Doctoral Thesis

Synthesis, dealumination, and adsorption behavior of mordenite extrudates

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SYNTHESIS, DEALUMINATION, AND ADSORPTION BEHAVIOR OF MORDENITE EXTRUDATES

A dissertation submitted to the

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# TABLE OF CONTENTS

ACKNOLEDGEMENTS 3

SUMMARY 9

ZUSAMMENFASSUNG 11

1. INTRODUCTION TO THE PROJECT 13

1.1 References 15

2. REVIEW ON ZEOLITES 17

2.1 Introduction 17

2.2 Structure types 19

2.2.1 Mordenite 19

2.2.2 Other zeolites 22

2.2.2.1 Faujasite (zeolite Y) 22

2.2.2.2 ZSM-5 23

2.3 Synthesis 24

2.3.1 Synthesis from gels 25

2.3.2 Synthesis from clay materials 25

2.4 Modification 28

2.4.1 Ion exchange 28

2.4.2 Dealumination 30

2.4.2.1 Dealumination with mineral acids 30

2.4.2.2 Dealumination with organic acids 31

2.4.2.3 Dealumination with steam 31

2.4.2.4 Dealumination with SiCl₄ 32

2.5 Applications 33

2.5.1 Ion exchange 33
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5.2</td>
<td>Catalysis</td>
<td>34</td>
</tr>
<tr>
<td>2.5.3</td>
<td>Adsorption</td>
<td>35</td>
</tr>
<tr>
<td>2.6</td>
<td>References</td>
<td>37</td>
</tr>
<tr>
<td>3.1</td>
<td>Nitrogen adsorption</td>
<td>39</td>
</tr>
<tr>
<td>3.1.1</td>
<td>Surface area determination; the Brunauer, Emmett and Teller (BET) method</td>
<td>39</td>
</tr>
<tr>
<td>3.1.2</td>
<td>The t-plot method</td>
<td>41</td>
</tr>
<tr>
<td>3.1.3</td>
<td>Mesopore size distribution; the BJH method</td>
<td>43</td>
</tr>
<tr>
<td>3.2</td>
<td>Nuclear magnetic resonance spectroscopy</td>
<td>44</td>
</tr>
<tr>
<td>3.2.1</td>
<td>General considerations</td>
<td>44</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Solid state NMR</td>
<td>46</td>
</tr>
<tr>
<td>3.2.2.1</td>
<td>Aluminum NMR</td>
<td>48</td>
</tr>
<tr>
<td>3.2.2.2</td>
<td>Silicon NMR</td>
<td>49</td>
</tr>
<tr>
<td>3.2.2.3</td>
<td>Proton NMR</td>
<td>52</td>
</tr>
<tr>
<td>3.3</td>
<td>Atomic absorption spectroscopy</td>
<td>53</td>
</tr>
<tr>
<td>3.4</td>
<td>X-ray diffraction</td>
<td>55</td>
</tr>
<tr>
<td>3.5</td>
<td>Scanning electron microscopy</td>
<td>56</td>
</tr>
<tr>
<td>3.6</td>
<td>References</td>
<td>57</td>
</tr>
<tr>
<td>4.1</td>
<td>Sample preparation</td>
<td>59</td>
</tr>
<tr>
<td>4.1.1</td>
<td>Synthesis of mordenite extrudates</td>
<td>59</td>
</tr>
<tr>
<td>4.1.2</td>
<td>Ion exchange and dealumination</td>
<td>60</td>
</tr>
<tr>
<td>4.2</td>
<td>Characterization</td>
<td>61</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Nuclear magnetic resonance</td>
<td>61</td>
</tr>
<tr>
<td>4.2.1.1</td>
<td>$^{27}$Al MAS NMR</td>
<td>61</td>
</tr>
<tr>
<td>4.2.1.2</td>
<td>$^{29}$Si MAS NMR</td>
<td>62</td>
</tr>
<tr>
<td>4.2.1.3</td>
<td>$^1$H MAS NMR</td>
<td>62</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Nitrogen adsorption</td>
<td>64</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Atomic absorption spectroscopy</td>
<td>64</td>
</tr>
</tbody>
</table>
4.2.4 X-ray diffraction
4.2.5 Scanning electron microscopy

4.3 References

5. DEALUMINATION OF MORDENITE

5.1 Introduction

5.2 Results and discussion
5.2.1 Bulk composition
5.2.2 Textural properties
5.2.3 NMR analyses
5.2.3.1 $^{27}\text{Al}$ MAS NMR
5.2.3.2 $^1\text{H}$ MAS NMR
5.2.3.3 $^{29}\text{Si}$ MAS NMR
5.2.4 XRD and IR
5.2.5 Identification of the oxalate species
5.2.5.1 Equilibrium distribution
5.2.5.2 Sample synthesis
5.2.5.3 Analysis of the aluminum complex

5.3 Conclusions

5.4 References

6. MORDENITE EXTRUDATES

6.1 Introduction

6.2 Synthesis of mordenite extrudates
6.2.1 Reaction temperature and time
6.2.2 Variation of the calcination temperature
6.2.3 Presence of quartz after transformation to mordenite
6.2.4 Variation of reactant composition
6.2.5 Effect of different silica and kaolin sources

6.3 Dealumination of mordenite extrudates
6.3.1 Preliminary results
Table of contents

6.3.2 Effect of sodium exchange 117
6.3.3 Effect of high temperature calcination 119
6.3.4 Steam calcination 120
6.3.5 Comparison of powder and extrudate dealumination 122

6.4 Adsorption experiments 125
  6.4.1 Introduction 125
  6.4.2 Experimental
    6.4.2.1 Adsorption unit 126
    6.4.2.2 The adsorption process 127
    6.4.2.3 Solvents employed 128
    6.4.2.4 Adsorbents properties 130
  6.4.3 Results and discussion 130
    6.4.3.1 Adsorption on mordenite powder 130
    6.4.3.2 Adsorption on exchanged mordenite extrudates 133
    6.4.3.3 Adsorption on extrudates dealuminated with nitric acid 135
    6.4.3.4 Adsorption on extrudates dealuminated with oxalic acid 137

6.5 Conclusions 138

6.6 References 140

CURRICULUM VITAE 143
Summary

The aim of our study was to find a practicable synthesis method for self-supported extrudates, i.e., zeolites directly synthesized as aggregates without a binder, and a method for their dealumination. For this purpose, first the dealumination of mordenite powder was studied using oxalic and nitric acid. The dealuminated samples were characterized using different techniques: their elemental composition was determined by atomic absorption spectrometry, their textural properties by nitrogen adsorption and scanning electron microscopy, their crystallinity by X-ray diffraction, their framework aluminum content by aluminum and hydrogen nuclear magnetic resonance, and their defect content by silicon NMR.

It was found that oxalic acid was more effective than nitric acid in dissolving framework aluminum. Other differences in the dealumination behavior were that oxalic acid left many defects and a fair amount of extra-framework aluminum in the zeolite structure. Nitric acid, on the other hand, dissolves all extra-framework aluminum and leads to the formation of a secondary pore structure in the zeolite. The Si(0Al) peak in the $^{29}$Si NMR is split in several peaks due to the presence of different crystallographically inequivalent sites. These peaks are broadened to a single peak by the presence of framework as well as extra-framework aluminum. An aluminum oxalato species found in the mordenite pores after dealumination with oxalic acid was identified as aluminum dioxalate.

Mordenite extrudates were prepared using a precursor made of clay, a silica source, and some waterglass. After calcination, these precursors were converted into self-supported mordenite extrudates in the presence of waterglass. The synthesis is mainly influenced by the reaction temperature and the precursor com-
Summary

position. A small amount of quartz is always present after transformation into mordenite extrudates, it originates from the calcination of kaolin. The pores of the mordenite extrudates were completely blocked after the synthesis. An ion exchange, however, was sufficient to obtain a highly porous material. Comparison of the as-synthesized and the exchanged material showed that the pore blockage is due to the presence of sodium as a counterion and some sodium silicate species left after the synthesis. Dealumination of mordenite extrudates was always less efficient than mordenite powder. This behavior is attributed to the presence of a hard-to-dealuminate unreacted precursor phase that acted as a matrix holding the extrudates together.

Dealuminated mordenite extrudates were used for the adsorption of a mixture of organic solvents composed of methanol, methyl ethyl ketone, n-pentane, toluene, and p-xylene. The adsorption capacity of the extrudates is comparable to that of mordenite powder, although the presence of the unreacted precursor slows the desorption of methanol and methyl ethyl ketone. Apolar molecules were found to desorb earlier than polar ones because they only weakly interact with the zeolite framework. The knowledge about mordenite dealumination helped explain the influence of hydroxyl groups and extra-framework aluminum on the adsorption behavior of polar molecules. In particular, methyl ethyl ketone is preferentially adsorbed on extra-framework aluminum and silanol groups, while water and methanol adsorb preferentially on acidic hydroxyl groups. In addition, water also compete with methanol and methyl ethyl ketone for adsorption on silanol groups.
Zusammenfassung

Ziel dieser Arbeit war die Suche nach einer Synthesemethode für verformte Zeolith-Extrudate, d. h. Zeolithe, die ohne Binder-Zusatz Aggregate bilden und eine Methode für deren Dealuminierung. Zu diesem Zweck wurde zuerst die Entaluminierung von pulverförmigem Mordenit untersucht. Die entaluminierten Proben wurden mittels verschiedener Verfahren charakterisiert: die Zusammensetzung mittels Atomabsorptionspektrometrie, die Oberfläche und die Porenverteilung mittels Stickstoffadsorption und Elektronenmikroskopie, die Kristallinität mit Röntgendiffraktion, die Menge Gerüstaluminium mit $^{27}$Al- und $^1$H-Festkörperkernresonanzspektroskopie und die Anzahl an Defekten mittels $^{29}$Si NMR.


