0.05 and 0.35. The \( V_{\text{mon}} \) value is proportional to the specific surface area of the adsorbent so the BET surface area is calculated as:

\[
S_{\text{BET}} = V_{\text{mon}} \cdot N_A \cdot \sigma \tag{2.5}
\]

where \( N_A \) is the Avogadro constant and \( \sigma \) the average area occupied by a nitrogen molecule (\( \sigma = 0.162 \text{ nm}^2 \)).

The micropore volume can be quantitatively determined by the \( t \)-plot method [5]. By plotting the ratio \( V_a/S \), where \( V_a \) is the volume of nitrogen adsorbed and \( S \) the surface area of the sample, as a function of the relative pressure (\( p/p_0 \)), a common curve was obtained for various non-porous solids [6]. The layer thickness is independent of the solid, but a function of the relative pressure. The statistical thickness of the adsorbed nitrogen multiplayer can be calculated by:

\[
t(nm) = 0.1 \sqrt{\frac{13.99}{-\log \left( \frac{p}{p_0} \right) + 0.034}} \tag{2.6}
\]

In the range of partial pressures between 0.1 and 0.8, equation 2.6 gives a good description of the common \( t \)-curve. The thickness of the adsorbed nitrogen multilayer in a porous sample is plotted against the adsorbed volume. The positive intercept of the linear part is indicative of the micropore volume. The slope of the linear branch is proportional to the external surface area. If mesopores are present, two linear segments may be observed. The extrapolation of the first linear segment corresponds to the micropore volume and the second one to the total pore volume of the sample. So the mesopore volume can be determined from the difference between the total pore volume and micropore volume.
In this study, the nitrogen physisorption measurements were performed at 77 K on a Micromeritics ASAP 2000 apparatus. Before the measurements, all samples were degassed overnight at 723 K unless noted otherwise.

2.3.3. X-ray powder diffraction (XRD)

X-ray powder diffraction is the most frequently used technique to identify crystalline compounds by their diffraction patterns. X-ray diffraction is the elastic scattering of X-ray photons by atoms in a periodic lattice. Constructive interference occurs when scattered monochromatic X-rays are in phase, which occurs only at particular angles. The lattice spacings, \( d \), can be derived from Bragg’s law:

\[
n\lambda = 2d \sin \Theta \tag{2.7}
\]

where \( \lambda \) is the wavelength of the X-ray, \( \Theta \) is the angle, under which the X-rays are constructively interfering, and \( n \) is the order of reflection. For crystals with cubic symmetry, the size of the unit cell \( a_0 \) can be determined by:

\[
a_0 = \frac{\lambda \sqrt{h^2 + k^2 + l^2}}{2 \sin \Theta} \tag{2.8}
\]

Where \( h, k, \) and \( l \) are the Millers indices representing the orientation of a lattice plane. The size of the unit cell in Faujasite structures has been correlated to the amount of framework aluminum atoms in the unit cell [7,8].

The XRD pattern of a powdered sample is obtained by applying a stationary X-ray source and a position-sensitive detector that detects the intensity of the diffracted X-rays as a function of the angle \( 2\Theta \) between the incoming and the diffracted beams. For the simplest case, the structure of a certain sample can be identified by comparing its experimental pattern with that of a reference one. The XRD patterns of known structure types of zeolites are compiled in the “Collection of Simulated XRD Patterns for Zeolites” [9] and in the online database of the IZA [10]. Because XRD is based on the interference between reflecting X-rays from the lattice planes, this technique requires a sample with a long-range order. It is not possible to obtain information on amorphous phases, such as amorphous silica-alumina.

In this study, XRD patterns were obtained by spinning capillaries of 0.3 mm diameter, filled with the samples, on a Siemens D-5000 powder X-ray diffractometer using Cu-K\(_{\alpha}\) radiation in a Bragg-Brentano geometry.
2.3.4. Solid state nuclear magnetic resonance (NMR)

NMR spectroscopy is based on the transitions induced between magnetic spin energy levels of certain atomic nuclei in a magnetic field. Nuclei with even mass number and even charge have zero spin so that they are no use for NMR spectroscopy. With introduction of the magic-angle spinning (MAS) technique, high-resolution NMR spectra of solids could be obtained and solid-state NMR has been widely applied to characterize the chemical and local structure of solid catalysts [11-13].

In this study, $^{27}$Al MAS NMR and $^{29}$Si MAS NMR were applied. $^{27}$Al MAS NMR characterizes the aluminum coordination in the sample. The $^{27}$Al MAS NMR spectra of zeolites are similar to those shown in Fig. 2.6.

![Fig. 2.6. Example of two typical $^{27}$Al MAS NMR spectra of zeolites, HY (top) and NH$_4$Y (bottom).](image)

The signal at about 60 ppm is assigned to tetrahedrally-coordinated aluminum and the one at about 0 ppm to the octahedrally-coordinated aluminum. Furthermore, a broad signal at around 20-40 ppm is often detected, especially in steam-treated samples, which is mostly ascribed to distorted tetrahedrally coordinated [14,15], although sometimes pentacoordinated aluminum is also observed [16].

$^{29}$Si MAS NMR enables the determination of the framework Si/Al ratio. This method is independent of the zeolite structure and the type of charge-balancing cations. In $^{29}$Si MAS NMR spectra of aluminium-rich zeolites, five peaks can be distinguished, which are assigned to silica atoms connected via oxygen atoms to four other framework T-atoms, which are either silicon or aluminum. These peaks are called $Q^4(n\text{Al})$ and $n = 0, 1, 2, 3, 4$. When one or two of the oxygen atoms are part of
a hydroxyl group, Q^3, respectively Q^2 peaks correspond to these species. Replacement of a silicon atom with an aluminum atom results in a shift of about 5 ppm to lower field as illustrated in Fig. 2.3.

![Fig. 2.3. ²⁹Si MAS NMR spectrum of zeolite NH₄Y.](image)

The Si/Al ratio can be determined by using the relative intensities of the Si(nAl) peaks:

\[
\frac{Si}{Al} = \frac{\sum_{n=0}^{4} I_{Si(nAl)}}{\sum_{n=0}^{4} 0.25n \cdot I_{Si(nAl)}}
\]  

(2.9)

MAS NMR spectra were measured at 104.287 MHz for ²⁷Al and at 79.49 MHz for ²⁹Si on a Bruker Avance AMX-400 spectrometer at a spinning rate of 12 kHz using a 4 mm probe. Prior to the MAS NMR measurements, the samples were hydrated by placing them in an atmosphere saturated with moisture from a solution of 1 M NH₄NO₃. In ²⁷Al MAS NMR, a single pulse length of π/6 and a relaxation delay of 1 s
Chapter 2

were used. In $^{29}$Si MAS NMR, a high-power decoupling pulse sequence (HPDEC) and a relaxation delay of 6 s were used. The $^{27}$Al chemical shifts were referenced to (NH$_4$)Al(SO$_4$)$_2$$\cdot$12H$_2$O and the $^{29}$Si chemical shifts to octakis-(trimethyl siloxy)silsesquioxane.

2.3.5. Infra-red spectroscopy

Infra-red spectroscopy is suitable for examining the zeolitic acid sites [17-19]. Both the direct characterization of the H-zeolite form, especially the O-H stretching frequencies, and the spectroscopic changes observed upon adsorption of molecules give useful information. Infra-red spectra are observed through the absorption of infra-red radiation by a molecule, caused by transitions between vibrational energy levels. To adsorb the radiation, a molecular must undergo a net change in dipole moment as a consequence of its vibration or rotation. Therefore, molecular asymmetry is required for excitation by infra-red radiation. The most useful frequencies of the radiation for zeolites characterization are between 4000 and 500 cm$^{-1}$ (wavenumbers).

For most types of zeolites the bridging hydroxyl groups, which correspond to the Brønsted acid sites, are observed between 3650 and 3550 cm$^{-1}$. In additional, terminal silanol OH groups are present in the range of 3745-3740 cm$^{-1}$ and Al-OH species in the range of 3680-3660 cm$^{-1}$. The frequency of the OH stretching vibration of the Brønsted acid site is strongly affected by the type of coordination of the oxygen, the local structure of the hydroxyl group, the type of zeolite lattice, and the Si/Al ratio [17]. The infra-red spectrum of dehydrated NH$_4$Y (Fig. 2.4) exhibits bands at 3640 and 3545 cm$^{-1}$ assigned to bridging OH's in the super cages (HF, high frequency), and bridging OH's in the sodalite cages (LF, low frequency), respectively. To compare the infra-red spectra from different samples, the spectra must be normalized by the amount of material irradiated by the infra-red beam, which is proportional to the sample thickness. For samples of identical structure, the overtone vibrations between 2000-1700 cm$^{-1}$ can be used.
For infra-red measurements, self-supporting pellets (2-4 mg) were positioned in a laboratory-constructed heated cell equipped with KBr windows and connected to a metal vacuum line capable of attaining a residual vacuum of \(< 10^{-3} \text{ Pa}\). The spectra were recorded at room temperature with 4 cm\(^{-1}\) resolution on a Galaxy 6020 FTIR spectrophotometer equipped with an MCT detector. Prior to measurement, the samples were activated for 1 h in vacuum at 773 K with a heating ramp of 2 K/min.

The infra-red spectroscopy after pyridine adsorption was performed in a flow cell on a Bio-Rad Excalibur FTS 3000 Infra-red spectrometer. After activation at 773 K, the samples were treated for 10 min at 393 K with a flow of 20 ml/min He which was saturated at 273 K with pyridine, which has a vapor pressure of 550 Pa. Infra-red spectra were recorded after flowing He for 1 h at 423 K. The number of Brønsted acid sites was determined by using the integrated molar extinction coefficients for the infra-red absorption band of pyridinium of 1.67 cm/"mol, mode 19b at 1545 cm\(^{-1}\) [20].

2.3.6. Temperature-programmed reaction of amines and thermogravimetric analysis (TPD-TGA)

TPD-TGA of amines is a technique for measuring the concentration of Brønsted acid sites in solid acids [21]. The method is based on the fact that alkylammonium ions, formed when alkyl amines are protonated by Brønsted sites, decompose to ammonia and olefins in a well-defined temperature range via a reaction similar to the Hofmann-elimination reaction. The adsorption and reaction can be described as follows:
It is assumed that the amine molecule is interacting with a single Brønsted acid site, so that the number of decomposed molecules, measured through the weight-loss, relates to the number of acid sites.

The technique can be applied to amorphous and crystalline solid acids. However, these materials have different structures. Amines of various sizes probe acid sites with different local structure. Therefore, both n-propylamine, which contains a primary alkyl group, and iso-propyl amine, with a secondary alkyl group, are employed in this measurement.

In the laboratory-constructed equipment, approximately 20-40 mg sample were activated at \( P < 10^{-4} \) Pa overnight by heating to 723 K with a ramp of 2 K/min. The sample was then exposed to propyl amine at 473 K for 2 h and cooled to room temperature. The sample was evacuated for about 2 h to remove the physically adsorbed propylamine. The decomposition experiment was performed with a heating rate of 10 K/min and a flow of 20 mL/min \( \text{Ar} \) in a Mettler Toledo TGA/SDTA851e instrument for thermogravimetric analysis (TGA). The amount of decomposed propylamine was obtained from the mass changes in the TGA curves between 573 and 650 K.

2.3.7. Transmission electron microscopy (TEM)

TEM is used to characterize the particle shape and size of amorphous silica-alumina samples described in Chapter 4. The measurements were performed on a Philips CM30 electron microscope using a super twin lens with a point resolution of 0.2 nm, operated at 300 kV. The samples were suspended in ethanol and deposited on a holey carbon foil prior to measurements.

2.3.8. Heat of adsorption of propane

The heat of adsorption was measured in a modified Setaram TG-DSC 111 instrument with a baratron pressure transducer. The sample was pressed into pellets and 10 to 15 mg of the sample was put into a quartz crucible. The sample was activated for 1 h at \( P < 10^{-4} \) Pa and at 823 K with a heating ramp of 10 K/min. After activation, alkanes were added in pulses at 323 and 343 K in two separate experiments. The system was allowed to equilibrate, which was confirmed by observation of the
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sample weight, heat flow, and pressure. The system was considered to be in equilibrium when stable for several minutes. The differential heats of adsorption were measured using the calorimeter. The heat of adsorption of propane on amorphous silica-alumina was determined using the same adsorption procedure. The heat of adsorption was determined by comparison of the isotherms at different temperatures, using the van’t Hoff equation (2.11):

$$\left( \frac{\Delta \ln p}{\frac{1}{T}} \right)_{\theta=\text{const.}} = -\frac{\Delta H_{\text{ads.}}}{R}$$ (2.11)

Here, $\Delta \ln P$ is the difference of natural logarithm of sorbate pressures at different temperatures, $\Delta H_{\text{ads.}}$ is the heat of adsorption, and $R$ is the gas constant.

2.4 Catalysts

2.4.1 Zeolites

ZSM5 was prepared by hydrothermal synthesis [22]. As-made ZSM-5 was calcined in air at 823 K for 5 h to remove the structure-directing agent and then converted to the NH$_4$-form by triple ion-exchange with 1 M NH$_4$NO$_3$ solutions at 353 K. Three Beta samples with Si/Al ratios of 10.5, 27, and 110 were described in an earlier study [23]. Template-free Beta samples were prepared by the stepwise calcination process [24]. In the first step, the as-synthesised Beta zeolite was calcined at 723 K in 10% NH$_3$ in He to remove the organic template. An ion exchange with a solution of NaCl was done to stabilize the framework structure, followed by washing and drying at 373 K. In the second step, calcination was performed in oxygen (O$_2$) at 723 K for easy oxidation of the charred template species, followed by ion exchange with NH$_4$Cl. MOR samples with Si/Al = 4.9, 9.9, and 16.7 in the Na form were obtained from Tosoh and a NaY with Si/Al = 2.6 was obtained from UOP, Molecular Sieve Division. All these samples were converted to the NH$_4$-form with procedures identical to the NH$_4$ZSM5 preparation. The residual Na content of each material determined by atomic absorption spectroscopy (AAS) was about 0.05 wt%.

Two high-silica zeolites Y were synthesized by the hydrothermal method with 15-crown-5 ether [25-28]. Y(3.6), was prepared using [25,27] 1.49 g sodium hydroxide (Aldrich, p.a., 99.998%), 0.57 g sodium fluoride (Sigma, p.a., 99%), and 3.03 g sodium aluminate (Riedel-de Haën, technical grade, 54 wt% Al$_2$O$_3$, 41 wt% Na$_2$O),
which were dissolved in 27 mL double deionized water. After stirring for 5 min, 3.53 g 15-crown-5 (Aldrich, 98%) and 24.11 g silica sol (Ludox AS-40, 40 wt% SiO₂) were added. After stirring continuously for 2 h, the mixture was transferred into an autoclave reactor to crystallize at 385 K for 7 days. A second sample (Y(3.3)) was made based on the procedure without adding sodium fluoride [26]. 1.04 g sodium hydroxide (Aldrich, p.a., 99.998%) was dissolved in 23 mL double deionized water and under stirring, 3.02 g sodium aluminate (Riedel-de Haën, technical grade, 54 wt% Al₂O₃, 41 wt% Na₂O), 2.42 g 15-crown-5 (Aldrich, 98%) and 23.89 g silica sol (Ludox AS-40, 40 wt% SiO₂) were added. The resulting gel was continuously stirred for 24 h. The crystallization was carried out in an autoclave reactor at 385 K for 7 days. Both as-synthesized samples were calcined in air at 823 K for 8 h to remove the template and then converted to the NH₄-form by triple ion-exchange with 1 M NH₄NO₃ solutions at 353 K. The residual Na content determined by AAS was less than 0.05 wt%. Part of both materials were calcined for 6 h at 823 K with a heating rate of 2 K/min and exposed to moisture after cooling to room temperature to form HY(3.6) and HY(3.3).