Zusammenfassung


1. Introduction to the project[1,2]

Nowadays exhaust fumes are mainly purified using activated carbon, however, zeolite are a good alternative. In fact, aluminum–poor zeolites are gaining a greater importance, opening new perspectives for the adsorption of volatile organic compounds (VOC) currently adsorbed over active carbon.

Active carbon has a different adsorption behavior than zeolites:

• exhaust fumes usually have a high water content. Water adsorption on activated carbon is one of the major drawbacks of this material since it reduces its adsorption capacity and generates high regeneration costs;
• carbon does not have a regular pore structure. This a disadvantage when a selective adsorption is needed;
• adsorption of a solvent that can polymerize, as for instance styrene, is also problematic, since the polymerized material can not be desorbed or burned away at the low regeneration temperatures that have to be employed for carbon;
• some solvents, as for instance some ketones, can react with impurities present in carbon, generating a dangerous exothermic reaction that can damage the adsorbent.

The use of zeolites for adsorptive waste gas purification was limited by the preferential uptake of water by conventional aluminum–rich zeolites. In the past years, however, zeolites with a high hydrophobicity have been developed. Their hydrophobic character can be tuned by varying the aluminum content, the higher the Si/Al ratio the more hydrophobic the zeolite.

Other advantages of zeolites are that they can be easily regenerated at high temperature so as to facilitate the desorption of polymerizing and high boiling
products, that they are not combustible, and that they are temperature-resistant and can therefore withstand employment temperatures up to 1000°C.

Possible applications could be the removal of VOC, as for instances in the purification of humid exhaust fumes of the food and paint industry, and the adsorption of oil traces in fluoro-carbons used in refrigerant systems; in oil refining processes, traces of substances resulting from preceding production steps, have to be removed in order not to influence the following processes.

Zeolites employed as adsorbents should be used in the form of aggregates, because the use of zeolite powder would cause a large pressure drop in an adsorber column. Other requirements of these aggregates are that they must have adequate crush strength and attrition resistance, and enough macroporosity to minimize diffusion resistance.

The most widely used method of aggregation is currently a post–synthesis treatment in which the zeolite is mixed with about 30 % by weight of binder, usually a clay. This, however, has two main disadvantages: it often influences the selectivity and kinetics of the adsorption process and it lowers the adsorption capacity of the final material due to the presence of an inactive component diluting the active zeolite phase.

The aim of this work is to find a practicable synthesis and dealumination method for self-supporting extrudates, i.e., zeolites directly synthesized as aggregates without a binder.
1.1 References


2. Review on zeolites

2.1 Introduction

Zeolites were first recognized as a new type of mineral in 1756 by the Swedish mineralogist A. F. Cronstedt [1]. The observation that certain minerals developed gas on strong heating led to the name “zeolites” to such materials from the Greek zeo (to boil) and lithos (stone).

Zeolites are crystalline, hydrated aluminosilicates with a three-dimensional framework structure which consists of four-connected TO₄ tetrahedra (T = Al, Si) linked through oxygen atoms. Substitution of Al for Si generates a charge imbalance necessitating the inclusion of non-framework cations. The cations, which are mobile and exchangeable, are mostly alkali metal or alkaline earth metal ions. Zeolites can therefore be represented by the formula:

$$M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot wH_2O$$

where M represents the non-framework metal cation, n is its valence, and w is the moles of water contained in the zeolitic voids. On heating, hydrated zeolites reversibly release water; many zeolites can be almost completely dehydrated without major alteration of their crystal structure by calcination at 400 – 500°C, leaving solids with a considerable free pore volume which may account to up to 50 % of the crystal by volume.

Most of the chemical and physical properties of the zeolites are essentially determined by the aluminum content of their framework, usually expressed as Si/Al ratio. According to the Loewenstein rule [2], Al–O–Al groups cannot oc-
cur in crystalline aluminosilicates. Hence, a Si/Al ratio lower than one is impossible for zeolites.

Many zeolites occur as minerals formed by the natural alteration of volcanic ash in alkaline environment over long periods of time, as for instance analcime (ANA), clinoptilolite (HEU), and mordenite (MOR). Zeolites became of industrial importance in the 1950s, when synthetic materials became available on an industrial scale. Since then, world consumption of synthetic zeolites in applications such as ion exchange, adsorption, and catalysis has grown continuously.

Depending on the structure type, zeolites contain regular channels or interlinked voids. The channel system is, in some instances, one dimensional whereas in other it is formed by intersecting channels producing a two- or three-dimensional channel system. The latter are preferred since they provide rapid intracrystalline diffusion in adsorption and catalytic application.

The principal characteristics of all zeolites are the regular structures and the dimensions of the cavities or channels which are of the same order of magnitude as molecular diameters, enabling the zeolites to function as molecular sieves. The various zeolite structures differ in the type and dimension of their pore system, as well as in the size of their pore aperture. Narrow-pore, medium-pore, and wide-pore zeolites have different pore apertures formed by rings of 8, 10, or 12 T atoms, with corresponding diameters of 3.5 – 4.5, 4.5 – 6.0, and 6.0 – 8.0 Å.

The description and classification of the topology of zeolites is based on the concept of larger units known as secondary building units. These can consist, for example, of simple rings and prisms of various size which are assembled from the primary building units, AlO₄ and SiO₄ tetrahedra, as depicted in Fig. 2.1.
Fig. 2.1: Secondary building units (SBU) of the zeolite structures. The dots represent the T atoms whereas the lines summarize the T–O–T bonds. Oxygen atoms are omitted for clarity.

2.2 Structure types

2.2.1 Mordenite

Mordenite is a large pore zeolite with two-dimensional pores, its structure, determined by Meier in 1961 [3], is built from 5 – 1 SBU’s. The pore system of mordenite, depicted in Fig. 2.2, consists of main elliptical channels with dimensions 6.5 x 7.0 Å oriented along the c axis which are connected by tortuous pores of 2.6 x 5.7 Å oriented in the b direction [4]. The latter are formed by 3.9 Å side pockets of the main channels which are connected by elliptical 8 rings.
Chapter 2

Fig. 2.2: Mordenite framework viewed along \([0 \ 0 \ 1]\)

Since these channels are too small for most molecules they do not participate in diffusion and catalysis processes and mordenite is therefore generally regarded as a monodimensional zeolite. The total estimated void volume in mordenite is 0.21 cm\(^3\)/g, of which the main channels enclose 0.11 cm\(^3\)/g [5].

Fig. 2.3: Framework unit cell structure of mordenite. The Arabic numerals denote tetrahedral positions as indicated by Meier [3] while the Roman numerals denote positions occupied by cations as suggested by Mortier et al. [6].
The unit cell is orthorhombic with space group Cmcm and cell constants $a = 18.13 \, \text{Å}$, $b = 20.49 \, \text{Å}$, and $c = 7.52 \, \text{Å}$. The ideal composition of the cell is $\text{Na}_8[\text{Al}_8\text{Si}_4\text{O}_{24}] \cdot 24 \, \text{H}_2\text{O}$. The framework density is 17.2 T atoms per 1000 Å$^3$.

In the mordenite unit cell four different crystallographic sites for the T atoms are present which are indicated in Fig. 2.3 with Arabic numerals. The roman numerals in the same picture denote the five positions occupied by cations in naturally occurring mordenites, as proposed by Mortier et al. [6]. The unit cell contains 16 T1, 16 T2, 8 T3, and 8 T4 sites.

In 1995 Takaishi et al. [7] studied the position of the aluminum atoms in the framework and introduced a new method to determine the ordered distribution of aluminum atoms in mordenite. They determined all the possible connectivity relations between the different T sites in a mordenite cell. Out of the hundreds of conceivable configuration patterns only one is realized in nature. They proposed a stability rule for the distribution of Al atoms complementing the Loewenstein's Al–Al avoidance rule. The new rule postulates that five-membered T–rings, plentifully contained in high-siliceous zeolites, can not contain two Al atoms. The new rule is generally valid for high-siliceous zeolites, but not always for low-siliceous ones.

Mordenite exists in two forms: Large Port (LP) and Small Port (SP) mordenite. The effective opening of the LP mordenite (8.0 Å) is consistent with the crystallographic data, while SP mordenite, on the contrary, can only adsorb molecules with a kinetic diameter smaller than about 4.2 Å, as reported by Barrer and Peterson [8]. To explain the difference between LP and SP mordenite three hypotheses have been proposed: the first one is related to the localization of the cations in SP mordenite, the second to the presence of amorphous material in the pores, and the last one to stacking faults which disrupt the continuity of the channels.
These three hypotheses were discarded by Raatz et al. [9,10]. The first one, which attributes the pore blocking to the presence of sodium cations, was rejected because an almost completely exchanged SP mordenite showed the same low adsorption of benzene as the starting material. The second hypothesis, which related the lower adsorption to the presence of amorphous material in the mordenite pores, was dismissed since a deep bed calcination of an ammonium exchanged SP mordenite that dealuminated the framework and formed extraframework aluminum species resulted in an adsorption capacity very close to that of a LP mordenite.

Defects of the glide vector [0 0 1/2], which do exist in SP mordenite, can not explain the pore blocking phenomenon since these defects are parallel to the direction of the main channel [0 0 1] [11] and also because the defects are still present after the SP–LP transition. Raatz et al. suggested that the pore constriction is due to the presence of framework aluminum in strategic sites (where defects are present) which must be removed in order to obtain LP characteristics. The authors observed that unblocking occurs if at least 20 % of framework aluminum was extracted.

2.2.2 Other zeolites

Although this work was focused on mordenite, a short review of some other types of zeolites is given here.

2.2.2.1 Faujasite (zeolite Y)

Zeolite Y has a three–dimensional zeolite structure, see Fig. 2.4. The Secondary Building Units are 6–6 double rings which are combined together to form a polyhedral structure consisting of linked sodalite cages. The diameter of the
latter is 6.6 Å. Only the smallest molecules can diffuse through the 2.2 Å six ring openings of the sodalite cages, however.

![Framework of zeolite Y viewed along [1 1 1]](image)

The main feature of this zeolite is the presence of a super cage with an internal diameter of 12.7 Å which can be entered through four twelve-membered oxygen rings having a diameter of 7.4 Å. Adsorbed molecules can then diffuse in every direction.

The faujasite crystallographic structure is cubic with the space group Fd3m. The unit cell dimension amounts to 24.74 Å [4].

### 2.2.2.2 ZSM–5

ZSM–5 is a medium port zeolite. The pore structure consists of a three-dimensional channel network with perpendicular intersections, as depicted in Fig. 2.5. In the b direction the channels have a zig-zag arrangement with pore openings of 5.5 x 5.1 Å, while the straight channels, perpendicular to the sinusoidal ones, have dimensions of 5.3 x 5.6 Å [4].
Chapter 2

Fig. 2.5: Channel system of ZSM–5

A post–synthesis treatment is generally not necessary since zeolite ZSM–5 can be directly obtained with a Si/Al that can vary over a wide range. Even a pure silicon framework can be synthesized (silicalite).

2.3 Synthesis

Synthetic zeolites are produced under conditions similar to those that led to formation of natural zeolites, i.e., by the mineralizing effects of water and OH–ions on reactive sources of silica and alumina in the presence of cations. However, the time required for their formation is shortened by using considerably higher temperatures and higher pH values. The synthesis limit of the Si/Al ratio of mordenite without using organic templates is presently about 10 [12], to obtain highly siliceous mordenite a post-synthesis treatment is necessary.

There are basically two methods for the commercial preparation of zeolites: the synthesis from gels and the synthesis from clay minerals.
2.3.1 Synthesis from gels

Various silica and alumina sources can be used as raw materials. The main silica sources used for the large-scale production of zeolites are sodium silicate solutions and precipitated amorphous silicas. The most common alumina source is sodium aluminate. A method for accelerating and directing crystal growth is the introduction of seed crystals; the induction period is eliminated and crystal growth starts immediately. A further reactant that provides $\text{OH}^-$ ions is also necessary. Sodium hydroxide solution is usually used except for those few cases in which the presence of $\text{Na}^+$ ions prevents the formation of the desired zeolite type.

The synthesis of high-silica zeolites often has to be carried out in the presence of organic templates, such as alkylammonium salts, alkylammonium hydroxides or amines.

2.3.2 Synthesis from clay materials

Clays are also suitable raw materials for the production of zeolites. The most important processes use minerals of the kaolin group. Kaolin, its structure reported in Fig. 2.6, has a two-layer crystal structure: a sheet of silica tetrahedra and an alumina sheet; adjacent cells are spaced about 7.1 Å across the [0 0 1] plane. In order to activate the clay for the reaction, it has been found necessary to convert the kaolin into metakaolin by thermal treatment.

Metakaolin is believed to be a defect phase in which tetrahedral silica layers of the original clay structure are largely retained; adjacent are the $\text{AlO}_4$ tetrahedral units derived from the original octahedral layer of the kaolin. Maximum reactivity for metakaolin can be obtained by producing a maximum concentration
Kaolin undergoes several transitions when heated in air as described by Breck [14]. The first of these takes place at about 550°C, and produces the disordered metakaolin phase by an endothermic dehydroxylation reaction. The metakaolin is then stable to about 925°C where it rearranges to give a defect aluminum–silicon spinel, also referred to as gamma–alumina type structure. This phase converts to mullite at about 1050°C.

\[
\begin{align*}
2 \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 & \xrightarrow{550-600^\circ\text{C}} 2 \text{Al}_2\text{Si}_2\text{O}_7 + 4 \text{H}_2\text{O} \\
2 \text{Al}_2\text{Si}_2\text{O}_7 & \xrightarrow{925-950^\circ\text{C}} \text{Si}_3\text{Al}_4\text{O}_{12} + \text{SiO}_2 \\
3 \text{Si}_3\text{Al}_4\text{O}_{12} & \xrightarrow{1050^\circ\text{C}} 2 \text{Si}_2\text{Al}_6\text{O}_{13} + 5 \text{SiO}_2
\end{align*}
\]

Since kaolin has a Si/Al ratio = 1, in order to form zeolites which have Si/Al ratios greater than 1, additional SiO\textsubscript{2} must be added to the reaction mixture. The
additional silica may be added in the form of sodium silicate or other sources, such as precipitated silica.

The synthesis of zeolites from kaolin is of industrial interest because it allows production of binder–free extrudates and granules. The initial kaolin may be shaped by extruding into pellets and subsequently dried and calcined at the appropriate temperature. This product can then be converted into a shaped zeolite. Typical zeolites produced this way are NaY and NaA.

The process for the in–situ production of zeolite Y, invented by Brown et al. [15], is of major importance. According to the authors the catalyst is prepared by first calcining kaolin at about 1000°C in order to convert it to a spinel. For two metakaolin moles, this process forms one mole of reactive silica that can be used as the silica source needed to form zeolite Y. Microgranules are then prepared from a mixture containing spinel, uncalcined kaolin, sodium silicate, and seed crystals. The next step is a calcination in order to transform kaolin into metakaolin. NaY zeolite is then formed by treatment with sodium hydroxide and sodium silicate at around 100°C. The role of the spinel is to function as an unreactive alumina source able to provide a stable matrix which binds the zeolite together.

Also zeolite NaA can be manufactured from clays, although this process is less often used, as the presence of impurities, especially iron, can impart an undesirable color to the product. With this method zeolite NaA is obtained by reacting metakaolin with sodium hydroxide at around 100°C [16]. A special variation is the process employed by Mizusawa Industrial Chemicals Ltd. in which an acid–treated clay is used [17]. By treating the clay with a mineral acid such as sulfuric acid, the metallic elements Al, Mg, Ca, Fe, and so on, are eluted, and the clay structure is destroyed into a silicic acid gel which has an activated reactivity. The zeolite is then obtained by mixing a dispersed solution of the gel with sodium aluminum solution and let it react to zeolite.
2.4 Modification

The synthesis step determines the structure type of the zeolite as well as the size and shape of its crystals. Only zeolites used as detergent builders can be used as-synthesized. For use as a catalyst or adsorbent, their properties must be fine tuned and this is mainly performed by ion exchange and dealumination.

2.4.1 Ion exchange

Beside being used in the production of zeolitic adsorbents for varying the pore size as will be described later in this chapter, ion exchange is also important in the synthesis of zeolite catalysts. The aim is usually to produce Brønsted acid sites. There are basically two ways to prepare a proton zeolite.

A direct treatment with diluted mineral acids, for instance with 1 M HCl at reflux temperature, as shown in Fig. 2.7, is generally only feasible for intermediate-silica or high-silica zeolites, because this treatment involves the risk of dealuminating the zeolite framework.

For aluminum–rich zeolites such as NaY, on the other hand, an indirect

![fig2.7](image)

Fig. 2.7: Direct ion exchange with a mineral acid
route has to be followed since dealumination in this case could result in a partial collapse of the zeolite framework. Zeolites, as depicted in Fig. 2.8, are ion-exchanged with an ammonium salt, usually ammonium nitrate resulting in the ammonium form of the zeolite, subsequently calcined at 500°C to remove NH₃ and obtain the Bronsted form.

![Sodium form](image1)

![Ammonium form](image2)

![H form](image3)

Fig. 2.8: Indirect ion exchange with an ammonium salt.

Not every zeolite can be exchanged to a good extent in one step. In zeolite NaY, in fact, sodium cations located in sodalite cages can not be replaced under mild conditions. Therefore, the zeolite is calcined after each exchange step causing the sodium ions to migrate out of the sodalite cages into the supercages where they are exchangeable. The procedure can be repeated several times until the desired degree of exchange is achieved.
2.4.2 Dealumination

The number and strength of acid sites depends on the Si/Al ratio of the zeolite framework. Decreasing framework aluminum content is associated with a decrease in the number of acidic OH groups, but generally the strength of the remaining sites increases.

Dealumination is mainly carried out on zeolites that have sufficient stability to survive the sometimes drastic treatment conditions without appreciable loss of crystallinity such as mordenite or zeolite Y. High-silica zeolite ZSM-5, on the other hand, can be directly produced by hydrothermal synthesis and a post synthetic treatment is not used. The catalytic properties of dealuminated zeolites differ from those with the same Si/Al ratio produced directly, since the dealumination of the structure can lead to the production of crystal defects, creation of a secondary pore system, and formation of extra-framework aluminum.

2.4.2.1 Dealumination with mineral acids

The simplest method, often carried out with mordenite, is to extract aluminum with a mineral acid such as nitric or hydrochloric acid as depicted in Fig. 2.9.

![Dealumination with mineral acids](image)

Fig. 2.9: Dealumination with mineral acids
This method can not be applied for zeolite Y because it causes defects leading to a destruction of the framework structure. For this zeolite, the process is only possible when used in combination with a preliminary dealumination by another method in which not only aluminum is forced to migrate out of the framework but also some isomorphic replacement of aluminum by silicon takes place.