A steamed commercial sample, HUSY (LZY-84), was used. Moreover, two treatments were applied on this sample. One is the adsorption of ammonia that converts part of the octahedrally-coordinated aluminum of HUSY to tetrahedrally-coordinated aluminum [29]. A flow of 10% NH₃ in He was adsorbed on HUSY at 423 K and the sample was cooled to room temperature in this flow to form H(NH₃)USY. The other treatment was the ethylenediaminetetraacetic acid (EDTA) treatment that further dealuminated the zeolite [30]. This sample, HUSY-NaEDTA, was obtained by refluxing with 0.1 M Na₂H₂-EDTA at 335 K for 24 h and then ion-exchanging with 1 M NH₄NO₃ at 353 K for 24 h [31].

2.4.2 Amorphous silica-alumina (ASA)

Three ASA samples were obtained from Shell with Si/Al ratios of 15, 7, and 3. All the samples were exchanged to their NH₄⁺ form. The sodium content of the samples was 0.01 wt%.

References


Chapter 2


Chapter 3

Catalytic Activity of Brønsted Acid Sites in Zeolites: Intrinsic Activity, Rate-Limiting Step, and Influence of the Local Structure of the Acid Sites

Abstract

The catalytic activity of Brønsted acid sites in zeolites was studied by the monomolecular conversion of propane on zeolites with different framework topologies and Si/Al ratios. The rates and apparent activation energies of cracking and dehydrogenation were determined. The activity of the Brønsted acid sites depends on the rate-limiting step of the reaction. In the cracking reaction, the protonation of the alkane is the rate-limiting step, and the heat of reactant adsorption dominates the differences in the observed activity. The similar intrinsic activities over the different zeolites show that the ability of zeolitic Brønsted acid sites to transfer a proton to an alkane does not vary much, which suggests that the acid sites that participate in the reaction have a very similar strength. In the dehydrogenation reaction, the rate-limiting step is the desorption of the alkoxide species. The rate is determined by the stability of the alkoxide species, which is influenced by the local geometric and electronic structure of the Brønsted acid site and is affected by zeolite structure and Si/Al ratio. Implications of these conclusions are related to other reactions such as catalytic cracking and alkylation.
3.1. Introduction

Acid-catalyzed hydrocarbon transformations, such as cracking, isomerization, and alkylation, are very important reactions in the petrochemical industry. Zeolites are used in several of these reactions, as well as in many reactions in the production of fine chemicals. The zeolitic Brønsted acid sites are the active species in many of these reactions [1,2]. Therefore, the characterization of the Brønsted acid sites in zeolites and the determination of the structure/activity relationship are of fundamental importance in understanding and improving of zeolites for the use as catalysts.

Alkanes can be activated by two mechanisms, which depend on the reaction conditions [3-5]. One is a monomolecular mechanism, and the other a bimolecular mechanism. In the monomolecular mechanism, an alkane is protonated by a Brønsted acid site [6-10] to form a five-coordinated carbon atom. This carbonium ion may undergo cracking to yield an alkane and an alkene regenerating the acid site or it may dehydrogenate to yield H₂ and an alkoxide species [11]. Desorption of the alkoxide yields an olefin and regenerates the acid site, or alkoxides may be reactive in bimolecular reactions. Scheme 3.1 shows the monomolecular reactions of propane. Reaction (1) represents cracking, whose rate-determining step is the protonation [12]; reaction (2) represents dehydrogenation, whose rate-determining step is olefin desorption [13]. Low reactant pressure, low conversion, and high temperature favor the monomolecular reaction and the product distribution is simple.

$$\text{C}_3\text{H}_8 + \text{H}^+ \text{OZ} \xrightarrow{\text{r.l.s.}} [\text{C}_3\text{H}_9]^+ \text{OZ} \rightarrow \text{CH}_4 + \text{C}_2\text{H}_4 + \text{H}^+ \text{OZ} \quad (1)$$

$$\text{C}_3\text{H}_8 + \text{H}^+ \text{OZ} \rightarrow [\text{C}_3\text{H}_9]^+ \text{OZ} \rightarrow \text{H}_2 + \text{C}_3\text{H}_7\text{OZ} \quad (2)$$

Scheme 3.1. Propane monomolecular reaction (r.l.s. = rate limiting step).
In the bimolecular mechanism, however, an alkane is activated by a hydride transfer between the alkane and the adsorbed alkoxide species [9,14-21]. This reaction may be followed by β-scission or isomerization [3,4,22]. The alkoxide species can be formed in the monomolecular dehydrogenation reaction or by adsorption of olefins present in the reactant feed or formed early in the reactor. The rate-limiting step in the bimolecular mechanism is the hydride transfer after the initial formation of the alkoxide species [11]. High reactant pressure, high conversion, and low temperature favor the reactions in the bimolecular mechanism and because of the di- and oligomerization, isomerization, and β-scission reactions, the product distribution is complicated.

The monomolecular conversion of small alkanes is a good reaction to characterize zeolites and to establish the relationship between their structure and catalytic activity. The reactants are physisorbed in the pores of the zeolites and at high temperature activated through proton transfer from the Brønsted acid sites. Because the rate-limiting step of monomolecular cracking is the protonation of the alkane, this reaction is an acid-base reaction between the zeolite and the alkane. Therefore, its intrinsic rate is a measure of zeolitic acidity. The intrinsic activation energy \( E_{\text{int}} \) equals the apparent activation energy \( E_{\text{app}} \) minus the heat of reactant adsorption \( \Delta H_{\text{ads}} \) [23] as given in eq. 3.1:

\[
E_{\text{int}} = E_{\text{app}} - \Delta H_{\text{ads}}
\]  

In contrast, the rate-limiting step in the dehydrogenation reaction is the desorption of the olefins [13]. The stability of the alkoxide species depends strongly on the local neighborhood of the Brønsted acid site [24], and the intrinsic reaction parameters of the dehydrogenation reflect the stability of the alkoxide species.

In several studies, the monomolecular cracking of hexane was used to characterize the Brønsted acid sites of different zeolites [25-27]. The results show that different zeolites have different activities. These differences were interpreted as being due to the different heat of reactant adsorption \( \Delta H_{\text{ads}} \) [25,27] and to the different acid strengths of the Brønsted acid sites in various zeolites [26]. Here, we report the intrinsic activity of the Brønsted acid sites and the influence of the local structure of the Brønsted acid sites by determining the cracking and dehydrogenation pathways of the conversion of propane. The influence of zeolite type and framework Si/Al ratio were studied.
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3.2. Experimental

Four different structure types (MFI, MOR, Beta, and FAU) of zeolites were used. Table 3.1 lists the samples and their physical properties. The sample preparation, characterization, and catalytic conditions were described in Chapter 2.

Table 3.1. Properties of zeolite samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al ratio&lt;sup&gt;a&lt;/sup&gt;</th>
<th>BET surface area (m&lt;sup&gt;2&lt;/sup&gt;/g)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Micropore volume (cm&lt;sup&gt;3&lt;/sup&gt;/g)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Bronsted acid sites (mmol/g)&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM5</td>
<td>39</td>
<td>370</td>
<td>0.13</td>
<td>0.42</td>
</tr>
<tr>
<td>4.9MOR</td>
<td>4.9</td>
<td>380</td>
<td>0.15</td>
<td>1.39</td>
</tr>
<tr>
<td>9.9MOR</td>
<td>9.9</td>
<td>510</td>
<td>0.20</td>
<td>0.90</td>
</tr>
<tr>
<td>16.7MOR</td>
<td>16.7</td>
<td>490</td>
<td>0.19</td>
<td>0.67</td>
</tr>
<tr>
<td>10.5Beta</td>
<td>10.5</td>
<td>490</td>
<td>0.17</td>
<td>0.90</td>
</tr>
<tr>
<td>27Beta</td>
<td>27</td>
<td>490</td>
<td>0.18</td>
<td>0.51</td>
</tr>
<tr>
<td>110Beta</td>
<td>110</td>
<td>370</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>Y</td>
<td>2.6</td>
<td>810</td>
<td>0.32</td>
<td>1.95</td>
</tr>
</tbody>
</table>

<sup>a</sup> determined by AAS  
<sup>b</sup> determined by N<sub>2</sub> physisorption  
<sup>c</sup> determined by the decomposition of i-propylamine

3.3. Results

Fig. 3.1 shows the <sup>27</sup>Al MAS NMR spectra of the zeolite samples. Only a single peak at around 60 ppm was observed for all the samples. This peak is assigned to tetrahedrally-coordinated framework Al. The position of the peak of the samples differs because of the different averaged Al-O-Si angles in the structures. None of the samples shows an octahedral coordination that is typical of non-framework Al.

The Arrhenius plots of the monomolecular conversion of propane over the MOR and Beta samples with different Si/Al ratios are shown in Figs. 2 and 3, respectively. For both the MOR and Beta zeolites, the Arrhenius plots of the cracking reaction are parallel, but the slopes of the dehydrogenation reaction increased with Si/Al ratio. Table 3.2 lists the apparent activation energies, the reaction rates, and the selectivities of the two reaction pathways at 823 K of all samples. The turnover frequencies based on the number of Bronsted acid site determined by i-propylamine decomposition (Table 3.1) and the rates per gram of cracking
of propane are given in Table 3.2. The activities per Brønsted acid site decreased in the order ZSM5 ≥ MOR > Beta > FAU. The Si/Al ratios of MOR and Beta affected the activities per Brønsted acid site at most by a factor of two, which is smaller than the difference in zeolite structure types. The different rates per Brønsted acid site are reflected in variations in the activation energies, which decreased in the opposite order: FAU > Beta > MOR ≥ ZSM5.

The rates of dehydrogenation per Brønsted acid site are also divided in four groups and decrease in the order ZSM5 ≥ MOR > Beta > FAU. The Si/Al ratio did not affect the rates more than a factor of two. Unlike cracking, the activation energies of dehydrogenation of propane showed no trend with the zeolite pore size. The activation energies significantly increased with Si/Al ratio for zeolites MOR and Beta. The selectivity to cracking decreased with increasing Si/Al ratio: 81, 71, and 67% for the MOR samples and 67, 58, and 56% for the Beta samples.
Fig 3.2. Arrhenius plots of monomolecular conversion of propane over MOR samples: (a) cracking and (b) dehydrogenation: 4.9MOR(■), 9.9MOR(▲), and 16.7MOR(●).

Fig 3.3. Arrhenius plots of monomolecular conversion of propane over Beta samples: (a) cracking and (b) dehydrogenation: 10.5Beta(■), 27Beta(▲), and 110Beta(●).
**Catalytic Activity of Brønsted Acid Sites in Zeolites**

Table 3.2. Reaction rates and apparent activation energies of monomolecular conversion of propane over zeolite samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate cracking $^a$ ($10^{-6}$ mol/g-s-bar)</th>
<th>Rate cracking $^b$ ($10^{-6}$ mol/g-s-bar)</th>
<th>Rate dehydr. $^a$ ($10^{-6}$ mol/g-s-bar)</th>
<th>Rate dehydr. $^b$ ($10^{-6}$ mol/g-s-bar)</th>
<th>$E_{app}^{cr}$ (kJ/mol)</th>
<th>$E_{app}^{de}$ (kJ/mol)</th>
<th>100$^*_{cr}$(cr+de)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM5</td>
<td>9.9</td>
<td>23.6</td>
<td>5.0</td>
<td>11.9</td>
<td>146</td>
<td>157</td>
<td>66</td>
</tr>
<tr>
<td>4.9MOR</td>
<td>32</td>
<td>23.0</td>
<td>7.6</td>
<td>5.5</td>
<td>145</td>
<td>123</td>
<td>81</td>
</tr>
<tr>
<td>9.9MOR</td>
<td>20</td>
<td>22.2</td>
<td>8.3</td>
<td>9.2</td>
<td>145</td>
<td>134</td>
<td>71</td>
</tr>
<tr>
<td>16.7MOR</td>
<td>6.9</td>
<td>10.3</td>
<td>3.4</td>
<td>5.1</td>
<td>149</td>
<td>172</td>
<td>67</td>
</tr>
<tr>
<td>10.5Beta</td>
<td>6.2</td>
<td>6.9</td>
<td>3.0</td>
<td>3.3</td>
<td>157</td>
<td>161</td>
<td>67</td>
</tr>
<tr>
<td>27Beta</td>
<td>3.2</td>
<td>6.3</td>
<td>2.3</td>
<td>4.5</td>
<td>159</td>
<td>169</td>
<td>58</td>
</tr>
<tr>
<td>110Beta</td>
<td>0.5</td>
<td>3.6</td>
<td>0.4</td>
<td>2.8</td>
<td>156</td>
<td>178</td>
<td>56</td>
</tr>
<tr>
<td>Y</td>
<td>0.29</td>
<td>0.15</td>
<td>0.24</td>
<td>0.12</td>
<td>165</td>
<td>173</td>
<td>55</td>
</tr>
</tbody>
</table>

$^a$rate at 823 K per gram (mol/g.s.bar)

$^b$rate at 823 K per Bronsted acid site determined by the decomposition of i-propylamine (mol/mmol.s.bar)

$^c$selectivity to cracking in percentage at 823 K

3.4. Discussion

3.4.1. Intrinsic activity per site: cracking

In protolytic cracking, alkane protonation is the rate-limiting step [13]. Because it involves the transfer of a proton to a weak base, the intrinsic activity of cracking is a way to measure the acid strength of the Brønsted acid sites [1,28-31]. All zeolite samples used in this study have only tetrahedrally-coordinated aluminum as shown by $^{27}$Al MAS NMR (Fig.3.1), which is the framework Al that generates the Brønsted acid site. Thus, the catalytic results are not influenced by extra-framework Al or Lewis acid sites. However, not all tetrahedral Al contribute to active Brønsted acid sites [32,33]. To determine the TOF, we determined the number of active sites via decomposition of i-propylamine assuming that those sites participate in the reaction, which may be an approximation.

Different structure types of zeolites have distinctly different propane activities per gram in monomolecular cracking. However, the activities per Brønsted acid site and the activation energies systematically vary with pore size: large pore zeolites show lower activities per Brønsted acid site and higher activation energies (Table 3.2), in agreement with previous reports [25,27,31]. The Si/Al ratios in MOR and Beta have no effect on activation energy. Alkanes are physisorbed in the pores of a zeolite and the dominant interactions are the dispersion forces (the van der Waals interaction). The strength of the adsorption depends on
the fit of alkane within the pore: the better the fit, the higher the heat of adsorption will be \([34,35]\). The activation of the alkane occurs through protonation at high temperature. Using Tempkin's equation (eq. 3.1), the intrinsic activation energies were calculated and are reported in Table 3.3.