2.4.2.2 Dealumination with organic acids

Instead of mineral acids, organic acids such as oxalic acid [18] or H₄EDTA [19], can be employed as dealuminating agents. The peculiarity of these acids is their ability to form strong complexes with aluminum. Due to its acidity constant pKₐ = 1.46, oxalic acid, for instance acts both as a hydrolyzing and as a chelating agent forming a trioxalato aluminum complex with a high complexation constant (log ß₃ = 15.1) [20]. This complexation is the driving force of the aluminum extraction by this acid.

2.4.2.3 Dealumination with steam

Calcination in the presence of water vapor is especially carried out on zeolite Y in the NH₄⁺ form [21]. This process, as shown in Fig. 2.10, causes aluminum atoms to migrate from the framework into the cavities, forming extra-framework aluminum which can be removed by washing with acids. Steaming causes the clustering of the defects, which can be detected by the formation of mesopores. The characteristic of this process is that the resulting lattice vacancies are filled by silicon atoms from amorphous SiO₂ originating from destroyed crystal domains. The resulting zeolites have a framework structure with an increased Si/Al ratio and a very high hydrothermal stability. They are today
known as ultrastable Y zeolite (USY) and are important components of fluid catalytic cracking (FCC) catalysts.

2.4.2.4 Dealumination with SiCl$_4$

Dealumination of zeolite Y and mordenite by complete isomorphous replacement of aluminum atoms by silicon atoms is possible using gaseous silicon tetra-chloride, see Fig. 2.11.
Fig. 2.11: Dealumination with SiCl₄

The reaction products are removed from the cavities by washing with water. It is important to notice that only zeolites in the sodium form are dealuminated this way, because the presence of Brønsted protons would result in the formation of HCl which could in turn dealuminate the framework.

In contrast with the hydrothermal dealumination, the formation of a secondary pore structure is not observed, the overall framework structure remains intact.

2.5 Applications

2.5.1 Ion exchange

The most important use of synthetic zeolites is as builders in detergents: 85% of zeolites produced in 1994 were used for this purpose [22].

Phosphates were long regarded as good builders for detergents. Their prime function in detergents is to reduce the activity of the hard ions such as Ca²⁺ and Mg²⁺ in the wash water by complexing. High phosphate levels in lakes and rivers, however, constitute an ecological problem, leading to eutrophication and excessive growth of algae. For this reason, restrictions on phosphate content of detergent and cleaning agents has been introduced in many countries. The
search for a replacement led to the development of zeolite NaA as a water-insoluble builder. This zeolite is able to replace Ca$^{2+}$ and Mg$^{2+}$ in solution with ions such as Na$^+$. 

### 2.5.2 Catalysis

10% of zeolites produced in 1994 were used in catalysis [22]. At present, FCC is the largest scale industrial process employing zeolite catalysts. The zeolite catalysts are more active and give higher gasoline yields and less coke formation than the amorphous silica–alumina catalyst formerly used. Today zeolite Y occupies the dominant position for FCC catalysts.

A unique feature of the use of zeolites as catalysts is that the reactions can be shape-selective. Shape-selectivity can be divided in three categories [23]:

In reactant shape selectivity, only reactants that can penetrate into the pore system by virtue of their slender shape and which can thus diffuse to the catalytic sites of the interior surfaces take part in the reaction (Fig. 2.12).

![Reactant shape selectivity](image)

Fig. 2.12: Reactant shape selectivity

Product shape selectivity is when the bulkier of the possible products cannot diffuse out of the pores. If the reaction is reversible as in Fig. 2.13 then the product is converted into the slimmest one, while when the reaction is irreversible the product accumulates in and thus blocks the pore.
Restricted transition-state shape selectivity occurs if the reaction pathway in the zeolite is directed by spatial requirements of the possible transition-state, as in Fig. 2.14.

2.5.3 Adsorption

About 5% of the zeolites produced in 1994 were estimated to have been used in adsorption [22]. Along with silica gels, alumina, activated carbons, carbon–molecular sieves, and organic resins, zeolites are important industrial adsorbents with a wide range of uses. Their diversity is due to the fact that zeolites not only have a high adsorption capacity but are also highly selective, so that substances may be separated and purified. Compared with other adsorbents, these zeolites have the advantage of a high thermal stability, nonflammability, and, depending on the Si/Al ratio, a pronounced hydrophobic charac-
ter. In addition to these, regeneration is possible by treating the zeolite at elevated temperatures.

Three factors can influence the adsorption behavior of zeolites. The first one is the size of the pores. The regular pores of zeolites allow separation of substances of different molecular dimensions. This selectivity can be influenced by post-synthesis treatment. For instance, the apparent pore size of zeolite NaA can be varied by exchanging its counterions: replacement of Na\(^+\) by Ca\(^{2+}\) increases the apparent pore size whereas replacement of Na\(^+\) by K\(^+\) narrows it.

The second factor is the adsorption kinetics, i.e. the selection according to differences in the rate of diffusion of two or more coadsorbed molecules into the zeolite pores.

The aluminum content is also a factor influencing the adsorption behavior. In aluminum-rich zeolites in which the negative framework charge is balanced by cations, electrostatic interactions predominate. This favors adsorption of substances with a large dipole moment, e.g. H\(_2\)O and NH\(_3\), or quadrupole moment, e.g. N\(_2\). In contrast, increasing silicon content leads to an increasingly hydrophobic character and the adsorption is then governed by van der Waals forces.
2.6 References


3. Zeolite characterization

3.1 Nitrogen adsorption

Textural properties of zeolites have a great importance. The analysis of nitrogen adsorption isotherms is therefore one of the most important technique since it allows the determination of the total surface area and the pore distribution in the measured material.

3.1.1 Surface area determination: the Brunauer, Emmett and Teller (BET) method

In 1938 Brunauer, Emmett and Teller were able to arrive at their well known equation for multimolecular layer adsorption by adopting the Langmuir model. This model postulates a state of dynamic equilibrium in which the rate at which molecules from the gas phase condense onto bare sites is equal to the rate at which molecules evaporate from occupied sites. Furthermore, they made the following simplifying assumptions:

- that in all layers except the first the heat of adsorption is equal to the molar heat of condensation;
- that in all layers except the first the evaporation–condensation conditions are identical;
- that when $p = p^*$, the adsorptive condenses to a bulk liquid on the surface of the solid, i.e. that the number of layers becomes infinite.
By summation for an infinite number of layers the following equation was obtained:

\[
\frac{p}{V \cdot (p^\circ - p)} = \frac{1}{V_m C} + \frac{(C - 1) \cdot p}{V_m C \cdot p^\circ}
\]

where \( V \) is the volume of the adsorbed molecules at pressure \( p \), \( V_m \) is the gas volume corresponding to the molecules adsorbed in a monolayer, and \( p^\circ \) the saturation vapor pressure of the gas at the measuring temperature.

The constant \( C \) depends exponentially on the heat of adsorption of the first and the next layers. \( V_m \) and \( C \) can be experimentally determined; by plotting \( p/V \cdot (p^\circ - p) \) vs. \( p/p^\circ \) a straight line can be found whose slope is \( (C-1)/V_m \cdot C \) and intercept \( 1/V_m \cdot C \).

The volume obtained for the monolayer allows the surface area of the sample to be determined using the area occupied by a single adsorbate molecule, a value derived from the assumption of close packing at the surface. For nitrogen a surface area of \( A_m = 16.2 \, \text{Å}^2 \) has been calculated.

The surface area of the adsorbent can therefore be found with the following equation:

\[
A_{\text{BET}} = \frac{V_m N_A A_m}{V_{\text{mol}}}
\]

where \( N_A \) is the Avogadro constant and \( V_{\text{mol}} \) the molar volume of the adsorbate.

In order to get proper results from this method it is necessary that the adsorption isotherm shows a distinct knee, meaning that the monolayer adsorption does not overlap with the multilayer one [1].

While the BET model of adsorption can be criticized for treating all adsorption sites on a surface as energetically identical, neglecting interactions among neighboring adsorbate molecules in the same layer, and not accounting for a
diminution of adsorption forces as outer layers build and distance from the surface increases, it has achieved wide usage for surface area evaluation.

3.1.2 The $t$-plot method

Since the profile of an isotherm depends on the properties of both the adsorbed gas and the adsorbent, a method for its normalization has been developed by Lippens and de Boer [2]. This method allows the determination of external surface area and pore volume.

For this purpose the experimental isotherm is compared with a standard isotherm (calculated or experimentally measured) of a non porous reference substance having the same surface characteristics as the analyzed material and, instead of the relative pressure $p/p^e$, the layer thickness of nitrogen $t$ is employed. $t$ is proportional to the number of adsorbed molecules and the mean thickness of a single layer. It is also assumed that $t$ increases continuously by raising the pressure.

$$ t = \frac{n}{n_m} \cdot \sigma $$

where $n$ is the number of adsorbed nitrogen molecules, $n_m$ the number of adsorbed molecules in a monolayer and $\sigma$ the mean thickness of a single layer (for nitrogen $\sigma = 3.54 \text{ Å}$). For a quantitative evaluation of the data the adsorbed gas volume is plotted against $t$.

In case the sample is a non porous substance, the $t$-plot is just a straight line through the origin whose slope can be used to calculate the surface area of the material.

If the adsorbent contains mesopores, capillary condensation will occur in each pore when the relative pressure reaches the critical condensation pressure,
a value which is related to the radius of the pore by the Kelvin equation. When capillary condensation takes place, the uptake at a given pressure will be enhanced by the amount of adsorbate condensing in the pores and the t-plot will therefore show an upward deviation commencing at the relative pressure at which the finest pores are just filled.