Table 3.3. Intrinsic activity of propane monomolecular cracking over zeolite samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pores</th>
<th>(\Delta H_{ads}^{c,tls}) (kJ/mol)</th>
<th>(E_{app}^{cr}) (kJ/mol)</th>
<th>(E_{int}) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFI</td>
<td>10 MR</td>
<td>5.1 x 5.5 Å</td>
<td>-46</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.3 x 5.6 Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MOR</td>
<td>8 MR</td>
<td>2.6 x 5.7 Å</td>
<td>-41</td>
<td>145-149</td>
</tr>
<tr>
<td></td>
<td>12 MR</td>
<td>6.5 x 7.0 Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beta</td>
<td>12 MR</td>
<td>6.6 x 6.7 Å</td>
<td>-42</td>
<td>157-159</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.6 x 5.6 Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FAU</td>
<td>12 MR</td>
<td>7.4 x 7.4 Å</td>
<td>-31</td>
<td>165</td>
</tr>
</tbody>
</table>

The values are very close to those reported by Narbeshuber et al. for cracking of alkanes of various lengths on ZSM5 \([12]\). The intrinsic activation energies vary less than the apparent ones, and the heat of adsorption is the major term in affecting the apparent activation energies. Previously, a compensation relation between the heat and entropy of adsorption over different zeolites was found \([36]\). In combination with the compensation relation for cracking \([27]\), it was suggested that the acid strength of the catalysts is much less important than the adsorption term or that the acid strength of the materials is more similar than assumed \([36]\). Our findings show that Si/Al ratios higher than Si/Al = 4.9 for MOR and Si/Al = 10.5 for Beta do not affect the acid strength of the Brønsted acid sites. We conclude that the differences in the heat of adsorption and, therefore, the size and shape of the pores are the dominant factors in determining the cracking activity of the Brønsted acid sites \([25,27,36]\). The better the fit between pore and reactant, the higher the observed rate per Brønsted acid site of the reaction will be.
3.4.2. Structure of active site: dehydrogenation

The apparent activities of dehydrogenation varied with the zeolite structure type (Table 3.2), but no relationship was found with pore size. Increasing the Si/Al ratio of zeolites increased the apparent activation energy. Monomolecular dehydrogenation proceeds via protonation on a C-H bond followed by the release of hydrogen and the formation of alkoxide species that desorb as olefins (Scheme 3.1) [6,17,37]. The rate-limiting step of monomolecular dehydrogenation differs from that of cracking. Theoretical calculations predicted that in the transition state of dehydrogenation a hydrogen molecule and an alkoxide species are being formed [9,10]. Hydrogen is desorbed and an alkoxide species is formed. The structure and, therefore, the stability of this transition state, strongly resembles that of the alkoxide. Biscardi and Iglesia [38] and Yu [39] et al. suggested that the predominant role of extra-framework cations like Zn and Co in Zn/H-ZSM5 and Co/H-ZSM5 was to enhance the recombinative desorption of hydrogen, which increased the rate of dehydrogenation compared to H-ZSM5. Kazansky et al. [40] showed experimentally that the role of Zn cations on Zn-ZSM5 is the dissociative adsorption of the hydrocarbon, forming an alkyl group and a Brønsted acid site, which differs from the theoretically predicted mechanism over H-ZSM5. Narbeshuber et al. [13] showed a dependence of the hydrocarbon chain length and amount of branching on the rates and apparent activation energies in dehydrogenation of hydrocarbons over H-ZSM5. Thus, in H-ZSM5, hydrocarbon species are involved in the rate-limiting step, in contrast to Zn/H-ZSM5 and Co/H-ZSM5 where the rate-limiting step may involve the formation of hydrogen. The presence of only a very small isotope effect in a steady state isotope transient (n-H10-butane to n-D10-butane) experiment suggested that desorption of the olefin represents the rate-limiting step [13]. Thus, the stability of alkoxide species determines the apparent activity of dehydrogenation and the reaction does not depend on the acid strength of the Brønsted acid sites to the same extent as cracking.

A quantum chemical study on the stability of C3-C5 alkoxide species, reported by Nieminen et al. [24], showed that the chemisorption energies of olefins differ by almost 150 kJ/mol. Moreover, the stability of the alkoxides increases with chain length (-137, -156, and -198 kJ/mol for C3, C4, and C5), which is in good agreement with experimental results by Narbeshuber et al. [13], who reported that the apparent activation energy of monomolecular dehydrogenation increases with carbon number, 95 (C3), 115 (C4), and 150 (C5) kJ/mol over
Chapter 3

HZSM5. Theory also predicted that a hindered local geometry around the active site of the zeolite has a destabilizing effect on the bulkier alkoxide species. Other theoretical calculations indicated that the alkoxide species interacts covalently with zeolites and is further stabilized by van der Waals interaction with the zeolite framework and that the nearby framework oxygens of the Brønsted acid sites also play a role in stabilization [41-43]. This means that not only the Brønsted acid sites, but also the region surrounding the sites participates in the reaction. Thus, changes in zeolite structure and properties such as the Si/Al ratio, framework ionicity, and framework flexibility strongly influence the stability of the alkoxide species.

Other reactions that involve alkoxide species may be similarly dependent on the stability of these species. One such reaction is alkylation, in which hydride transfer from an alkane to an alkoxide largely determines the product distribution over the catalyst. Various publications have reported that high rates of hydride transfer and stable alkylation catalysts require a high Brønsted acid site density [44,45]. Sanchez-Castillo et al. [44] showed that the activation energy is lower for zeolites with higher Brønsted acid site density, similar to our observation for the dehydrogenation reaction, which may suggest that this reaction also depends on the stability of alkoxide species involved in the reaction. In another study [45], it was found that the rate of hydride transfer is slowed down by a higher Si/Al ratio of zeolite Beta compared to Y and that a high Brønsted acid site density causes high hydride transfer and favors a long catalyst life. This is in line with catalytic cracking experiments, in which lower framework Si/Al ratios gave higher hydride transfer rates [46].

3.5. Conclusion

Different reactions depend differently on the strength and local structure of the Brønsted acid sites in zeolites. The activity of Brønsted acid sites in zeolites is strongly affected by the rate-limiting step of the reaction. The monomolecular cracking of alkanes proceeds via protonation of the alkane as the rate-limiting step. This reaction is affected by the size and shape of the pores that affect the heat of adsorption; the intrinsic reaction parameters are much more similar than the apparent values, which are not corrected for the heat of adsorption. The rate-limiting step in dehydrogenation of alkanes is desorption of the alkoxide species and the rate is determined by the stability of the alkoxide species. This stability
Catalytic Activity of Brønsted Acid Sites in Zeolites

depends on the local structure of the Brønsted acid site and the Si/Al ratio of the zeolite framework.

References

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    (1989) 2052.


Chapter 4

Strong Brønsted Acidity in Amorphous Silica-Aluminas

Abstract

Monomolecular cracking of propane was used to investigate the activity of the Brønsted acid sites in amorphous silica-aluminas with three different Si/Al ratios. The reaction rates increased with increasing aluminum content, but the apparent activation energies were identical. Compared to zeolite ZSM5, the ASA catalysts showed much lower activity both per weight and per total aluminum content. However, after correction for the heat of adsorption, the intrinsic activation energies of ASA and ZMS5 were similar. This indicates that the ability of the active Brønsted acid sites to protonate propane is similar for amorphous and crystalline structures and that the much lower activity of the ASAs is caused by a lower heat of adsorption and by a small number of active sites. A small number of Brønsted acid sites was detected using pyridine infra-red and a broad band around 3600 cm$^{-1}$ was observed in the infra-red region of the hydroxyl stretch vibrations.
4.1. Introduction

Amorphous silica-aluminas (ASAs) and zeolites are widely applied as solid acid catalysts in cracking, dehydrogenation, isomerization, and alkylation reactions, which are very important in the petrochemical and refining industry \[1,2\]. These catalysts consist of corner-sharing tetrahedral \( \text{AlO}_4^- \) and \( \text{SiO}_4 \) units that form three-dimensional structures that contain micropores. Charge balance requires the presence of extra-framework cations. If protons compensate the framework charge, these materials show Brønsted acidity. The framework of zeolites is ordered and crystalline, containing pores and cages with sizes between 4 and 20 Å. ASAs lack long-range order and are XRD amorphous. The catalytic activity of zeolites is generally much higher than that of ASA. It was proposed that the zeolite crystal readjusts the bond structure of the Brønsted acid sites to maintain long-range order and that this produces strong Brønsted acid strength \[3-5\]. This readjustment is much smaller pronounced in amorphous structures so that the acid strength of the amorphous material is thought to be weaker \[3\]. Many methods, such as Hammett titrations, solid-state nuclear magnetic resonance spectroscopy, infra-red spectroscopy, temperature-programmed desorption, microcalorimetry, and reactivity measurements have been used to characterize the acidity of crystalline zeolites and ASAs. Often the lower activity of ASA compared to zeolites was explained by lower acidity \[6-8\]. Other reports suggested that the acid strength of ASA is between that of zeolite Y and Mordenite \[9\] or equal to zeolite Y \[10,11\], equal to Beta \[12\], or to dealuminated zeolite Y \[12\]. In addition, a comparison between ASA and zeolites showed that the low catalytic activity of ASA is due to its lower number of Brønsted acid sites and not because of a special property of zeolites \[13\].

For zeolites, it has been observed that the intrinsic activity of the Brønsted acid sites in monomolecular cracking is independent of the zeolite structure and that the sorption of the reactant dominates the catalytic activity \[14-20\]. As the rate-limiting step in monomolecular cracking is the alkane protonation \[21\], the intrinsic activity should be conceptually related to the concentration and strength of the Brønsted acid sites in the catalysts. In this study, we therefore explore the concentration and strength of Brønsted acid sites in ASA compared to those of ZSM5 by means of the monomolecular cracking of propane together with a variety of physicochemical methods.
4.2. Experimental

The sample preparation, characterization, and catalytic conditions were described in Chapter 2. The sample names are given as ASA(M), where M represents the Si/Al ratio.

4.3. Results

The $N_2$ physisorption isotherms of the ASAs are shown in Fig. 4.1. That of ASA(15) was a typical Type IV isotherm [22]. This indicates the presence of mesopores. Increasing the aluminum content changed the isotherm to a Type I isotherm, with a smaller mesopore volume. The BET surface areas and pore volumes are compiled in Table 4.1. The surface area decreased from 590 to 310 m$^2$/g and the mesopore volume from 0.60 to 0.29 cm$^3$/g with decreasing Si/Al ratio. A contribution of micropores to the total pore volume was not detected.

![N$\text{\textsubscript{2}}$ isotherm of ASAs: ASA(15)(■), ASA(7)(●), and ASA(3)(▲).](image)

The TEM photos in Fig. 4.2 showed that the three ASAs are amorphous and consist of agglomerated worm-like particles. The estimated particle sizes for the three samples increased with increasing Si/Al ratio from 5, 7, to 10 nm, which correlated with the BET surface areas.
Table 4.1. The properties of ASAs

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)ᵃ</th>
<th>Micro pore volume (cm³/g)ᵇ</th>
<th>Meso pore volume (cm³/g)ᵇ</th>
<th>Al (mmol/g)ᵇ</th>
<th>Brønsted acid sites (mmol/g)ᶜ</th>
<th>Lewis acid sites (mmol/g)ᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASA(15)</td>
<td>590</td>
<td>0</td>
<td>0.60</td>
<td>1.0</td>
<td>0.016</td>
<td>0.106</td>
</tr>
<tr>
<td>ASA(7)</td>
<td>460</td>
<td>0</td>
<td>0.49</td>
<td>2.1</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>ASA(3)</td>
<td>310</td>
<td>0</td>
<td>0.29</td>
<td>4.2</td>
<td>0.011</td>
<td>0.075</td>
</tr>
</tbody>
</table>

ᵃ determined by N₂ physisorption
ᵇ determined by AAS
c pyridine infra-red after desorption at 423 K

Fig. 4.2. TEM pictures of ASAs.

The $^{27}$Al MAS NMR spectrum (Fig. 4.3) showed a single peak at around 54 ppm for ASA(15), which is assigned to tetrahedrally-coordinated aluminum. The width of the tetrahedral aluminum peak was about 15 ppm, which is larger than that observed in spectra of highly crystalline NH₄⁺-zeolites that are measured at the same magnetic field. This indicates a large spread of Al-O-Si angles in the ASAs. ASA(7) and ASA(3) also showed the broad tetrahedral aluminum peak and a small peak at around 0 ppm, which is assigned to octahedrally-coordinated aluminum. The intensity of the octahedral aluminum peak was larger in ASA(3). The $^{29}$Si MAS NMR spectra are presented in Fig. 4.4. With increasing aluminum content, the intensity of the peak at around −120 ppm decreased and that at around
-105 ppm increased. The former peak corresponds to silicon atoms with no or one aluminum next neighbor (Q^4(0)Al and Q^4(1)Al), the latter peak to silicon with two or three aluminum neighbors (Q^4(2)Al and Q^4(3)Al). In contrast to ^29Si MAS NMR spectra of zeolites, the peaks are very broad and overlap strongly. Therefore, no attempt was made to determine the Si/Al ratios from these spectra, although the spectra indicated that the framework aluminum content increased in the order ASA(15) < ASA(7) < ASA(3).

![Fig. 4.3. ^27Al MAS NMR of ASAs.](image)

The infra-red spectra of the dehydrated ASAs are shown in Fig. 4.5. Ammonia had been completely removed and the sample was in the protonic form. In the spectra recorded at room temperature, there was a high intensity peak at ca. 3743 cm\(^{-1}\) assigned to the silanol OH vibration; its intensity increased with increasing Si/Al ratio. At approximately 3600 cm\(^{-1}\), a broad peak was observed in all spectra, which increased in intensity with decreasing aluminum content. In parallel to the assignment of the infra-red spectra of zeolites, this peak is assigned to Brønsted acidic OH groups.

The Arrhenius plots of the monomolecular cracking of propane were all parallel (Fig. 4.6). Table 4.2 compiles the reaction rates at 823 K, the apparent activation energies of the cracking reaction, and the selectivities to cracking. The rates per gram increased in the order ASA(15) ≈ ASA(3) < ASA(7). The apparent activation energies were independent of the Si/Al ratio: 182 to 186 kJ/mol. The selectivity to cracking varied from 24 to 36%.
Fig. 4.4. $^{29}$Si MAS NMR of ASAs.

Fig. 4.5. FT-Infra-red spectra of ASAs.
Fig 4.6. Arrhenius plots of propane monomolecular cracking over ASAs: ASA(15)(●), ASA(7)(▲), and ASA(3)(●).