On the other hand, if micropores are present in a solid, the uptake is enhanced in the low pressure region and the isotherm is correspondingly distorted, as in Fig. 3.1. The high-pressure branch is still linear (provided mesopores are absent), but when extrapolated to the adsorption axis it gives a positive intercept which is equivalent to the micropore volume (MV). The slope of the linear branch is now proportional to the external surface area (ESA) of the solid.

![Fig. 3.1: Typical t-plot of a zeolite sample. From this plot the micropore volume and the external surface area can be determined.](image)

Fig. 3.1: Typical t-plot of a zeolite sample. From this plot the micropore volume and the external surface area can be determined.
3.1.3 Mesopore size distribution: the BJH method

Mesopores generally are defined as pores having widths between 20 and 500 Å and macropores as pores with widths greater than 500 Å. It is well established that the pore space of a mesoporous solid fills with condensed adsorbate at pressures somewhat below the prevailing saturated vapor pressure of the adsorptive. When combined with a correlating function that relates pore size with critical condensation pressure, this knowledge can be used to characterize the mesopore size distribution of the adsorbent. The correlating function most widely used is the Kelvin equation:

$$\ln \left( \frac{p^*}{p^o} \right) = -\left( \frac{2\gamma v \cos \theta}{R T r_m} \right)$$

where $p^*$ is the critical condensation pressure, $\gamma$ the liquid surface tension, $v$ the molar volume of the condensed adsorptive, $\theta$ the contact angle between the solid and condensed phase, and $r_m$ the mean radius of curvature of the liquid meniscus.

The procedure for calculating pore size distributions using the Kelvin equation involves an imaginary emptying of condensed adsorptive in the pores in a stepwise manner as the relative pressure is likewise decreased. The calculation method follows generally that described by Barrett, Joyner, and Halenda [2], hence called the BJH method.

When calculating from the desorption branch of the isotherm, the amount of adsorptive lost in each step (after conversion from a gas volume at standard conditions to a liquid volume) represents the core volumes of the pores emptied in that step. On the pore walls, however, there is still an adsorbed layer with thickness $t$. By substituting $(r-t)$ for $r_m$ in the above equation, a value of the pore radius $r$ is calculated.
Chapter 3

3.2 Nuclear magnetic resonance spectroscopy

In 1946 the discovery of nuclear magnetic resonance (NMR) led to the development of NMR spectroscopy. Since then this technique has gained increased popularity due to the unique information that can often be derived from the analysis of the spectra and due to the relative easy of use thanks to the introduction of other techniques as for instance Fourier transformation and high magnetic fields.

From a NMR spectrum we can typically obtain information on the surroundings of the atom (from the chemical shift) and the number of equivalent nuclei (from the integral of the signal).

3.2.1 General considerations

Many nuclei, assumed to be spherical and to rotate about an axis, possess spin angular momentum $\vec{p}$ and a magnetic moment $\vec{\mu}$ which are associated with the following equation:

$$\vec{\mu} = \gamma \cdot \vec{p}$$

where $\gamma$, the magnetogyric ratio, is a coefficient of proportionality specific for each nucleus that can be experimentally determined.

The magnitude of the angular momentum is quantized according to:

$$p = \frac{h}{2\pi} \sqrt{I \cdot (I + 1)}$$

where $h$ is Planck's constant and $I$ the nuclear spin. Nuclei with $I = 0$, such as $^{12}$C and $^{16}$O, do not possess a nuclear magnetic moment and can not be observed by NMR spectroscopy.
If a nucleus is placed in a static magnetic field $B_0$, the angular momentum takes up an orientation such that its component $P_z$ along the direction of the field is a multiple $m$ of $\hbar/2\pi$, where $m$ is the magnetic or directional quantum number, and can take any of the values $m = 1, 1-1, \ldots, -1$. This behavior is called directional quantization.

Each value of $m$ corresponds to a different orientation of the nuclear spin and therefore of the nuclear magnetic moment too. From this follows that the $(2I + 1)$ orientations of the nucleus have different energies. When the sample is exposed to electromagnetic radiation of frequency $\nu_1$, resonance occurs if the energy separation of the levels matches the energy of the photons in the electromagnetic field. At resonance there is strong coupling between the nuclear spins and the radiation, and strong absorption occurs as the spins make the transition from one energy level to the other, i.e. they reverse their orientation. This is ob-

![Diagram](image_url)

Fig. 3.2: Transitions between the two levels $E_{-\frac{1}{2}}$ and $E_{+\frac{1}{2}}$ will be induced by electromagnetic radiation of frequency $\nu_1$, provided that $\hbar \nu_1 = \Delta E$. 

\[
\Delta E = E_{-\frac{1}{2}} - E_{+\frac{1}{2}} = \frac{\hbar}{2\pi} \gamma \cdot B_0 = \hbar \cdot \nu_1
\]
served as a signal (Fig. 3.2)

The resonance condition is therefore satisfied when:

\[ v_1 = \frac{\gamma}{2\pi} B_0 \]

Modern methods of detecting the energy separation between nuclear spin states are more sophisticated, however, than simply looking for the frequency at which resonance occurs. The decisive step forward was achieved through pulsed NMR spectroscopy. This method uses a radiofrequency pulse to excite simultaneously all nuclei of one species in the sample. In fact, instead of having a generator that operates at a fixed frequency, the generator is switched on for only a short time \( \tau_p \) so as to obtain a pulse which contains not just the frequency \( v_1 \) but a continuous band of frequencies symmetrical about the center frequency \( v_1 \). The bandwidth is proportional to \( \tau_p^{-1} \). The choice of the generator frequency \( v_1 \) is determined by \( B_0 \) and the nuclide to be observed. With this method we do not obtain a typical NMR spectrum, only an interferogram or free induction decay curve (FID) with a time axis as abscissa that can not be directly interpreted in this form. It can, however, easily be transformed into a spectrum where the abscissa is a frequency axis by a common mathematical operation called Fourier transformation.

### 3.2.2 Solid state NMR

The principal difficulty with the application of NMR to solids is the low resolution that is characteristic of solid samples. In solids the rapid, random motion characteristic of liquids is strongly constrained and the nuclear spin interactions causing large line broadening are not averaged. This means that in a
solid system the interactions are anisotropic, i.e. they depend on the orientation of the crystal.

Problems of resolution and linewidth are not the only features that plague NMR studies of solids. In a pulse experiment lengthy delays are necessary, of several seconds, between successive pulses so that the spin system has time to revert to equilibrium. Moreover, because lines are so broad, very high powers of radiofrequency radiation may be required.

Fortunately, there are techniques available for reducing the linewidth of solid samples. One of these, magic angle spinning (MAS), makes use of the fact that the two principal contributions to the line broadening in solids, i.e. dipole–dipole interaction and chemical shift anisotropy, both depend on the term $(1 - 3\cos^2\theta)$. The so-called magic angle is the angle at which $1 - 3\cos^2\theta = 0$, and corresponds to $54.74^\circ$. In the technique, the sample is spun at high speed at the magic angle to the applied field: dipole–dipole interaction and chemical shift anisotropy average to zero. Magic angle spinning yields the same isotropic chemical shift as does the random motion in fluids.

Another technique which is often used in solid state NMR is cross polarization. Because spectra of rare nuclei and/or nuclei having a low resonance frequency are usually difficult to detect and require long measuring times, the use of cross polarization, i.e. the repeated transfer of polarization from a more abundant species (usually protons) to a rare one, can enhance the NMR visibility of the latter. It should be noticed, however, that cross polarization does not affect the widths of the signals and therefore the resolution of the spectra, and that the resulting enhancement may be completely different for structurally different crystallographic sites, which renders the quantitative evaluation of such spectra difficult [3].
3.2.2.1 Aluminum NMR

There are two features which make $^{27}$Al a very favorable nucleus for NMR investigations: the 100% natural abundance and the fast relaxation generally observed for quadrupolar nuclei. Therefore, short pulse repetition can be applied, and $^{27}$Al MAS NMR spectra of good quality with relatively high signal-to-noise ratios can normally be obtained within comparatively short measurement times. These advantages may be partly compensated by the large linewidths usually observed in the $^{27}$Al MAS NMR spectra due to second-order quadrupolar interactions.

The most prominent structural effect on isotropic $^{27}$Al chemical shifts of aluminosilicates is the coordination number of the aluminum atom. For tetrahedral coordinated Al(OSi)$_4$ units, chemical shifts of about +60 ppm are observed, while octahedral AlO$_6$ groups resonate at about 0 ppm [3]. Furthermore, a broad signal at about 30 to 50 ppm is often detected which has not yet been unambi-

![Fig. 3.3: $^{27}$Al MAS NMR spectrum of a zeolite sample. The signals of tetrahedral aluminum at 55 ppm and of octahedral aluminum at 0 ppm are clearly visible. In addition to these, a signal at around 30 ppm is also recognizable.](image)
guously assigned: Gilson et al. [4] and Sanz et al. [5] ascribed this signal to penta-coordinated aluminum, whereas Samoson et al. [6] explained this signal with the presence of tetrahedral extra-framework aluminum. A typical spectrum is given in Fig. 3.3

In general, these well separated shift ranges permit the coordination number of the aluminum present in the aluminosilicates samples to be determined unambiguously from the $^{27}$Al MAS NMR spectra, even from relatively broad lines and incorrect chemical shift data.

### 3.2.2.2 Silicon NMR

The chemical shift is the most informative parameter in structural studies of

![Diagram of Si chemical shifts ranges of aluminosilicates, from [7].](image)

Fig. 3.4: $^{29}$Si chemical shifts ranges of aluminosilicates, from [7].
aluminosilicates by $^{29}\text{Si}$ MAS NMR since it reflects very sensitively the immediate structural surroundings of a silicon atom.

In a first approximation, neglecting the presence of crystallographically nonequivalent Si(nAl) sites, the $^{29}\text{Si}$ MAS NMR spectrum of a zeolite may consist of one to five peaks corresponding to the five possible Si(nAl) sites with $n = 0 - 4$ environments in the zeolite framework. With increasing number of Al atoms (n) in the first tetrahedral coordination sphere of the silicon atom, the peaks are systematically shifted to low field, while each Al substitution results in a shift contribution of about 5 ppm, as depicted in Fig. 3.4.

From careful analysis of the individual chemical shifts and peak intensities, the specific types and relative populations of the distinct Si(nAl) units present in the zeolite under study can, in principle, be determined, as in Fig. 3.5.

Provided that the $^{29}\text{Si}$ MAS NMR spectrum is correctly interpreted in terms of Si(nAl) units and no AlOAl linkages are present in the zeolite studied (i.e.

![Fig. 3.5: $^{29}\text{Si}$ MAS NMR spectrum of a dealuminated zeolite. Only the signals attributed to Si(0Al) and Si(1Al) can be distinguished.](image-url)
Loewenstein’s rule applies), the quantitative ratio of tetrahedral Si and Al in the zeolite framework can be directly calculated from the Si(nAl) peak intensities, \( I_{Si(nAl)} \), according to the equation [8]:

\[
\frac{\text{Si}}{\text{Al}}_{Si} = \frac{N_{Si}}{N_{Al}} = \frac{\sum_{n=0}^{4} n I_{Si(nAl)}}{4 \sum_{n=0}^{4} I_{Si(nAl)}}
\]

The Si/Al ratios calculated this way are in agreement with the real values only if there are no framework defects, because of the overlapping of the signals of silicon bound to aluminum and of silicon atoms bearing hydroxyl groups. Since the Si(1Al) signal has the same shift as Si(1OH) [7], the calculated (Si/Al)\(_{Si}\) will be lower for a sample having many defects.

The spectral analysis is complicated when the silicons in a certain Si(nAl) environment occupy different, i.e. crystallographically inequivalent, framework sites. This may lead to additional splittings and partial overlap of the Si(nAl) peaks, which renders the spectral assignment difficult. On the other hand, valuable information on the presence of crystallographically non-equivalent Si sites can be derived from those peak splittings and their intensity distributions, especially if highly dealuminated zeolites containing preferably Si(0Al) units are investigated.

The presence of SiOH groups in defect centers of the framework or on amorphous regions of the crystallites can be detected by application of the cross-polarization (CP) technique with which the signal intensities of silicon atoms bearing hydroxyl groups are enhanced.
3.2.2.3 Proton NMR

Hydrogen atoms may be present in zeolites in several structurally distinct forms. With respect to the catalytic properties of zeolites, the acidic protons of hydroxyl groups associated with framework aluminum Si(OH)Al (called “bridging” or “structural” hydroxyl groups) are most important. Hydrogen atoms may also be present in SiOH groups (“terminal” or “silanolic” hydroxyl groups) at the outer surface of the zeolite crystallites, in defect sites of the framework or in amorphous material occluded in the zeolite. Studies on their distribution may provide important information on lattice defects or lattice destruction and amorphization. Zeolites may further contain hydrogen atoms in chemically or physically adsorbed water molecules, in AlOH groups of nonframework

Fig. 3.6: $^1$H MAS NMR spectrum of a dealuminated zeolite. The signal of isolated silanols at 2 ppm, with shoulders at lower field attributed to OH groups associated with EFAI and bridged silanols, and of isolated Brønsted protons at around 4 ppm, with a shoulder at lower field attributed to Brønsted protons interacting with the framework could be distinguished.
hydroxoaluminum species formed by framework dealumination, and in NH$_4^+$ cations. All these different kinds of protons can, in principle, be studied by $^1$H NMR.

$^1$H MAS NMR of zeolites is complicated by interactions of the protons with the quadrupolar $^{27}$Al nuclei and by the narrow range of $^1$H chemical shifts. Moreover, adsorbed water has a disturbing effect on the spectra, and therefore samples have to be dehydrated and carefully protected against moisture by spinning them in tightly closed capsules.

$^1$H MAS NMR has proved to be very effective in obtaining highly resolved $^1$H NMR spectra displaying distinct and well separated signals of different types of protons in zeolites. Since the line broadening due to dipolar interaction with the $^{27}$Al nucleus decreases and the chemical shift dispersion increases with increasing magnetic field strength, it is advantageous to measure the $^1$H MAS NMR spectra of zeolites at high magnetic fields.

The spectra were analyzed according to the literature with the following assignments: 1.2 – 2.0 ppm silanol groups [9], 2.4 – 2.5 ppm OH groups associated with EFAI [10], 2.9 – 3.0 hydrogen bridged silanol groups [11], 3.9 – 4.1 ppm isolated Brønsted protons [9], 5.0 ppm Brønsted protons interacting with oxygen atoms of the framework [12], and at 7.0 ppm the signal of ammonia protons [13], as depicted in Fig. 3.6.

### 3.3 Atomic absorption spectroscopy

Atomic absorption spectroscopy (AAS) is one of the most used technique for the determination of the elemental composition of zeolites thanks to its reliability and easy of use. It is based upon the absorption of radiation by free atoms, usually in the ground state. By selecting a wavelength for a given element that corresponds to an optical transition between atoms in the ground state and
atoms in an excited level, the absorption of the radiation leads to a depopulation of the ground state. The value of the absorption is related to the concentration of the atoms in the ground state, and therefore, to the concentration of the element.

An atomic absorption spectrometer will therefore consist of a primary radiation source which produces the radiation to be absorbed, a source of free atoms with an associated sample introduction system, an optical dispersive system, a detector, and electronics for data acquisition, processing, and editing. The presence of free atoms must be obtained in the path between the primary radiation source and the detector.

The most commonly-used primary radiation source is the hollow-cathode lamp which consists of a hollow cathode made of a highly pure metal whose spectrum is to be produced.

The role of an atomizer is to efficiently convert the sample to free atoms mostly in the ground state. An ideal atomizer would result in a complete atomization of the sample. Among the possible flames used the air–acetylene and the nitrous oxide (N₂O)–acetylene flames are the most common. The air–acetylene flame was used for the determination of sodium; whereas the nitrous oxide–acetylene flame was used for aluminum and silicon because of its higher temperature (> 2600°C).

So as to avoid the ionization of some element, as for instance aluminum and sodium, which would lower their absorption, an easily ionizable element, potassium in our case, was added to the solution.

Quantitative analysis is possible in AAS if the absorption of the radiation can be related to the concentration of the element to be analyzed. The absorption of light with a specific wavelength by the neutral atoms in the gas phase gives rise to a signal which is linearly proportional to their amount in solution.
(Lambert–Beer law). By measuring the amount of radiation absorbed, a quantitative determination of the amount of analyte can be made.

### 3.4 X–ray diffraction

The phenomenon of diffraction is due to the interference caused by an object in the path of waves, and the pattern of varying intensity that results is called diffraction pattern. Diffraction occurs when the dimensions of the diffracting object are comparable to the wavelength of the radiation.

X-rays have wavelengths comparable to bond lengths in molecules and the spacing of atoms in crystals. By analyzing an X-ray diffraction pattern, it is possible to draw up a detailed picture of the location of atoms even in complex crystal structures.

A crystal is built up from regularly repeating "structural motifs", which may be atoms, molecules, or group of atoms. The unit cell is an imaginary parallelepiped characterized by three vectors $\vec{a}$, $\vec{b}$ and $\vec{c}$ that contains one unit of the translationally repeating pattern. A unit cell can be thought of as the fundamental region from which the entire crystal may be constructed by purely translation displacements. The external appearance of crystals is controlled by their internal periodic structure. Characteristic faces develop by addition of atoms to a crystal nucleus in an ordered stepwise manner. These faces may be characterized by their Miller indices.

Crystal lattices provide an excellent diffraction grating for X–rays. Bragg demonstrated in 1913 that constructive interference can only occur when the parallel diffracted waves all display a path difference of $\lambda(2\pi)$ to the nearest neighbor. The Bragg equation:
$d = \frac{n \cdot \lambda}{2 \sin \theta}$

relates the interplanar distances $d$ to an integer number of wavelengths $n\lambda$ and the glancing angle $\theta$.

During powder diffraction the samples are compressed on a sample holder. The large number of crystallites in the sample and the rotation of the sample holder during exposure guarantee that all crystallite orientations are present. The diffraction pattern is registered as counts per second with the help of a Röntgen detector.

### 3.5 Scanning electron microscopy

The scanning electron microscope achieves its resolution by scanning a finely focused beam of very short-wavelength electrons, about 10–100 Å in diameter, across a surface and by detection of either the back-scattered or secondary electrons in a raster pattern in order to build up an image on a television monitor. Because of its very low numerical aperture, the SEM has an extreme depth of field so that thick objects can be visualized in focus from top to bottom. The SEM, unlike light microscopes, is limited to a surface view only. Nothing is learned visually about the interior of the specimen. It does, however, permit the production of dramatic black-and-white images.
3.6 References


4. Experimental

4.1 Sample preparation

4.1.1 Synthesis of mordenite extrudates

The synthesis procedure described by Whittemore [1] was modified by adding some mordenite in the mixture as seed in order to accelerate the transformation to mordenite. The direct synthesis of mordenite in form of extrudates consists of three steps: a) preparation of the precursors; b) calcination of these precursors; c) reaction to mordenite.