Table 4.2. Reaction rates and apparent activation energies of propane monomolecular conversion over ASAs and ZSM5

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate-cracking a</th>
<th>Rate-cracking b</th>
<th>E_{app} (kJ/mol)</th>
<th>100*cr/(cr+de)d</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASA(15)</td>
<td>0.040*10^{-6}</td>
<td>3.8 *10^3</td>
<td>182</td>
<td>36</td>
</tr>
<tr>
<td>ASA(7)</td>
<td>0.062</td>
<td>2.9</td>
<td>186</td>
<td>24</td>
</tr>
<tr>
<td>ASA(3)</td>
<td>0.047</td>
<td>1.2</td>
<td>183</td>
<td>28</td>
</tr>
<tr>
<td>ZSM5</td>
<td>9.9</td>
<td>2000</td>
<td>146</td>
<td>66</td>
</tr>
</tbody>
</table>

a rate at 823 K per gram  
b rate at 823 K per total Al  
d selectivity to cracking in percentage at 823 K  
e from ref. [20]

Fig. 4.7 shows the sorption isotherms of propane on ASA(15) at 343 and 323 K and the differential heat of propane adsorption as a function of the propane uptake. The amount of propane adsorbed per gram of ASA was much lower than typically adsorbed on zeolitic samples, which prevented an accurate determination of the calorimetric signal. The heats of propane adsorption as determined using equation (2.11) increased linearly with the propane uptake, which indicates that there are sorbate-sorbate interactions. Extrapolation to an uptake...
of zero resulted in an initial heat of adsorption of propane of about 11 kJ/mol. This compares to 46 kJ/mol on the ten-membered ring zeolite ZSM5 [23].

![Graph](image)

Fig. 4.7. Sorption isotherms of propane on ASA(15) at two temperatures; (a) and the differential heat of propane adsorption as a function of the propane coverage on ASA(15) (b).

The acid sites measured by the infra-red of adsorbed pyridine of the ASAs are shown in Table 4.1. At 423 K, 0.016 mmol/g Brønsted acid sites and 0.106 mmol/g Lewis acid sites were detected in ASA(15). 0.040 mmol/g of Lewis acid sites were retained after pyridine desorption at 723 K; all pyridine had desorbed of the Brønsted acid sites. For ASA(3), at 423 K the concentration of the Brønsted acid sites was 0.011 mmol/g and that of the Lewis acid sites 0.075 mmol/g. At 723 K, 0.013 mmol/g Lewis acid sites and no Brønsted acid sites were observed.

4.4. Discussion

ASA is an amorphous silica-alumina mixed oxide without micropores (Table 4.1), while in the crystalline ZSM5 micropores are dominating. Aluminum may be tetrahedrally coordinated in the framework of both materials giving rise to bridging hydroxyl groups that act as strong Brønsted acid sites. In zeolites the hydroxyl groups give rise to an infra-red around 3600 cm⁻¹, while for dehydrated ASA distinct infra-red bands of Brønsted acidic hydroxyl groups were not observed [10-12,24]. However, by sorption of bases, strong Brønsted acidic hydroxyl groups were probed and the strength of at least a fraction of these sites is comparable to those in zeolites [12,25].
Various models have been advanced to explain this ambiguity in the attribution of strong Brønsted acidic hydroxyl groups in ASAs. Most are based on the observation that silanol groups are heterogeneous depending on their environment [25,26]. It has been suggested that the silanol groups with an aluminum atom as a neighbor show strong Brønsted acidity [12,25]. Crepeau et al. [12] proposed that a paired silanol and a tetrahedral aluminum atom, either on the surface or in the bulk, provide strong Brønsted acidity. Trombetta et al. [25] claimed that strong Brønsted acidity was formed by the interaction of a base molecule with the silanol group neighboring a Lewis site (Al\(^{3+}\)). Only after adsorption of a base, a bond between the hydroxyl of the silanol and the aluminum atom will be formed. However, a recent study [27] reported an infra-red band of Si-(OH)-Al groups at 3600-3610 cm\(^{-1}\) in ASA with a Si/Al = 10 ratio, synthesized via atrane complexes, and that part of these groups are resistant to dehydroxylation and behave like zeolitic hydroxyl groups. In our ASAs a broad hydroxyl band of low intensity was observed at approximately 3600 cm\(^{-1}\). Although in these samples the majority of aluminum atoms is in tetrahedral coordination, a relation between the concentrations of tetrahedral framework aluminum and Brønsted acid sites in the infra-red spectra is not evident like in zeolites. We speculate that this is related to the fact that ASAs do not have open micropores and that hence many of the hydroxyl groups of the Brønsted acid sites may not be located at the external surface and will interact with nearby oxygen atoms in closed inner voids. Pyridine infra-red indicated a small number of Brønsted acid sites on the surface of the ASA. The amount was 1 % or less of the total aluminum concentration.

In agreement with previous reports, our ASAs have a much lower activity than zeolites, [6-9,28,29]. The reaction rate per gram of ASA is about 200 times lower than that of the ZSM5. Normalized to the total aluminum content, the rate of ZSM5 is around 1000 times higher than that of ASA. The apparent cracking activation energies of ASA were 182-186 kJ/mol. Typical values that were measured over zeolites are 145 to 165 kJ/mol. For zeolites, the differences in the catalytic activities for cracking of alkanes are caused by differences in the adsorption of alkanes in the pores. Several papers have shown that the intrinsic activation of alkanes by Brønsted acid sites is independent of the pore structure, if the rate-limiting step of the reaction is the protonation of the alkane [16,18,19]. However, the heat of adsorption of a certain reactant depends on the pore size and shape of the zeolite [19,30,31]. The better the
fit of the reactant in a pore or cage, the larger the heat of adsorption will be. The heat of adsorption for ZSM5 is 46 kJ/mol and 11 kJ/mol for ASA (see Table 4.3) indicating that the interaction of the alkane is much weaker with the external surface of the ASA than with the micropore of a zeolite.

Table 4.3. Intrinsic activity of propane monomolecular cracking over ASA and ZSM5

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\Delta H_{\text{ads}}^{\text{cr}}$ (kJ/mol)</th>
<th>$E_{\text{app}}$ (kJ/mol)</th>
<th>$E_{\text{int}}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASA</td>
<td>-11</td>
<td>182-186</td>
<td>193-197</td>
</tr>
<tr>
<td>ZSM5$^a$</td>
<td>-46</td>
<td>146</td>
<td>192</td>
</tr>
</tbody>
</table>

$^a$ from ref. [20]

As the monomolecular cracking is first order with respect to the partial pressure of propane, true activation energies of 193-197 kJ/mol were obtained for the ASAs by adding the values of the apparent (measured) activation energy and the heat of adsorption of propane (Table 4.3). This is very similar to the intrinsic activation energy of 192 kJ/mol observed for ZSM5. This indicates that the intrinsic activity of the active Bronsted acid sites in ASA is the same as that of zeolites, suggesting that also the nature of the strong Bronsted acid sites is identical in these two materials. The different heats of reactant adsorption dominate the differences in reactivity. The lower heat of adsorption on ASA leads to the smaller propane coverage on the surface and, thus, to a lower activity per active site. This implies that the nature of the active Bronsted acid sites is very similar in both materials and that an active zeolitic-like Bronsted acid site in ASA is responsible for the cracking of propane. Like in zeolites [17], the Si/Al ratio did not influence the intrinsic activity.

Although the intrinsic activity of an active Bronsted acid site in ASA is very similar to that in a zeolite, its activity per gram is much lower. Because of the lower heat of adsorption of ASA, the rate per Bronsted acid site is lower than that in zeolites. The very low number of the Bronsted acid sites detected by pyridine infra-red suggests that only a small percentage of the total aluminum atoms contributes to Bronsted acid sites. We propose that a small number of bridging hydroxyl groups on the surface of ASA have a zeolite-like structure and, hence, zeolite-like intrinsic activity. These sites might correlate to the low-intensity band at round
3600 cm\(^{-1}\) in Fig. 4.5 and the Brønsted acid sites detected by pyridine infra-red. However, unlike generally observed in zeolites, all pyridine had desorbed from the sample after heating to 723 K, which could also be related to a lower adsorption strength on the external surface of the ASA. The absence of micropores causes most of the hydroxyl groups to be inaccessible to the reactant and not all aluminum atoms introduce strong Brønsted acidity. Bridging hydroxyl groups most likely interact with nearby oxygen atoms and are therefore not detected in the infra-red stretching region at around 3600 cm\(^{-1}\) and do not contribute to activity. Our results imply that the activity of ASA could be enhanced by increasing their surface areas by the formation of additional mesopores or, preferentially, micropores.

4.5. Conclusion

ASAs contain a small number of Brønsted acid sites that have intrinsic activities that are similar to those in zeolites. This implies that the acid strength of Brønsted acid sites is independent of the crystallinity of the structure. A small percentage of the aluminum atoms form zeolite-like hydroxyl groups that dominate the activity of ASA in a demanding reaction like monomolecular cracking of alkanes.

References


Chapter 5

Reversibility of Structural Collapse in Zeolite Y: Alkane Cracking and Characterization

Abstract

The structural collapse and the reconstruction of Bronsted acid sites in zeolite Y were investigated by combining propane monomolecular cracking with various structural characterization techniques. Destruction of Bronsted acid sites, together with a loss of catalytic activity, was found after calcination and exposure to moist at room temperature. A loss in long-range structure was observed by XRD. Adsorption of NH₃ before exposure to air prevents the structural collapse of Bronsted acid sites and the loss of the catalytic activity. The collapsed Bronsted acid sites and long-range order recover fully after thermal treatment with NH₃ at moderate temperature; the catalytic activity also recovers fully. Reheating of HY causes further structural collapse. Water molecules are involved in structural destruction, but they are also shown to play a role in structural recovery with ammonia. The structure of zeolites is very sensitive to temperature and presence of moisture. Because various characterization methods are preceded by various pretreatment methods, the zeolite structure probed by these methods is not necessarily the same.
Chapter 5

5.1. Introduction

Because Brønsted acid sites are active in cracking, alkylation, and isomerization reactions [1,2], protonic zeolites are important catalysts in oil refining, in petrochemistry, and in the production of fine chemicals. As new zeolite structures and new applications demonstrate, zeolites are a major topic in scientific and industrial research [3-8]. Because of the susceptibility of the Al-O bonds to hydrolysis, acidic zeolites are unstable to heating in the presence of steam. The stability depends on the structure and the Si/Al ratio. Hydration leads to the removal of aluminum atoms from the framework to create non-framework aluminum and Lewis acid sites, whose structure and location are still being debated [9-11]. Mesopores often form during dealumination [12-18] and XRD reveals a loss of crystallinity [18]. For example, dealumination of zeolite Y in its own moisture or with controlled addition of steam, leads to ultra-stable zeolite Y (USY) [19,20], which is used widely in catalytic reactions, of which fluid catalytic cracking (FCC) is the most important.

Brønsted acid sites are directly related to tetrahedrally-coordinated framework aluminum species, indicated by a peak in the $^{27}\text{Al}$ MAS NMR spectrum of a zeolite at about 60 ppm. In 1967, Kerr [21] reported that H-Y zeolite is unstable in the presence of water at room temperature. Octahedrally-coordinated aluminum forms and can be converted to tetrahedral aluminum by adsorption of basic molecules such as ammonia as well as by the substitution of the protons by sodium and potassium cations [22]. The presence of aluminum species that reversibly convert coordination upon ammonia adsorption was also found in the zeolites ZSM-5 [10], MOR [23], and Y [24]. Similar behavior of amorphous silica-aluminas was observed [23]. In acidic zeolites, the transformation of the coordination of aluminum from tetrahedral to octahedral occurs at room temperature after contact with moisture; octahedral coordination is unstable at temperatures above 400 K [25,26] and reverts back to tetrahedral, although the Brønsted acid site is not restored [23].

The change in aluminum coordination alters the number of Brønsted acid sites in the catalyst, which is directly related to the catalytic activity [27]. It has been reported that the catalytic activity increases with the number of Brønsted acid sites in hexane cracking over zeolite Y [28,29] and ZSM5 [9,30], and in isobutene cracking over zeolite Y [31]. Steam activation is generally applied to activate zeolites [18,31]. Increased catalytic activity is
generally explained by enhanced acidity of the remaining Brønsted acid sites [32,33].
Recently, enhanced participation of catalytically active sites by augmented adsorption of reactants has been proposed [34,35]. An important parameter in zeolite catalysts is the number of Brønsted acid sites that participate in the reaction. For example, it has been proposed that in zeolites Y and Beta not all tetrahedral aluminum atoms contribute to strong Brønsted acid sites and activity [36]. Biaglow et al. showed that strong Brønsted acid sites in zeolite Y that decompose propyl amine molecules are associated with the high-frequency hydroxyl stretch vibration at 3640 cm⁻¹ [37], which are the Brønsted acid sites pointing into the supercage.

In this study, the reversibility of structural changes of acidic zeolite Y is investigated by means of various characterization techniques and the structural changes are related to the catalytic activity of the zeolitic materials. The catalytic activity of the Brønsted acid sites is determined by monomolecular cracking of propane. Cracking of alkanes is a model reaction. When performed in the monomolecular reaction regime, the alkane is protonated by the zeolitic proton and, in the case of propane, cracked into methane and ethylene or dehydrogenated to propene and hydrogen:

\[
C_3H_8 \overset{\text{cracking}}{\rightarrow} CH_4 + C_2H_4 \quad (5.1)
\]

\[
\overset{\text{dehydrogenation}}{\rightarrow} H_2 + C_3H_6 \quad (5.2)
\]

Running the reaction at high temperature and low conversion prevents bimolecular reactions [38,39].

5.2. Experimental

Table 5.1 shows the treatments and nomenclature of the samples. To investigate the effect of moisture on the acid sites, about half of all NH₄Y was calcined for 6 h at 823 K with a heating rate of 1 K/min and, after cooling to room temperature, exposed to air to form HY. To investigate the recovery of the original structure, several treatments were performed on the samples NH₄Y and HY. (NH₃)HY was obtained by calcination of NH₄Y at 823 K and switching to a flow of 10% NH₃ in He during the cooling of the sample from 423 K to room temperature [40,41]. Ammonia was adsorbed from a flow of 10% NH₃ in He on HY at 423 K to yield H(NH₃)Y. HY-723-423NH₃ was formed by heating HY to 723 K
and switching to a flow of 10% NH₃ in He while cooling the sample from 423 K to room temperature. Calcination of HY at 723 K produced sample HY-723-RT. The influence of H₂O and temperature on this treatment was studied by infra-red spectroscopy on HY. Adsorption of ammonia was carried out at room temperature following two procedures: 1) after activation at 723 K for 1h producing HY-723-RTNH₃ and 2) after activation at 723 K and subsequent room-temperature adsorption of 2-2.7 kPa of H₂O giving HY-723-RTH₂O+NH₃.