Kaolin (Fluka AG), silica powder FK 320 (Degussa AG), and sodium silicate solution (Fluka AG) were the ingredients for the preparation of the precursors. Typically 50 g kaolin, 53 g FK 320, and 142 g waterglas were kneaded till homogeneity upon addition of 25 g deionized water and 2.5 g well-crystalline mordenite (PM22–Na) as seed. The thus obtained mixture was then shaped by extrusion through 1/16" holes. Water content of the mixture was a critical factor and a too low or a too high water content hinders the extrusion. The resulting extrudates were dried for some hours at ambient temperature and then at 130°C overnight. In order to obtain a non-agglomerated material, drying had to be carried out in flowing air and a heating rate lower than 0.5°C/min. The extrudates were finally subjected to calcination at 600°C for 1 h (heating rate 10°C/min) in order to transform kaolin in the more reactive metakaolin as described in Chapter 2.3.2.
Chapter 4

The molar composition of the precursors (excluding water) was 1.00 Al : 0.95 Na : 4.85 Si with about 1.5 wt % seed.

In order to transform the precursors in self-supported mordenite samples, 20 g of the calcined material was sealed in a teflon lined autoclave together with 30 g sodium silicate and reacted under autogeneous pressure at 220°C (heating rate 10°C/min) during 18 h without stirring. The thus obtained mordenite extrudates were thoroughly washed with deionized water till a neutral pH, dried at 120°C overnight (10°C/min), and finally calcined at 500°C. The result was a material with a molar composition of 1.00 Al : 2.50 Na : 5.70 Si (excluding water).

4.1.2 Ion exchange and dealumination

All investigations on mordenite powder were done on mordenite PM22–Na provided by CU Chemie Uetikon. The procedure for ion exchange and dealumination were similar for mordenite extrudates and mordenite powder, the only difference being the use of a sieve when treating extrudates that prevented them to be crushed by the stirrer during the treatment.

In a typical run, 10 g of mordenite were ion exchanged using 300 ml of a 1 M solution of hydrochloric acid at reflux temperature (100°C) during 1 h, followed, after filtration and washing, by ion–exchange with a 1 M solution of ammonium nitrate under the same conditions. Samples were then dried at 120°C for 10 h. This method allowed a 95 % exchange of sodium.

Dealumination was carried out using nitric acid, a mineral acid, and oxalic acid, an organic one. Prior to dealumination the exchanged samples were calcined at 750°C in a shallow bed for 2 h. Aluminum was then removed by acid leaching of 5 g of calcined mordenite stirred together with 60 ml of solution of acid at reflux temperature; samples were collected after different reaction times. The thus obtained zeolite samples were washed with water, dried at 120°C dur-
ing 10 h, and calcined for 3 h at 500°C. The dealumination step before the leaching with acids is necessary in order to facilitate to washing of aluminum out of the zeolite. In fact this high temperature treatment permits the migration of aluminum from the lattice to the pores forming an extra-framework species.

4.2 Characterization

4.2.1 Nuclear magnetic resonance

Solid-state MAS NMR spectra were recorded on a Bruker AMX400 spectrometer at a magnetic field of 9.4 T. Experiments were carried out using ZrO$_2$ rotors with tight fitting Kel-F caps filled with mordenite samples.

4.2.1.1 $^{27}$Al MAS NMR

Spectra were recorded at a resonance frequency of 104.26 MHz. The $^{27}$Al chemical shifts were referenced to Al(H$_2$O)$_6^{3+}$ in an 0.1 M aqueous solution of Al(NO$_3$)$_3$ using (NH$_4$)Al(SO$_4$)$_2$ · 12 H$_2$O (-0.4 ppm) as a secondary reference. At least 512 scans were acquired for each spectrum with a recycling time of 10 s. Rotors were spun at 10 kHz with pulse lengths of 0.8 μs (10° flip angle) and an irradiation power of 63 kHz.

In order to quantitatively analyze the spectra all samples were weighed and the spectra calibrated by measuring a known amount of ammonium aluminum sulfate under the same conditions. The intensity of its central bands has been integrated and the average intensity of the first spinning sideband located on each side of that band has been subtracted so as to correct for the contribution of the satellite transition to the center band. This way we could determine the intensity per aluminum atom.

Aluminum, having a nuclear spin $I = 5/2$, possesses a quadrupole moment.
which renders its quantitative determination troublesome. In fact this causes a broadening of the signal and this is sometimes so large that some signal contribution is scattered over the whole spectra and cannot be detected \[2,3\], aluminum nuclei becomes then NMR invisible. However, this broadening depends on the symmetry of the nucleus and affects therefore only octahedral aluminum, i.e. extra-framework aluminum. Its amount can be indirectly calculated from the bulk composition of the sample.

After deconvolution of the spectra the amount of framework aluminum was determined by dividing the area under its peak by the intensity per aluminum atom. The amount of extraframework aluminum was then established by subtracting the amount of framework aluminum from the total amount as found with AAS. Müller et al. \[4\] have established that tetrahedrally coordinated Al in the zeolite lattice, under the analysis conditions reported before, is completely NMR visible.

4.2.1.2 \(^{29}\)Si MAS NMR

\(^{29}\)Si MAS NMR spectra were recorded at a resonance frequency of 79.49 MHz. The \(^{29}\)Si chemical shifts were referenced to tetramethylsilane (TMS) (0.0 ppm). At least 1024 scans were acquired for each spectrum with a pulse length of 2.9 \(\mu\)s (30° flip angle) and recycling time of 5 s. Rotors were spun at 5 kHz and proton decoupling was applied. Cross polarization experiments were acquired using at least 4096 scans with the same recycling time. Protons were excited for 7 \(\mu\)s and silicon nuclei for 5 ms.

4.2.1.3 \(^{1}\)H MAS NMR

Before investigation, zirconia rotors containing the sample were dehydrated by evacuation for 6 h at 350°C (heating rate 60°C/min) at a pressure below 0.1 Pa and then sealed using tight fitting Kel–F caps. The rotors were spun at 10 kHz.
Experimental during MAS NMR experiments. The resonance frequency for $^1$H NMR measurements was 400.13 MHz at a magnetic field of 9.4 T. Single pulse excitation with pulse lengths of 6.0 μs (70° flip angle) and 10 s relaxation delays was applied. $T_1$ relaxation times were found to be shorter than 5 s. Chemical shifts were referenced to TMS (0.0 ppm). At least 256 scans were acquired for each spectrum. For the determination of quantitative results, all samples were weighed and the spectra were calibrated by measuring a known amount of 1,1,1,3,3,3-hexafluoro-2-propanol under the same conditions. By measuring an empty rotor it was observed that the probe and rotor themselves gave rise to a broad background signal which had to be subtracted from the $^1$H spectra measured for the different samples.

The analysis of $^1$H NMR spectra is easier than that of $^{27}$Al NMR since every proton induces the same signal intensity. However, even here a direct determination of the amount of extra-framework aluminum is not possible since the amount of hydroxyl groups per aluminum atom in extra-framework position can vary. The procedure is then similar to the one described before in the case of aluminum: by determining the area under the two proton signals of the external standard and by weighing the standard we were able to determine the intensity per proton which was then used to quantify the amount of aluminium in the framework, after integration of the two peaks assigned to Brønsted hydroxyls, i.e. the one belonging to unperturbed Brønsted protons and to Brønsted protons interacting with oxygen atoms of the framework. The quantification of EFAI is then possible by comparing the bulk Si/Al ratio obtained from AAS measurements with the framework (Si/Al)$_n$ ratio obtained from the $^1$H MAS NMR spectrum [4].
4.2.2 Nitrogen adsorption

Nitrogen adsorption isotherms were measured at liquid nitrogen temperature (-196°C) using a Micromeritics ASAP 2010 instrument; prior to analysis the samples were outgassed at 400°C for 3 h at a pressure below 1 Pa.

4.2.3 Atomic absorption spectroscopy

This technique requires the elements to be in solution. For that reason about 750 mg of zeolite was first dissolved using 5 ml 40 % (by weight) hydrofluoric acid at 0°C; 25 ml 25 % sulfuric acid were then added. In order to prevent the corrosion of the absorber hydrofluoric acid in excess needs to be complexed with 40 ml 2.5 % boric acid. The solution was finally diluted to 100 ml using bidistilled water and the desired concentration determined on a Varian SpectrAA-10.

For the determination of the aluminum concentration the standard addition method has to be employed since the presence of silicon in solution causes a lowering of the aluminum signal. For that purpose three different solutions were prepared by adding, in addition to the sample solution, 0, 10 and 20 ppm aluminum, respectively. The concentration was then determined by extrapolation to zero absorption. Elements and their measurement methods are summarized in Tab. 4.1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Range</th>
<th>Wavelength</th>
<th>Ion suppressant</th>
<th>Gas</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>10 ppm</td>
<td>309.3 nm</td>
<td>2000 ppm K⁺</td>
<td>N₂O</td>
<td>St. addition</td>
</tr>
<tr>
<td>Si</td>
<td>150 ppm</td>
<td>251.6 nm</td>
<td>-</td>
<td>N₂O</td>
<td>Calibration line</td>
</tr>
<tr>
<td>Na</td>
<td>0.5 ppm</td>
<td>589.0 nm</td>
<td>2000 ppm K⁺</td>
<td>Air</td>
<td>Calibration line</td>
</tr>
</tbody>
</table>

Tab. 4.1: Measuring conditions for AAS
An error of about 10%, taking in account errors during dilution and measurement, had to be considered.