Table 5.1. Sample treatments and nomenclature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Starting material</th>
<th>Treatment</th>
<th>Exposed to air after treatment?</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄Y</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HY</td>
<td>NH₄Y</td>
<td>calcination at 823 K</td>
<td>yes</td>
</tr>
<tr>
<td>(NH₃)HY</td>
<td>NH₄Y</td>
<td>calcination at 823 K; cooled from 423 K to RT under NH₃</td>
<td>yes</td>
</tr>
<tr>
<td>H(NH₃)Y</td>
<td>HY</td>
<td>exposed to NH₃ at 423 K</td>
<td>yes</td>
</tr>
<tr>
<td>HY-723-423NH₃</td>
<td>HY</td>
<td>heated at 723 K in He; cooled from 423 K to RT under NH₃</td>
<td>yes</td>
</tr>
<tr>
<td>HY-723-RT</td>
<td>HY</td>
<td>heated at 723 K in He</td>
<td>yes</td>
</tr>
<tr>
<td>HY-723-RTNH₃</td>
<td>HY</td>
<td>heated at 723 K in vacuum; RT exposure to NH₃</td>
<td>no</td>
</tr>
<tr>
<td>HY-723-RTH₂O+NH₃</td>
<td>HY</td>
<td>heated at 723 K in vacuum; RT exposed to H₂O and NH₃</td>
<td>no</td>
</tr>
</tbody>
</table>

* Treatments were performed in the infra-red apparatus

The source of NH₄Y, characterization, and catalytic conditions were described in Chapter 2.

5.3. Results

5.3.1. Reaction kinetics

Table 5.2 lists the reaction rates at 823 K, the apparent activation energies, and the selectivity to cracking of all the samples. At 823 K, the reaction rates of cracking of the parent sample NH₄Y and of (NH₃)HY are the same, while the reaction rate of H(NH₃)Y is slightly lower. The rate of HY is much lower than that of NH₄Y, (NH₃)HY, and H(NH₃)Y. The reaction rate of HY-723-423NH₃ is slightly higher than that of HY.
Table 5.2. Reaction rates and activation energies of monomolecular cracking of propane over treated zeolite samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate-Cracking *10^{-6} (mol/g.s.bar)^a</th>
<th>Activitation Energy (kJ/mol)</th>
<th>100*cr/ (cr+de)^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH_4 Y</td>
<td>0.29</td>
<td>165</td>
<td>60</td>
</tr>
<tr>
<td>HY</td>
<td>0.05</td>
<td>208</td>
<td>38</td>
</tr>
<tr>
<td>(NH_3)HY</td>
<td>0.30</td>
<td>168</td>
<td>70</td>
</tr>
<tr>
<td>H(NH_3)Y</td>
<td>0.21</td>
<td>162</td>
<td>57</td>
</tr>
<tr>
<td>HY-723-423NH_3</td>
<td>0.08</td>
<td>269</td>
<td>42</td>
</tr>
</tbody>
</table>

^a at 823 K
^b selectivity to cracking (in %) at 823 K

Fig. 5.1 shows the Arrhenius plots of the monomolecular cracking of propane of the three samples NH_4 Y, H(NH_3)Y, and HY. The apparent activation energies of NH_4 Y and H(NH_3)Y are 165 and 168 kJ/mol (Table 5.2), obtained by averaging three measurements on newly prepared samples. These values are within the uncertainty of the measurement (±5 kJ/mol). The value for (NH_3)HY is very similar: 162 kJ/mol. The apparent activation energies of the samples HY and HY-723-423NH_3 are much higher, 208 and 269 kJ/mol respectively. The cracking selectivity also differs for the samples NH_4 Y, (NH_3)HY, and H(NH_3)Y and the samples HY and HY-723-423NH_3. The former samples have a higher selectivity to cracking and the latter to dehydrogenation.

![Arrhenius plots of monomolecular cracking of propane over NH_4 Y, HY, and H(NH_3)Y.](image-url)

Fig. 5.1. Arrhenius plots of monomolecular cracking of propane over NH_4 Y (■), HY (●), and H(NH_3)Y (▲).
5.3.2. Characterization

The BET surface areas and micropore volumes after degassing at 723 K are presented in Table 5.3 (columns 6 and 7). NH4Y had the highest surface area (810 m²/g). (NH3)HY and H(NH3)Y had identical values (770 m²/g). The micropore volumes were also very similar (0.32, 0.31, and 0.31 cm³/g respectively). HY had a much lower surface area (450 m²/g) and micropore volume (0.18 cm³/g). Degassing HY at 423 K yielded essentially the same values. HY-723-423NH3 had the lowest surface area (230 m²/g) and micropore volume (0.09 cm³/g), less than half the values of the parent sample NH4Y. The number of Brønsted acid sites, determined with infra-red after the adsorption of pyridine and desorption at 423 and 623 K, shows that NH4Y and H(NH3)Y had a high concentration of Brønsted acid sites and that the amount depended on the temperature of pyridine desorption. HY contained less than 20% of the amount of Brønsted acid sites in NH4Y.

Table 5.3. Characteristics of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al</th>
<th>Si/Al</th>
<th>%Td Al</th>
<th>Unit Cell a₀ (Å)</th>
<th>Surface Area (m²/g)</th>
<th>µ-pore Volume (cm³/g)</th>
<th># acid sites e</th>
<th># acid sites f</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH4Y</td>
<td>2.6</td>
<td>2.4</td>
<td>100</td>
<td>24.720 (52)</td>
<td>810</td>
<td>0.32</td>
<td>1.1</td>
<td>0.6</td>
</tr>
<tr>
<td>HY</td>
<td>2.6</td>
<td>2.6</td>
<td>93</td>
<td>24.643 (43)</td>
<td>450</td>
<td>0.18</td>
<td>0.2</td>
<td>0.07</td>
</tr>
<tr>
<td>(NH3)HY</td>
<td>2.6</td>
<td>n.d.</td>
<td>100</td>
<td>24.705 (50)</td>
<td>770</td>
<td>0.31</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>H(NH3)Y</td>
<td>2.6</td>
<td>n.d.</td>
<td>100</td>
<td>24.705 (50)</td>
<td>770</td>
<td>0.31</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>HY-723-423NH3</td>
<td>2.6</td>
<td>n.d.</td>
<td>-</td>
<td>24.580 (36)</td>
<td>230</td>
<td>0.09</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

a The corresponding numbers of aluminum per unit cell are given in brackets
b Determined by AAS
c Determined by 29Si MAS NMR
d Only the narrow peak at about 60 ppm is considered in 27Al MAS NMR
e The number of Brønsted acid sites determined from pyridine infra-red after desorption at 423 K (mmol/g)
f The number of Brønsted acid sites determined from pyridine infra-red after desorption at 623 K (mmol/g)

Fig. 5.2 shows the XRD patterns of NH4Y and the treated samples. The samples were not pretreated before the measurement. NH4Y, (NH3)HY, and H(NH3)Y showed similar patterns and high crystallinity. The patterns of HY, HY-723-423NH3, and HY-723-RT

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showed less intense and broader diffraction peaks, indicating a loss of crystallinity especially for the latter two. In HY, the loss of crystallinity is likely due to increased disorder and loss of long-range order because of the formation of local defect sites and partial dealumination of the structure (vide infra). The unit cell parameters are given in Table 5.3. The corresponding number of aluminum atoms per unit cell was with 43 significantly lower in HY than in NH₄Y, (NH₃)HY, and H(NH₃)Y, where it was about 50. Heating HY and exposure to air resulted in a further decrease in aluminum content of the framework; samples HY-723-423NH₃ and HY-723-RT had 36 aluminum atoms per unit cell.

Fig. 5.2 shows the XRD patterns of NH₄Y and the treated samples. The samples were stored in a controlled wet environment prior to measurement. For NH₄Y, (NH₃)HY, and H(NH₃)Y, a single peak at 60 ppm was observed, which is assigned to tetrahedrally-coordinated framework aluminum. The width of the peak in the spectrum of H(NH₃)Y was larger than that of the other two samples. The spectrum of HY showed two peaks, one at 60 ppm, attributed to tetrahedrally-coordinated aluminum and, the other at 0 ppm, assigned to octahedrally-coordinated aluminum. The peak for tetrahedrally-coordinated aluminum was slightly broadened, showing disorder in the structure. HY-723-423NH₃ had a broad tetrahedral peak and a small fraction of octahedrally-coordinated
aluminum. Moreover, a low-intensity signal at 20 to 40 ppm was detected and was attributed to pentacoordinated aluminum or distorted tetrahedrally-coordinated aluminum [42]. HY-723-RT showed enhanced intensity of octahedrally and pentacoordinated or distorted tetrahedrally-coordinated aluminum. Assuming that the sharp tetrahedrally-coordinated aluminum peak in the spectra of NH₄Y, HY, (NH₃)HY, and H(NH₃)Y correlates to framework aluminum, 49 aluminums per unit cell are estimated for HY and 53 for NH₄Y, (NH₃)HY, and H(NH₃)Y.

![Fig. 5.3. ²⁷Al MAS NMR of NH₄Y and the treated samples.](image)

From ²⁹Si MAS NMR data [43], the Si/Al ratios of all silica-alumina phases in the samples can be estimated. These phases are the crystalline zeolite and any amorphous silica-aluminas that may have been formed during the treatments. For selected samples, ²⁹Si MAS NMR data are presented in Fig. 5.4. Analysis of the spectrum of NH₄Y gave a Si/Al ratio of 2.4 (Table 5.3), which is close to the bulk value as determined from atomic absorption spectroscopy. The spectrum of HY showed a decreased intensity of the peak at about 97 ppm, which is ascribed to a silicon atom with two aluminum next-nearest neighbors (Q⁴(2Al)). A corresponding increase in the Si/Al ratio to 2.6 of the silica-alumina phases was observed, which correlates to a decrease of less than 10% of the framework aluminum content, in reasonable agreement with a content of 7% octahedrally-coordinated aluminum. The spectrum of HY-723-RT showed broadened peaks and more intensity at
the more negative ppm values, indicative of significant dealumination, which is also shown by the higher Si/Al ratio of 3.4.

![Fig. 5.4. $^{29}$Si MAS NMR spectra of NH$_4$Y, HY, and HY-723-RT.](image)

The infra-red spectra of NH$_4$Y, HY, H(NH$_3$)Y, and HY-723-423NH$_3$, measured at room temperature after vacuum activation at 723 K (Fig. 5.5), showed that ammonia was completely removed and that the samples were in the protonic form. To compare the intensities of the OH peaks of the different samples, all the spectra were normalized in intensity, by giving the overtones and combination modes of the zeolitic framework at about 1700-2000 cm$^{-1}$ equal intensity. The parent sample, NH$_4$Y, exhibited bands at 3640 and 3545 cm$^{-1}$, assigned to Brønsted acid sites in the super cages (HF, high frequency) and Brønsted acid sites in the sodalite cages (LF, low frequency) respectively [44]. The band at 3745 cm$^{-1}$ is assigned to the silanol OH vibration. The infra-red spectrum of H(NH$_3$)Y was almost identical to that of NH$_4$Y. The spectrum of HY showed a much lower intensity of the HF and LF bands and a higher intensity of the silanol band at 3745 cm$^{-1}$. Compared to HY, the spectrum of HY-723-423NH$_3$ showed even weaker HF and LF bands. Fig. 5.6 shows the infra-red spectra of HY and of the in-situ treated samples recorded at room temperature after re-activation and ammonia removal at 723 K. The number of Brønsted acid sites in these samples decreased in the order HY-723-RT/H$_2$O+NH$_3$ > HY > HY-723-
RTNH₃, which indicates that Brønsted acid sites are restored only when small amounts of H₂O are present.

![FT-Infra-red spectra](image)

Fig. 5.5. FT-Infra-red spectra of NH₄Y and the treated samples in the region of OH stretching vibration.

![FT-Infra-red spectra](image)

Fig. 5.6. FT-Infra-red spectra of HY and its treated samples in the region of OH stretching vibration.
5.4. Discussion

5.4.1. Catalytic activity

The propane cracking activities and the apparent activation energies of samples NH₄Y, (NH₃)HY, and H(NH₃)Y are very similar. In contrast, the calcined sample, which was exposed to air at room temperature (HY), showed a much lower cracking activity per gram and a higher apparent activation energy, which indicate that the structure and number of the catalytically active sites had changed. Fig. 5.7 compares the catalytic activities per gram of NH₄Y, HY, and H(NH₃)Y with the catalytic activities normalized by the number of Brønsted acid sites, as determined by infra-red after pyridine adsorption and desorption at 623 K. The activities per Brønsted acid site for NH₄Y and H(NH₃)Y are the same and slightly lower than for HY. The activity per site and the number of sites in NH₄Y and H(NH₃)Y are very similar. The activity per site in HY differs, which was also indicated by its different activation energy (Table 5.2).

Fig. 5.7. Catalytic activity per gram (solid bars) and normalized per H⁺ site, as determined by infra-red after pyridine adsorption, (dashed bars) (See text for details).

All the characterization methods indicate that HY is partially dealuminated and has low crystallinity and surface area and a decreased number of Brønsted acid sites. Its structure is a function of temperature (vide infra). Structural collapse occurs at room temperature after exposure to water, which has previously been shown by in-situ Al XAS, which showed the formation of octahedrally-coordinated aluminum at room temperature after the exposure of
an acidic Y zeolite to moisture [25]. Heating this zeolite causes further structural damage as shown by the loss of crystallinity and intensity in the stretching OH region in the infra-red spectra (Fig. 5.5). The catalytic measurements were performed at high temperature, so characterization after additional heat treatment is most representative of the structures under catalytic reaction conditions.

H(NH₃)Y was made from HY by adsorption of gaseous ammonia at 423 K; its very similar kinetic parameters as the parent sample NH₄Y show that treatment with NH₃ results in the virtually full recovery of the catalytic activity of HY. The characterization results of these samples are also very similar. The catalytic behavior of sample (NH₃)HY, which was made by calcining the parent sample NH₄Y and exposure to NH₃ before exposure to air, confirmed that the NH₃ treatment maintained the catalytic activity of the parent sample NH₄Y after calcination, as previously proposed [40,41,45,46].

In summary, the catalytic cracking of propane over zeolite Y and the treated samples shows that the activity does not change when the material, in its acidic form, is not exposed to air. An inactive catalyst can be recovered by NH₃ treatment at 423 K. However, if this catalyst is heated first, recovery will be incomplete.

5.4.2 Reversibility of the structure of Brønsted acid sites of zeolite catalysts

Based on the spectroscopic results and according to previous proposals [22-24], we present the structures of the Brønsted acid sites in every state (NH₄Y, HY, and the ammonium treated HY) in Scheme 5.1. Species (a) represents the structure of the catalytically active site in the ammonium form of the zeolite. The aluminum is tetrahedrally coordinated. Species (b) contains the bridging hydroxyl group of a Brønsted acid site, formed after NH₃ removal. In this state, the OH vibration of the Brønsted acid sites was detected by infra-red (Fig. 5.5) and tetrahedrally-coordinated aluminum detected by Al K edge XAS measurements [47]. This sample is catalytically active. After calcination and exposure to moisture in air at room temperature, some of the Brønsted acid sites are converted into species (c), which are identified by octahedrally-coordinated aluminum in the ²⁷Al MAS NMR (Fig. 5.3) and Al K edge XAS [47]. The exact structure of the octahedrally-coordinated aluminum remains unknown. However, the peak in the ²⁷Al MAS NMR spectrum is very sharp (500 Hz). This strongly suggests that either a symmetric
species or a very mobile species forms, which is highly dehydroxylated, almost ion-like, and strongly hydrated. Theoretical calculations suggested that the dehydroxylation of aluminum in the framework can occur and that an extra-framework species forms, which is coordinated to its original position by a network of hydrogen bonds [48]. The presence of octahedrally-coordinated aluminum correlates with the results of Si MAS NMR and XRD that indicate a higher Si/Al ratio in this sample. A comparison of the amount of Brønsted acid sites of the parent sample NH\textsubscript{4}Y and HY, determined in the hydroxyl region in the infra-red spectra and the py-H\textsuperscript{+} region after pyridine adsorption, indicates that few Brønsted acid sites remain in HY and that a large number of silanol groups are formed (Fig. 5.5 and Table 5.3). These few Brønsted sites explain the strong decrease of the catalytic activity of this sample. A similar phenomenon has been observed on NH\textsubscript{4}-beta and H-beta zeolites [45].

\begin{equation}
\text{NH}_{3} \rightarrow \text{structure (a)}
\end{equation}

\begin{equation}
\text{species (c) } \text{H}_{2}\text{O} \rightarrow \text{further structural collapse}
\end{equation}

\begin{equation}
\text{high T } \text{NH}_{3} \rightarrow \text{partial recovery}
\end{equation}

Scheme 5.1. Structure of Brønsted acid sites during activation and deactivation of NH\textsubscript{4}Y (a) NH\textsubscript{4}Y; (b) [HY] formed after ammonia removed from NH\textsubscript{4}Y; (c) change of the aluminum coordination from tetrahedral to octahedral by room temperature exposure of calcined NH\textsubscript{4}Y to air [23].

The structural collapse of zeolite HY can be reverted by ammonia treatment at temperatures below 423 K, resulting in species (a) [22-24, 49, 50], as indicated by tetrahedral aluminum in \textsuperscript{27}Al MAS NMR and Al K edge XAS [47], the high intensity of the
Børnsted acid sites in infra-red, a high crystallinity, recovered unit cell parameters, and microporous volume with XRD and nitrogen physisorption. However, treating HY at high temperature causes further structural damage even more when it is exposed to air afterwards, which can no longer be fully repaired by ammonia (Scheme 5.1). $^{27}\text{Al}$ and $^{29}\text{Si}$ MAS NMR, Infra-red, and XRD all showed further structural damage after re-exposure to air of the high temperature-activated zeolite HY.

In HY that is exposed to air, a significant fraction of the Al-O and Si-O bonds are hydrolyzed and broken leading to a partially amorphous structure and a considerable loss of long-range order and micropore volume. However, a large part of the network of the Si-O-T bonds remains intact, which enables full recovery of the structure.

This and previous reports [21-24,49,50] show that moist partially destroys an acidic zeolite; with a base like ammonia and pyridine, the collapsed structure fully recovers. Our infra-red measurements indicate that $\text{H}_2\text{O}$ also plays a role in structural recovery. If HY is heated to 723 K and completely dehydrated, adsorption of gaseous ammonia at 393 K does not result in the reconstruction of the Børnsted acid sites (HY-723-RTNH$_3$, Fig. 5.6) and the structure collapses further (Scheme 5.1). Partial reconstruction of the Børnsted acid sites occurs only after first adding a small amount of $\text{H}_2\text{O}$ (Fig. 5.6 and Scheme 5.1). $\text{H}_2\text{O}$ may enable atom mobility by formation of hydroxyl groups on the zeolite surface, thus enabling the reconstruction with NH$_3$. Hydroxylation reactions are base-catalyzed and the role of NH$_3$ is therefore to catalyze this reaction. Moreover, NH$_4$OH may form, which aids the formation of the Børnsted acid sites and produces NH$_4^+$ ions, which charge-compensate the zeolite framework. Reversible structural changes are a general property of zeolites [10,22,26] and amorphous silica-aluminas [23,51]. The amount of octahedrally-coordinated aluminum is a function of structure type [10,22-24] and of the Si/Al ratio of the framework [52]. Different structure types have different T-connectivities, aluminum proximities, and various pore sizes, which affect the stability of the structure. Zeolites with a high framework Si/Al ratio are very hydrophobic, which may protect the zeolite framework from attack by water molecules. The low Si/Al ratio and, therefore, the high aluminum content of zeolite NH$_4$Y make this zeolite particularly unstable and sensitive to moisture. The high proton density leads to partial dealumination already at room temperature after exposure to moist from the air.
5.4.3 Different characterization techniques reveal different states of zeolite catalysts

Spectroscopic measurements are preceded by sample pretreatment, which often differs for each characterization technique. Because the structures of zeolites are sensitive to their environment, they alter during the pretreatment of the characterization methods. $^{27}$Al MAS NMR is generally used to study the hydrated state of the catalysts. The dehydrated state of the catalysts is studied by techniques such as nitrogen physisorption, FTIR, $^1$H MAS NMR, and kinetic measurements, all of which are performed after the activation of the catalysts at high temperature. Because different techniques reveal different zeolite structures, a direct comparison of the results of various techniques is often difficult. True in-situ methods are essential to determine the zeolite structure under catalytically relevant conditions. Several techniques, such as X-ray absorption spectroscopy, XRD, and, to some extent, NMR, can determine the zeolite structure under well-defined conditions, aiding a direct comparison of results of other characterization techniques and providing structure-performance relationships.

5.5. Conclusion

The conditions that induce the destruction and reconstruction of zeolitic Brønsted acid sites are described. Some of the Brønsted acid sites in the acidic form of the zeolites collapse after contact with moisture from the air. Heating this partially dealumminated zeolite causes further structural collapse and a loss of catalytic activity at high temperature. However, treatment of the collapsed Brønsted acid sites with NH$_3$ results in a recovery of the catalytic activity. The presence of H$_2$O molecules aids the structural recovery. Different characterization methods reveal different zeolite structures, because of structural changes that occur during sample preparation.

References

Reversibility of Structural Collapse in Zeolite Y


[27] N. Katada, T. Kanai, M. Niwa  

[28] P.O. Fritz, J.H. Lunsford  

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Chapter 6

Effect of Framework and Extra-framework Aluminum on the Catalytic Activity of Zeolite Y

Abstract

The effect of framework Si/Al ratio on the intrinsic activity of Brønsted acid sites in zeolite Y was investigated by monomolecular cracking of propane and various physicochemical characterization methods. Samples had different Si/Al ratios from synthesis or from post-synthesis treatments. Two samples with Si/Al ratios 3.3 and 3.6 were synthesized and exhibited similar characteristic features as commercial zeolite Y that had a Si/Al ratio of 2.6. An ultrastable Y (HUSY) was treated with ammonia and ethylenediaminetetraacetic acid (EDTA) to remove extra-framework aluminum (EFAI). The rates per gram increased with Si/Al ratio. However, the activation energies were independent of the Si/Al ratio and the presence of EFAI. This implies that the acidity of the Brønsted acid sites in all samples that participate in the reaction is identical. The enhanced activity of the samples with higher Si/Al ratio (up to 5) is attributed to the creation of more isolated Brønsted acid sites, which are active in this demanding reaction. Removing EFAI did not affect the intrinsic catalytic activity, but increased the number of Brønsted acid sites.
6.1. Introduction

Zeolite Y (FAU) is the most widely used zeolite in the refinery industry [1]. Its large pore openings and high surface area make it the catalyst of choice in the fluid catalytic cracking (FCC), which is one of the most important reactions in oil refining. However, the thermal and hydrothermal stability of zeolite Y is limited. Even at room temperature, the structure of acidic zeolite Y partially collapses when exposed to moisture [2-4]. It is well known that the higher the Si/Al ratio, the more stable a zeolite structure is. Therefore, a thermally stable Y, so called ultra-stable zeolite Y (USY), was developed by dealumination of the framework via the controlled addition of steam [5]. The reduced ion-exchange capacity and a smaller unit cell are indications of a removal of aluminum from the framework [6]. Extra-framework phases are formed [7-10].

Except for its higher thermal stability, HUSY exhibited a much higher catalytic activity than the non-activated samples [11-16]. Many explanations have been put forward. First, the next-nearest neighbour effect [17-20] suggests that strong Brønsted acid sites occur only on acid sites of which the aluminum atom has no aluminum atoms as next-nearest neighbour. Second, extra-framework aluminum has been suggested to modify the catalytic activity because of stabilization of the lattice [21]. It forms an active phase [22], or it has a synergistic effect on nearby Brønsted acid sites [21,22]. Sites of enhanced strength have been attributed to a hydroxyl band located at 3600 cm\(^{-1}\) in infra-red spectra of HUSY [11,23-25]. Finally mesopores are generated during steam-activation that have been shown to alleviate diffusion limitations [26].

Cracking and isomerization of hydrocarbons are catalyzed by the Brønsted acid sites in the zeolites [27] and the catalytic activity increases with the number of Brønsted acid sites [11,16,23], which is related to the number of framework aluminum atoms. Alkane cracking is a model reaction to be used to probe the nature of Brønsted acid sites in zeolites. Depending on the reaction condition, there are two reaction mechanisms: monomolecular and bimolecular [28,29]. The monomolecular pathway involves the protonation of an alkane by the Brønsted acid site to form a carboxation, which subsequently undergoes cracking or dehydrogenation [30]. The bimolecular pathway involves hydride transfer between an alkane and an adsorbed alkoxide species followed by isomerization and/or \(\beta\)-scission [28,31]. The hydride transfer does not involve a direct interaction between alkane
and the Brønsted acid sites. The monomolecular reaction, however, involves a proton transfer from the zeolite to the alkane, which is sensitive to the nature of the Brønsted acid sites. The monomolecular cracking is a first-order reaction and when catalyzed by zeolites its rate-limiting step is the protonation of the alkane [32,33]. Therefore, the intrinsic activity of this reaction is a measure of the strength of Brønsted acid sites in the catalyst. The intrinsic activation energy (E_{act}) equals the apparent activation energy (E_{app}) minus the heat of reactant adsorption (\Delta H_{ads}) [34]. The activation energy is indicative of the nature of the active site; only looking at the activity will not provide insight into the intrinsic activities of the catalytic active sites.

Previously, the intrinsic reactivity of zeolitic Brønsted acid sites was determined by the monomolecular cracking of alkanes [32,33,35-37]. The common conclusion was that the variations in activities are mainly due to the different sorption of reactant and that the intrinsic activity of Brønsted acid sites is identical and independent of the structures.

In this work, we determined the effect of the framework Si/Al ratio on the intrinsic activity of zeolite Y. Samples with different framework Si/Al ratios were obtained either from synthesis or from post-synthesis treatments. The Brønsted acid sites in these samples were investigated by the monomolecular cracking of propane and various physicochemical characterization techniques.

### 6.2. Experimental

The sample preparation, characterization, and catalytic conditions were described in Chapter 2. Table 6.1 compiles the samples and their nomenclature. The samples’ names were given as Y(N) and HY(N), which correspond to the NH₄ and proton forms, respectively. N is the Si/Al ratio determined by atomic absorption spectroscopy (AAS). We used the samples’ names of the starting materials prior to the pretreatments in the characterization and kinetic measurements.
Table 6.1. Sample treatments and nomenclature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Starting material</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(2.6)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HY(2.6)</td>
<td>Y(2.6)</td>
<td>calcined at 823 K in air</td>
</tr>
<tr>
<td>Y(3.3)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HY(3.3)</td>
<td>Y(3.3)</td>
<td>calcined at 823 K in air</td>
</tr>
<tr>
<td>Y(3.6)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HY(3.6)</td>
<td>Y(3.6)</td>
<td>calcined at 823 K in air</td>
</tr>
<tr>
<td>HUSY</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H(NH₃)USY</td>
<td>HUSY</td>
<td>at 423 K NH₃ admitted, cooled in NH₃</td>
</tr>
<tr>
<td>HUSY-NaEDTA</td>
<td>HUSY</td>
<td>washed with 0.1 M Na₂H₂-EDTA at 335 K for 24 h; ion-exchanged with 1 M NH₄NO₃ at 353 K for 24 h</td>
</tr>
</tbody>
</table>

6.3. Results

6.3.1. Characterization

The Si/Al ratios of all the samples determined by AAS are listed in Table 6.2 (column 2). High-silica zeolites Y, Y(3.3) and Y(3.6) had Si/Al ratios of 3.3 and 3.6 respectively. The steamed sample (HUSY) had a Si/Al ratio of 2.5, which did not change with ammonia treatment (H(NH₃)USY). The sample treated with Na₂H₂EDTA had a Si/Al ratio of 5.0, which indicated that EDTA removed aluminum from the sample. The BET surface areas and micropore volumes after degassing at 723 K are presented in Table 6.2 (columns 3 and 4). Zeolites Y(3.3) and Y(3.6) had very similar surface areas of 670 and 650 m²/g and micropore volumes of 0.27 and 0.26 cm³/g. The values were lower than that of Y(2.6) (810 m²/g and 0.31 cm³/g). The surface areas and micropore volumes of the calcined samples decreased in the order of increasing aluminum content: HY(3.6) > HY(3.3) > HY(2.6). HUSY and HUSY-NaEDTA showed very similar surface areas of 700 and 730 m²/g, and identical micropore volumes of 0.27 cm³/g. The ammonia treated sample H(NH₃)USY, had an evidently smaller surface area (640 m²/g) and micropore volume (0.24 cm³/g) [38].
Table 6.2. Characteristics of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al $^a$</th>
<th>Surface Area (m$^2$/g)</th>
<th>$\mu$-pore Volume (cm$^3$/g)</th>
<th>%Td Al$^b$</th>
<th>Unit cell $a_0$ (Å)</th>
<th>FWA1 /u.c.</th>
<th>#acid sites$^d$</th>
<th>#acid sites$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(2.6)$^f$</td>
<td>2.6</td>
<td>810</td>
<td>0.32</td>
<td>100</td>
<td>24.720</td>
<td>52</td>
<td>1.10</td>
<td>1.95</td>
</tr>
<tr>
<td>HY(2.6)$^f$</td>
<td>2.6</td>
<td>450</td>
<td>0.18</td>
<td>93</td>
<td>24.643</td>
<td>43</td>
<td>0.20</td>
<td>1.0</td>
</tr>
<tr>
<td>Y(3.3)</td>
<td>3.3</td>
<td>670</td>
<td>0.27</td>
<td>100</td>
<td>24.660</td>
<td>45</td>
<td>0.90</td>
<td>1.76</td>
</tr>
<tr>
<td>HY(3.3)</td>
<td>3.3</td>
<td>540</td>
<td>0.22</td>
<td>94</td>
<td>24.628</td>
<td>42</td>
<td>0.29</td>
<td>n.d.</td>
</tr>
<tr>
<td>Y(3.6)</td>
<td>3.6</td>
<td>650</td>
<td>0.26</td>
<td>100</td>
<td>24.580</td>
<td>37</td>
<td>0.71</td>
<td>1.54</td>
</tr>
<tr>
<td>HY(3.6)</td>
<td>3.6</td>
<td>600</td>
<td>0.25</td>
<td>93</td>
<td>24.524</td>
<td>31</td>
<td>0.40</td>
<td>n.d.</td>
</tr>
<tr>
<td>HUSY</td>
<td>2.5</td>
<td>700</td>
<td>0.27</td>
<td>40</td>
<td>24.537</td>
<td>32</td>
<td>0.30</td>
<td>1.06</td>
</tr>
<tr>
<td>H(NH$_3$)USY</td>
<td>2.5</td>
<td>640</td>
<td>0.24</td>
<td>89</td>
<td>24.545</td>
<td>33</td>
<td>0.36</td>
<td>1.13</td>
</tr>
<tr>
<td>HUSY-NaEDTA</td>
<td>5.0</td>
<td>730</td>
<td>0.27</td>
<td>93</td>
<td>24.517</td>
<td>30</td>
<td>0.54</td>
<td>1.40</td>
</tr>
</tbody>
</table>

$^a$ determined from AAS
$^b$ only the narrow peak at about 60 ppm is considered in $^{27}$Al MAS NMR
$^c$ determined from the unit cell size
$^d$ The number of Brønsted acid sites determined by pyridine infra-red after desorption at 423 K (mmol/g)
$^e$ The number of Brønsted acid sites determined by the decomposition of i-propylamine (mmol/g)
$^f$ data taken from ref. [39]

n.d. not determined

Fig. 6.1 shows the $^{27}$Al MAS NMR spectra of the high-silica zeolite Y, HUSY, and the treated samples. These spectra were recorded after equilibration in a controlled wet condition. The spectra of Y(3.3) and Y(3.6) showed a single peak at 60 ppm, which is assigned to tetrahedrally-coordinated framework aluminum. The spectra of the calcined samples, HY(3.3) and HY(3.6), showed two peaks, one at 60 ppm, attributed to tetrahedrally-coordinated aluminum and one at 0 ppm, assigned to octahedrally-coordinated aluminum. There was about 6-7% octahedral aluminum, similar to that in HY(2.6) [39]. The peak for tetrahedrally-coordinated aluminum was broadened, showing disorder in the structure. The spectrum of HUSY consisted of three parts: a broad tetrahedral peak at 60 ppm, a distorted tetrahedral peak from 20 to 40 ppm [7], and an octahedral peak at 0 ppm. The spectrum of H(NH$_3$)USY showed a broad tetrahedral peak at 60 ppm and a weak octahedral signal at 0 ppm. The spectrum of HUSY-NaEDTA contained an asymmetric tetrahedral peak and a small broad peak at 20-40 ppm. The tetrahedral peaks in the spectra of HUSY, H(NH$_3$)USY, and HUSY-NaEDTA were broad, indicating a large spread in average T-O-T angles. The percentage of tetrahedral aluminum in HUSY that corresponded to the peak at 60 ppm was 40% (Table 6.2, column 5), which increased to 89% after
ammonia treatment. After the EDTA treatment, the percentage of tetrahedral aluminum was about 93% of the total aluminum.

Fig. 6.1. $^{27}$Al MAS NMR of high silica Y, HUSY, and the treated samples.

Fig. 6.2 shows the XRD patterns of zeolite Y(2.6), the high-silica zeolites Y, HUSY, and the treated samples. The samples were not pretreated before the measurement. All the samples showed similar patterns and high crystallinity in agreement with N$_2$ physisorption. The unit cell parameters and the corresponding numbers of framework aluminum atoms per unit cell are given in Table 6.2 (column 6 and 7). The unit cell decreased in size with dealumination and so the number of framework aluminum atoms per unit cell. Zeolite Y contains 192 T atoms per unit cell. Thus, the numbers of framework aluminum atoms per unit cell determined from the XPD patterns and AAS are more or less similar for the samples with 100% tetrahedral aluminum. The calcined samples had significantly lower framework aluminum atoms per unit cell, which corresponded to the $^{27}$Al MAS NMR that contained octahedral aluminum.
The $^{29}$Si MAS NMR data are presented in Figs. 6.3 and 6.4 and Table 6.3. The spectra of the high-silica zeolites Y showed decreased intensity of the peak at about -97 ppm and increased intensity of the signals at about -103 ppm and -107 ppm compared to those of Y(2.6). They are assigned to $(Q^4(2Al))$, $(Q^4(1Al))$, and $(Q^4(0Al))$ species, where $Q^4$ represents a Si atom connected to four T atoms via bridging oxygen; nAl indicates the number, n, of aluminum atoms in the second coordination shell. Analysis of the spectra of the high-silica zeolites Y gave a Si/Al ratio of 3.2 for Y(3.3) and 4.3 for Y(3.6) (Table 6.3), which follow the trend of the bulk values determined from atomic absorption spectroscopy. The Si/Al ratios in HUSY and H(NH$_3$)USY were 4.8 and 5.1; after EDTA treatment it increased to 5.5. Most likely, HUSY contains ASA phases that interfered with the $^{29}$Si MAS NMR and that were washed out during the EDTA treatment. The numbers of framework aluminum atoms per unit cell determined from the $^{29}$Si MAS NMR are also given in Table 6.3 (column 3). They followed the same trends as those predicted by $^{29}$Si MAS NMR, XRD and the combination of AAS and $^{27}$Al MAS NMR.
Chapter 6

Fig. 6.3. $^{29}$Si MAS NMR of high silica Y zeolite samples.

Fig. 6.4. $^{29}$Si MAS NMR of HUSY and the treated samples.
**Effect of Framework and Extra-framework Aluminum in Zeolite Y**

Table 6.3. $^{29}$Si MAS NMR data of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al$^a$</th>
<th>FWAl/u.c.</th>
<th>Si(0Al)</th>
<th>Si(1Al)</th>
<th>Si(2Al)</th>
<th>Si(3Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(2.6)$^b$</td>
<td>2.4</td>
<td>56</td>
<td>4</td>
<td>42</td>
<td>37</td>
<td>17</td>
</tr>
<tr>
<td>HY(2.6)$^b$</td>
<td>2.6</td>
<td>53</td>
<td>11</td>
<td>35</td>
<td>42</td>
<td>12</td>
</tr>
<tr>
<td>Y(3.3)</td>
<td>3.2</td>
<td>46</td>
<td>11</td>
<td>38</td>
<td>24</td>
<td>7</td>
</tr>
<tr>
<td>HY(3.3)</td>
<td>3.6</td>
<td>42</td>
<td>20</td>
<td>47</td>
<td>33</td>
<td>0</td>
</tr>
<tr>
<td>Y(3.6)</td>
<td>4.3</td>
<td>36</td>
<td>36</td>
<td>30</td>
<td>49</td>
<td>20</td>
</tr>
<tr>
<td>HY(3.6)</td>
<td>5.3</td>
<td>30</td>
<td>37</td>
<td>50</td>
<td>13</td>
<td>0</td>
</tr>
<tr>
<td>HUSY</td>
<td>5.1</td>
<td>31</td>
<td>51</td>
<td>35</td>
<td>14</td>
<td>0</td>
</tr>
<tr>
<td>H(NH$_3$)USY</td>
<td>4.8</td>
<td>33</td>
<td>42</td>
<td>33</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>HUSY-NaEDTA</td>
<td>5.5</td>
<td>29</td>
<td>46</td>
<td>38</td>
<td>13</td>
<td>3</td>
</tr>
</tbody>
</table>

$^a$ from $^{29}$Si MAS NMR.

$^b$ from ref. [39].

The number of Brønsted acid sites, determined with infra-red after the adsorption of pyridine and desorption at 423 and the decomposition of i-propylamine (Table 6.2, columns 8 and 9), showed that the concentration of Brønsted acid sites decreased with decreasing aluminum content. For HUSY and its treated samples, both ammonia and EDTA treatment lead to a higher number of Brønsted acid sites. HUSY-NaEDTA had more Brønsted acid sites than H(NH$_3$)USY. For H(NH$_3$)USY, the higher number of Brønsted acid sites corresponds to its higher framework aluminum content compared to the parent sample as determined by other techniques (NMR and XRD). For HUSY-NaEDTA, a higher number of Brønsted acid sites per gram were detected, because extra-framework aluminum had been removed from the sample. The number of Brønsted acid sites determined by decomposition of i-propylamine gave consistently higher values than that determined by infra-red after pyridine adsorption and desorption.

The infra-red spectra of Y(2.6), Y(3.3), and Y(3.6), measured at room temperature after vacuum activation at 773 K, are shown in Fig. 6.5. To compare the intensities of the OH peaks of the different samples, all the spectra were normalized in intensity by giving the overtones and combination modes of the zeolitic framework at about 1700-2000 cm$^{-1}$ equal intensity. The spectra of Y(2.6) and its calcined sample (HY(2.6)) were taken from [39]. The spectrum of Y(2.6), after in-situ removal of ammonia, exhibited bands at 3644 and 3545 cm$^{-1}$, assigned to Brønsted acid sites in the super cages (HF, high frequency) and Brønsted acid sites in the sodalite cages (LF, low frequency) respectively [40]. The small band at 3745 cm$^{-1}$ is assigned to the silanol vibration. The HF peak shifted to lower
wavenumber in the spectra of Y(3.3) (3636 cm\(^{-1}\)) and Y(3.6) (3630 cm\(^{-1}\)). A higher Si/Al ratio caused a band shift \([25,41,42]\). The intensity of the HF and LF bands decreased with increasing Si/Al ratio, which is in line with the number of Brønsted acid sites determined. The spectra taken after in-situ temperature treatment of HY(2.6), HY(3.3), and HY(3.6) showed much lower intensity of the HF and LF bands and a higher intensity of the silanol band at 3745 cm\(^{-1}\). Compared to HY(2.6), the spectra of HY(3.3) and HY(3.6) showed more intense HF and LF bands and a less intense silanol band. Fig. 6.6 compares the infrared spectra of HUSY, H(NH\(_3\))USY, and HUSY-NaEDTA after in-situ heat treatment. The spectrum of HUSY is more complex than the spectrum of untreated zeolite Y. In addition to the bands assigned to silanols (3745 cm\(^{-1}\)), HF (3625 cm\(^{-1}\)), and LF (3560), two shoulders at 3700 and 3525 cm\(^{-1}\) and two distinct bands at 3670 and 3600 cm\(^{-1}\) are observed. The shoulder at 3700 cm\(^{-1}\) and the peak at 3670 cm\(^{-1}\) are ascribed to internal silanols and to partial extra-framework aluminum (EFAl) species, respectively \([43]\), which are both formed during the steam activation. The distinct band at 3600 cm\(^{-1}\) has been ascribed to Brønsted acid sites in interaction with EFAl, and has been suggested to be responsible for enhanced catalytic activity (HF') \([44]\). The spectra of H(NH\(_3\))USY and HUSY-NaBDTA after activation at 773 K showed an increase in overall intensity in the hydroxyl region. The HF and LF bands increased and those at 3600 and 3670 cm\(^{-1}\) decreased in intensity. The low-frequency shoulder on the LF peak virtually disappeared and the peak at 3600 cm\(^{-1}\) (HF') can hardly be distinguished.

6.3.2. Reaction kinetics

Fig. 6.7 shows the Arrhenius plots of the monomolecular cracking of propane of Y(2.6), Y(3.3), and Y(3.6). Table 6.4 lists the reaction rates at 823 K, the apparent activation energies, and the selectivity to cracking of all the samples. At 823 K, the cracking rates of high-silica zeolites Y are much higher than that of Y(2.6); the rate increased with Si/Al ratio. For Y(3.6), the rate per gram is about 16 times higher than that of Y(2.6) and for Y(3.3) it is about four times higher. For the calcined samples, the rate of HY(2.6) is about six times lower than that of Y(2.6), while the rate of HY(3.3) is about 3 times less than that of parent sample Y(3.3) and for HY(3.6) it is about 1.5 times. The apparent activation energies of Y(2.6), Y(3.3), and Y(3.6) are virtually equal at 165-166 kJ/mol (Table 6.4).
The apparent activation energies of the calcined samples are higher, 208, 186, and 176 kJ/mol respectively for HY(2.6), HY(3.3), and HY(3.6). The high-silica zeolite Y had selectivities to cracking of 79 and 81%, which is higher than for Y(2.6) (60%). Compared to their parent samples, the calcined samples had a lower selectivity to cracking. The
catalytic results of HUSY and the treated samples are also presented in Table 6.4. H(NH\textsubscript{3})USY had a higher cracking rate than HUSY. The rates of both HUSY and H(NH\textsubscript{3})USY were higher than that of Y(2.6) and Y(3.3), but lower than Y(3.6). The apparent activation energies of HUSY and H(NH\textsubscript{3})USY are similar, respectively 166 and 161 kJ/mol and within limits of accuracy equal to that of zeolites Y samples irrespective of the Si/Al ratio. The selectivity to cracking is lower for H(NH\textsubscript{3})USY. HUSY-NaEDTA had a reaction rate per gram about 3 times that of HUSY. Its apparent activation energy is 162 kJ/mol, which is the same as that of HUSY and H(NH\textsubscript{3})USY. The selectivity to cracking of HUSY-NaEDTA is 84%, very similar to HUSY and the high-silica Y samples.

![Image](image_url)

Fig.6.7. Arrhenius plots of monomolecular cracking of propane over Y(2.6) (■), Y(3.3) (●), and Y(3.6) (▲).

6.4. Discussion

6.4.1 Site isolation

The XRD patterns of directly synthesized high-silica zeolites Y (Y(3.3) and Y(3.6)) were the same as that of normal zeolite Y (NH\textsubscript{4}Y), which indicates that their structures belong to FAU (Fig. 6.2). Both AAS and MAS NMR showed that their Si/Al ratios are higher than normal zeolite Y. All aluminum atoms in these samples were in tetrahedral coordination (Fig. 6.1), which implies that all the aluminum atoms are in the framework. In zeolite Y, although not all tetrahedral aluminum atoms contribute to the strong Brønsted acid sites [45, 46], the number of sites still correlates to the content of tetrahedral framework aluminum.
Table 6.4. Reaction rates and activation energies of monomolecular cracking of propane of zeolite Y samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate-cracking(^a) ×10(^{-6})</th>
<th>Rate-cracking(^b) ×10(^{-6})</th>
<th>Rate-cracking(^c) ×10(^{-6})</th>
<th>(E_{\text{app}}) (kJ/mol)</th>
<th>100×cr/(cr+de)(^d)</th>
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<tr>
<td>Y(2.6)(^e)</td>
<td>0.29</td>
<td>0.26</td>
<td>0.15</td>
<td>165</td>
<td>60</td>
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<tr>
<td>HY(2.6)(^e)</td>
<td>0.05</td>
<td>0.25</td>
<td>0.05</td>
<td>208</td>
<td>38</td>
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<tr>
<td>Y(3.3)</td>
<td>1.3</td>
<td>1.5</td>
<td>0.8</td>
<td>166</td>
<td>81</td>
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<tr>
<td>HY(3.3)</td>
<td>0.49</td>
<td>1.7</td>
<td>n.d.</td>
<td>186</td>
<td>64</td>
</tr>
<tr>
<td>Y(3.6)</td>
<td>5.4</td>
<td>7.6</td>
<td>3.5</td>
<td>165</td>
<td>79</td>
</tr>
<tr>
<td>HY(3.6)</td>
<td>3.3</td>
<td>8.3</td>
<td>n.d.</td>
<td>176</td>
<td>77</td>
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<tr>
<td>HUSY</td>
<td>2.0</td>
<td>6.7</td>
<td>1.9</td>
<td>166</td>
<td>81</td>
</tr>
<tr>
<td>H(NH(_3))USY</td>
<td>2.2</td>
<td>6.1</td>
<td>1.9</td>
<td>161</td>
<td>69</td>
</tr>
<tr>
<td>HUSY-NaEDTA</td>
<td>6.8</td>
<td>13.2</td>
<td>4.9</td>
<td>162</td>
<td>84</td>
</tr>
</tbody>
</table>

\(^a\) rate at 823 K per gram(mol/g.s.bar)
\(^b\) rate per Brønsted acid site determined by pyridine infra-red after desorption at 423 K (mol/mol.s.bar)
\(^c\) rate per Brønsted acid site determined by the decomposition of i-propylamine (mol/mol.s.bar)
\(^d\) selectivity to cracking in percentage at 823 K
\(^e\) data taken from ref. [39]

Compared to normal zeolite Y, a lower number of framework aluminum atoms per unit cell in high-silica samples leads to fewer Brønsted acid sites, which is experimentally shown by the intensity in the infra-red OH stretching bands, by infra-red after pyridine adsorption, and by decomposition of i-propylamine. The infra-red spectra of high-silica samples contain three types of hydroxyl bands that are silanol, HF, and LF, which are the same as that of normal zeolite Y except that the HF band of the high-silica sample is at lower frequency indicative of their lower aluminum framework content [25]. The calcined high-silica samples, HY(3.3) and HY(3.6) showed a large decrease in intensity of the stretching hydroxyl groups, similar to HY(2.6) that is not stable and shows structural collapse after exposure to moisture [39].

Because the rate-limiting step of monomolecular cracking on zeolites is the protonation of the alkane by the accessible Brønsted acid sites [32], this reaction probes the ability of the zeolite to protonate a weak base. We consider the intrinsic activation energy a measure of acidity of the Brønsted acid sites that participate in the reaction. The high-silica zeolites Y had almost identical apparent activation energies as Y(2.6) in the monomolecular cracking of propane. Therefore, sites of equal strength dominate the reactivity in Y(2.6), Y(3.3), and Y(3.6). However, the high-silica samples exhibited much higher cracking rates.
Chapter 6

expressed per gram and per acid site than normal zeolite Y and the rate increased with Si/Al ratio. Generally it is believed that the catalytic activity increases with the number of Bronsted acid sites \([11,12,23,27,47]\), as shown by poisoning and chemical substitution of aluminum by silicon in the framework \([23,33,48,49]\). The catalytic activity decreased faster than the number of sites that are poisoned \([45,48-50]\). Clearly, not all Bronsted acid sites contribute to activity. The identical activation energies suggested that the higher activity of the high-silica samples originates from the number of Bronsted acid sites that participate in the reaction. Even though the samples had lower framework aluminum contents, more catalytic active sites are present.

The number of Bronsted acid sites measured by infra-red with the adsorption of pyridine and the decomposition of \(i\)-propylamine in the high-silica samples were lower than in \(Y(2.6)\), which is consistent with the changes in framework aluminum content. Normalized by these numbers the rates per Bronsted acid sites for zeolites Y samples decreased in the order: \(Y(3.6) > Y(3.3) > Y(2.6)\). It is known that the Bronsted acid sites in the FAU structure are heterogeneous due to different framework structures and chemical composition \([51]\) and that strong bases like pyridine are not able to distinguish the different Bronsted acid sites \([43]\). The monomolecular cracking of propane is a highly demanding reaction and was performed at high temperatures (675 to 875 K), so this reaction likely probes only the strongest active Bronsted acid sites \([52]\). We suggest that the numbers of Bronsted acid sites that were determined either by pyridine or isopropylamine are higher than the numbers of sites that participate in the reaction, which is in agreement with the previously mentioned poisoning studies. The lower the framework aluminum content, the higher the number of strong Bronsted acid sites.

An experimental study of the acidity of FAU-like zeolites by Beaumont and Barthomeuf \([41]\) showed that the effective Bronsted acidity increased with Si/Al ratio and reached a maximum at Si/Al = 6. Assuming that all the aluminums are in the framework, the sample with Si/Al ratio 6 has about 27 framework aluminum atoms per unit cell. A model was developed to interpret the observation that the strength of Bronsted acid sites depends on the aluminum environment \([53]\) and only aluminum atoms with no next-nearest neighbor aluminum exhibit strong acidity \([49,54]\). Since then, theoretical modeling and experimental measurements reported the next-nearest neighbor effect in zeolites and the catalytic activity
increases with the framework aluminum content to a maximum at around 30 framework aluminum atoms per unit cell and then decreases with increasing framework aluminum content [11,13,23,55-61]. The catalytic results of our samples are in line with these suggestions. $^{29}$Si MAS NMR indicated that Si(1Al) increased in the order: Y(2.6) (42%) < Y(3.6) (49%) < Y(3.3) (58%), and Si(0Al) increased with Si/Al ratio from 4% to 30%. The high-silica samples contain more isolated Bronsted acid sites [49,54,62,63]. We attribute the enhanced catalytic activity of high-silica samples to the increased number of isolated framework aluminum.

All the characterization methods showed that the calcined samples, HY(3.3) and HY(3.6) were partially dealuminated and had smaller unit cell size and lower numbers of Bronsted acid sites, which was also observed in HY(2.6) [39]. However, HY(2.6) had only around half the surface area and micropore volume of that of the parent sample, whereas for HY(3.3) it was about 80% and for HY(3.6) its surface area and micropore volume are close to the parent sample. Moreover, the intensity of hydroxyl groups of the Bronsted acid sites for these calcined samples was lower than that of their respective parent samples and increased with Si/Al ratio (Fig. 6.6). These observations were corroborated by the catalytic results. The cracking rate of HY(2.6) was about 17% of that of its parent sample, for HY(3.3) and HY(3.6) it was 38% and 61% respectively. Their activation energies increased in the order: HY(3.6) < HY(3.3) < HY(2.6) and the values were all higher than that of the parent samples, which implied that structural collapse had occurred. It has been shown that octahedral aluminum in acidic zeolites forms at room temperature after exposure to moisture [3,4,10,64-67]. The results indicated that the structure collapse is a function of Si/Al ratio and that frameworks with lower aluminum contents are more stable [68]. Al MAS-NMR spectra of HY(2.6), HY(3.3), and HY(3.6) showed a similar percentage of octahedral aluminum. This disagrees with zeolite Beta where the amount of octahedral aluminum is a function of the Si/Al ratio [68], which may be caused by the influence of the structure types.

6.4.2 HUSY and the treated samples

HUSY, a commercial sample with a framework Si/Al ratio of 5.1, was also studied in its protonic form, after ammonia adsorption, and after EDTA treatment. Steamed zeolites
generally show enhanced catalytic activity, also shown in this study. The catalytic results of HUSY showed that the activation energy was independent of these treatments and within the limits of accuracy identical to that of untreated zeolite Y. The cracking rates per gram of HUSY were in the range of those of high-silica zeolite Y. The identical activation energies of all these samples show that the structures of the catalytic active sites in all these samples are the same. Zeolites with lower framework aluminum contents can exhibit higher catalytic activity as shown by Y(2.6), Y(3.3), and Y(3.6), which is caused by a higher number of isolated framework aluminum. The large amount of octahedrally-coordinated aluminum in HUSY can be washed out by EDTA treatment (Fig. 6.1) [69]. This treatment results in a sample (HUSY-NaEDTA) with a higher number of Brønsted acid sites [69] and increased activity. Its activation energy remained unaltered. This indicates that the higher activity of HUSY compared to untreated zeolite Y is not due to the extra-framework aluminum, which was supposed to be the active site or the enhancing site for increasing the catalytic activity of HUSY [12,21,23,70,71].

After adsorption of ammonia on HUSY, the \(^{27}\)Al MAS NMR data (Fig. 6.1 and Table 6.2) showed that some of the octahedrally-coordinated aluminum had converted to tetrahedral coordination [10]. Thus, the framework aluminum content increased (Tables 6.2 and 6.3). The infra-red data (Fig. 6.6) on HUSY and H(NH\(_3\))USY after activation at 773 K indicated that the number of Brønsted acid sites represented by the HF band at 3625 cm\(^{-1}\) increased at the cost of the 3600 cm\(^{-1}\) peak (HF'). We ascribe the enhanced catalytic activity of H(NH\(_3\))USY to a higher number of Brønsted acid sites. The band at 3600 cm\(^{-1}\) has been suggested to be related to the enhanced catalytic activity [44,72]. However, a decrease in its intensity is paralleled by a higher activity. This suggests that it may play a minor role in catalytic activity. The similar activation energy of H(NH\(_3\))USY indicates that the treatment did not change the properties of the active sites that created more active sites by bringing extra-framework aluminum back to the framework. This suggests that the catalytic potential of a steamed zeolite is not fully utilized and that structural collapse can be reversed [39].

It was reported that EDTA treatment was used to obtain ultrastable zeolites from Y zeolites by dealumination [73,74]. The sample showed a higher catalytic activity, and it was suggested that new strong Brønsted acid sites were created by the treatment [69,75]. Our HUSY sample after EDTA treatment had the same structure as the parent sample as shown...
Effect of Framework and Extra-framework Aluminum in Zeolite Y

by nitrogen physisorption and XRD. The number of Brønsted acid sites was higher [69] and so was the activity. Its activation energy remained unaltered. This implies that the sites that participated in the reaction do not possess a special property, and are the same as that of untreated zeolite Y. XRD and $^{29}$Si MAS NMR results showed it had 30 framework aluminum atoms per unit cell, which explains its higher activity [41]. The infra-red spectrum of HUSY-NaEDTA (Fig. 6.6) does not exhibit a distinct band at 3600 cm$^{-1}$, which confirms that this band may not be important for the catalytic activity.

6.5. Conclusion

The strong Brønsted acid sites in zeolite Y of various Si/Al ratios and with different contents of extra-framework aluminum are identical and show the same catalytic activity. Their intrinsic activities are independent of Si/Al ratio and extra-framework aluminum. Only isolated sites that have no aluminum next-nearest neighbor are strong Brønsted acid sites. Their number is higher in zeolites Y with higher Si/Al ratio up to Si/Al = 5, the maximum studied.

References


*Chem. 31* (1986) 190.


Conclusions and outlook

The aim of the doctoral work was to elucidate the structure-performance relation in aluminosilicates. Since the catalytic performance of zeolites and amorphous silica-aluminas (ASAs) is largely affected by their structure, understanding structure-performance relationships is important for designing better catalysts. To determine this relationship, the structure and stability of the solid-acid catalysts were studied by kinetic measurements and physicochemical characterization.

The observed activity and selectivity of aluminosilicates depended strongly on the rate-limiting step (r.l.s.) in the monomolecular conversion of propane. Two separately occurring reactions took place: protolytic cracking and dehydrogenation. The r.l.s. in the protolytic cracking was the protonation of the alkane. Therefore, its intrinsic activity is a measure of the acidity of the Brønsted acid sites. The intrinsic activity of Brønsted acid sites in aluminosilicates did not depend on crystallinity or the structure type of the material. Only isolated Brønsted acid sites were active in this demanding reaction; the non-framework aluminum did not affect the intrinsic activity. An open question remains how many Brønsted acid sites participate in the reaction. Pore size and shape strongly affected the observed rates of reaction by causing changes in the sorption of the reactant onto the catalytically active sites. The better the fit between the reactant and the pore of the catalyst, the higher the observed activity will be. The more favorable thermodynamic equilibrium of sorption of the alkane in the pores of 10 MR zeolite ZSM5 is responsible for its higher cracking rates per active site compared to the larger pore zeolites like mordenite, beta, and zeolite Y.

In ASA, only a small percentage of the framework aluminum atoms generated Brønsted acid sites and those sites have low rates because of the low adsorption of alkane on its flat surface. Introducing micropores could enhance the rates of monomolecular cracking of alkanes by enhancing the sorption of alkanes. Such pores are preferentially introduced during the synthesis of high-silica ASA. Because the synthesis of zeolites requires thermal conditions and usually the use of expensive structure-directing agents, highly active ASAs would be attractive alternatives to zeolites. The stability of such material requires high Si/Al ratios.

The r.l.s. in the dehydrogenation of alkanes was the desorption of an alkene from the alkoxide species. Because the stability of this species is affected by the steric hindrance around the Brønsted acid site and by the flexibility of the framework, this
reaction depended on the framework type and ionicity, which is determined by the Si/Al ratio.

One important conclusion of this study is that the structural dependence of the reaction rates is affected by the species involved in the r.i.s. There is no general relationship between zeolite acidity and activity. A strong dependence on the Si/Al ratio will be observed when the stability of the alkoxide species is involved in the r.i.s. First-order reactions that involve proton transfer between the zeolite and the reactant depend on the pore size via the adsorption of the reactant. Building on these insights will eventually lead to the a priori prediction of the catalytic performance of existing and new types of zeolite structure.

The stability of aluminosilicates depended on the structure type and the Si/Al ratio. High-aluminum zeolites are instable when exposed to moisture, even more so when the Si/Al ratio is low. Both the structure and activity recovered after adsorption of a strong base, in agreement with earlier reports. The presence of water was essential for the complete recovery of the structure. To determine structure-performance relationships, a variety of structure-determining methods must be applied. In comparing the results of these methods, it must be kept in mind that different pretreatments often lead to different structures. For example, MAS NMR is performed after equilibrating the sample in an environment saturated with moisture, and infra-red is performed after heat-treatment under vacuum; these methods lead to a different structure.
List of publications and presentations

Chapter 3:
“Catalytic Activity of Brønsted Acid Sites in Zeolites: Intrinsic Activity, Rate-Limiting Step, and Influence of the Local Structure of the Acid Sites”
B. Xu, C. Sievers, S.B. Hong, R. Prins, J.A. van Bokhoven

Chapter 4:
“Strong Brønsted Acidity in Amorphous Silica-Aluminas”
B. Xu, C. Sievers, J.A. Lercher, J.A. Rob van Veen, R. Prins, J.A. van Bokhoven
Manuscript in preparation

Chapter 5:
“Reversibility of Structural Collapse in Zeolite Y: Alkane Cracking and Characterization”
B. Xu, F. Rotunno, S. Bordiga, R. Prins, J.A. van Bokhoven

Chapter 6:
“Effect of Framework and Extra-framework Aluminium on the Catalytic Activity of Zeolite Y”
B. Xu, S. Bordiga, R. Prins, J.A. van Bokhoven
Manuscript in preparation

Presentations:
“Solid-Acid Catalysts Characterized by Monomolecular Conversion of Propane”
B. Xu, R. Prins, J.A. van Bokhoven
*Fall Meeting of the SCS*, Zurich, Switzerland, October 2004 (Poster)

“Activity of Brønsted Acid Site in Solid-Acid Catalysts Characterized by Monomolecular Conversion of Propane: Amorphous Silica-Alumina & Zeolites”
B. Xu, J.A. van Bokhoven
*15th International Zeolite Conference*, Beijing, China, August 2007 (Oral)
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**Curriculum Vitae**

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<tr>
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<th>Xu Bin</th>
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<tbody>
<tr>
<td>Date of birth:</td>
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</tr>
<tr>
<td>Place of birth:</td>
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<td>Nationality:</td>
<td>P.R. China</td>
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