### 4.2.4 X-ray diffraction

X-ray powder diffraction patterns of the modified zeolites were recorded from 5° to 45° 2θ on a Siemens D5000 diffractometer using CuKα radiation at a step size of 0.02°. The unit cell parameters were determined using LATCON, a program for the refinement of lattice constants [5]; peak positions were corrected using silicon powder as a standard.

The method for the determination of zeolite crystallinity consists of dividing the sum of several specific peak areas by the respective sum found for a highly crystalline zeolite, such as PM22–Na, measured under the same conditions.

### 4.2.5 Scanning electron microscopy

Scanning electron microscopy images of the samples coated with a 3 nm thick platinum layer were recorded with an electron acceleration voltage of 10 kV.
4.3 References


5. Dealumination of mordenite

5.1 Introduction

The synthesis limits of the Si/Al ratio of mordenite are presently about 10 [1], to obtain highly siliceous mordenite a post-synthesis treatment is necessary. The most common procedure for the dealumination of mordenite is a high temperature shallow bed calcination followed by a leaching with a mineral acid such as hydrochloric acid or nitric acid; this way a silicon-to-aluminium ratio up to 600 has been obtained [2].

Some patent applications for the dealumination of ferrierite [3], ECR-17 [4], Beta [5], and mordenite [6] with oxalic acid were filed. In 1996 Apelian et al. published a detailed description of dealumination of zeolite Beta by oxalic acid [7]. Liu et al. [8] described the dealumination of zeolite Y by oxalic acid in 1998. In the case of Beta, up to 90% of the aluminum could be removed without loss of crystallinity and oxalic acid was effective for the removal of both tetrahedral and octahedral aluminum: $^{27}$Al NMR analysis did not detect any extra-framework aluminum species. NMR and IR analyses showed that the dealumination was accompanied by the formation of silanol groups. Apelian et al. [7] proposed a two-step mechanism for the dealumination which involved first the hydrolysis of aluminum from the framework owing to the high acidity of the solution and then the chelation of each aluminum ion with three oxalic acid molecules.

Liu et al. [8], by dealuminating zeolite Y with oxalic acid, observed a retaining of the overall crystallinity; IR investigations revealed the presence of hydroxyls group due to aluminum vacancies in the framework. In addition to this, adsorption of pyridine and CO showed the production of extraframework alumi-
num species. The presence of secondary pores larger than the aluminum vacancies was disclosed by nitrogen adsorption.

In this chapter the dealumination behavior of mordenite using nitric acid is compared with that using oxalic acid. The dealuminated samples were characterized by elemental analysis, nitrogen adsorption, scanning electron microscopy, X-ray diffraction, nuclear magnetic resonance and infrared spectroscopy.

5.2 Results and discussion

5.2.1 Bulk composition

In order to limit the parameters influencing the dealumination, in all experiments the same batch of mordenite and the same mordenite/acid volume ratio were used. The parent zeolite was dealuminated using three different concentr-
Dealumination of mordenite

tions of each acid: 6 M, 2 M and 1 M of nitric acid, 2 M, 1 M, 0.5 M of oxalic acid and treatment times up to 20 h. Si/Al ratios of the dealuminated samples are reported in Fig. 5.1 and Fig. 5.2.

![Graph showing Si/Al ratios versus leaching time with different acid concentrations](image)

**Fig. 5.2:** Bulk composition versus leaching time with 2 M, 1 M and 0.5 M oxalic acid; sample at $t = 0$ is HM

At the highest concentrations tested for both acids the silicon-to-aluminium ratio leveled out after an initial steep increase; at lower concentrations the Si/Al ratio increased gradually with time. Oxalic acid was the more effective of the acids. Si/Al ratios up to 120 could easily be reached using 2 and 1 M solutions, using 6 M or 2 M nitric acid the ultimate Si/Al ratio was about 70.

The difference in dealumination behavior can be explained by the dual nature of oxalic acid, it acts both as a hydrolyzing and as a chelating agent forming a trioxalato aluminum complex with a high complexation constant ($\log \beta_3 = 15.1$) [9]. The dealumination mechanism proposed by Apelian et al. [7] involves two steps: first aluminum is hydrolyzed from the framework due to the acidity of
the solution, then each aluminum cation is chelated by three oxalic acid molecules.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modification</th>
<th>(Si/Al)$_b$</th>
<th>MSA$^a$</th>
<th>ESA$^b$</th>
<th>MV$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaN</td>
<td>Parent material</td>
<td>5.8 ± 0.6</td>
<td>361</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>HM-nc</td>
<td>Na exch., not calcined</td>
<td>6.7 ± 0.7</td>
<td>511</td>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td>HM</td>
<td>Na exch., calcined 750°C</td>
<td>6.7 ± 0.7</td>
<td>495</td>
<td>12</td>
<td>0.2080</td>
</tr>
<tr>
<td>M-HN-2</td>
<td>2 h with 6 M HNO$_3$</td>
<td>50 ± 5</td>
<td>572</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>M-HN-20</td>
<td>20 h with 6 M HNO$_3$</td>
<td>77 ± 8</td>
<td>467</td>
<td>32</td>
<td>0.1960</td>
</tr>
<tr>
<td>M-Ox-2</td>
<td>2 h with 2 M oxalic acid</td>
<td>29 ± 3</td>
<td>577</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>M-Ox-4</td>
<td>4 h with 2 M oxalic acid</td>
<td>79 ± 8</td>
<td>597</td>
<td>13</td>
<td>0.2518</td>
</tr>
<tr>
<td>M-Ox-8</td>
<td>8 h with 2 M oxalic acid</td>
<td>119 ± 12</td>
<td>601</td>
<td>14</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$: micropore surface area (m$^2$/g)
$^b$: external surface area (m$^2$/g)
$^c$: micropore volume (cm$^3$/g)

Tab. 5.1: Bulk Si/Al and nitrogen adsorption results

Samples leached with nitric acid (M-HN-20) and with oxalic acid (M-Ox-4 and M-Ox-8) were subjected to a thorough characterization. These materials are typical for each acid and had a similar Si/Al ratio. The ion exchanged (HM) was used as reference. An explanation of the sample names, the modification applied, the bulk Si/Al ratio, and the N$_2$ adsorption results are given in Tab. 5.1.

### 5.2.2 Textural properties

The adsorption isotherms of HM, M-HN-20 and M-Ox-4 in Fig. 5.3 clearly show the formation of secondary pores. The mordenite treated with oxalic acid has a higher sorption capacity than the other material, in fact its isotherm is shifted to higher value; the overall shape of the isotherm, however, equals that of HM. This does not apply to the sample treated with nitric acid: the shape of the curve is different, and with increasing p/p$^0$ the slope of the adsorption isotherm increases and the hysteresis loop widens. Considering that an ideal mi-
croporous material has an adsorption isotherm which shows a sharp knee and then a horizontal plateau, any deviation from this behavior, in particularly an increased uptake of nitrogen at higher partial pressures, is an indication of the presence of mesopores in the sample: the more mesopores, the steeper the curve and the wider the hysteresis loop [10].

Fig. 5.3: Nitrogen adsorption isotherms of HM, M-HN-20 and M-Ox-4

The micropore and external surface areas of the dealuminated samples are reported in Fig. 5.4 and Fig. 5.5. They were determined by nitrogen adsorption and by applying the t–plot method [11] in the linear branch of the plot, usually in the 6 – 12 Å region. The main difference between the two acid treatments is that the external surface area (ESA) remained constant at about 14 m²/g when using oxalic acid. With nitric acid, on the other hand, the external surface area increased with increasing acid strength and dealumination time, reaching a maximum of 35 m²/g. The micropore surface area (MSA) reached a value of about 470 m²/g using 6 M and 580 m²/g using 2 M nitric acid. The MSA values
Fig. 5.4: Micropore (MSA, dashed lines) and external surface area (ESA, solid lines) of samples treated with nitric acid. ◯: 6 M, □: 2 M, O: 1 M; sample at t = 0 is HM of the oxalic acid treated samples were in the 570 – 600 m²/g range.

An increase in the micropore surface area is observed upon ion exchange due to the removal of sodium and dissolution of some amorphous silica-alumina left after the synthesis [12]. Calcination of the exchanged mordenite caused a 3% lowering of the MSA. This was explained with the migration of aluminum from framework in extra-framework positions due to the high calcination temperature thus partially blocking the pore system. The strong increase in ESA observed in the mordenite samples leached with 2 and 6 M nitric acid is attributed to the formation of a secondary pore system in the crystal. Since this increase in ESA was specific for nitric acid and since, as will be shown in the following NMR section, according to $^1$H and $^{27}$Al MAS NMR oxalic acid extracted more aluminum from the framework, the additional ESA can not be attributed only to aluminum removal, otherwise the M-Ox-4 sample would have
Fig. 5.5: Micropore (MSA, dashed lines) and external surface area (ESA, solid lines) of samples treated with oxalic acid. ◆: 2 M, □: 1 M, ○: 0.5 M; sample at t = 0 is HM had a larger external surface area. In fact, besides the aluminum extraction from the framework, the most important factor in the increase of the ESA is the simultaneous dissolution of silica units from the framework due to the high acidity of the employed solution (pH = -0.8 in the case of 6 M nitric acid) [13]. This dissolution was probably initiated by lattice defects created by dealumination which weakened the structure locally. Ajot et al. [14] have already ascribed the structural defects to the formation of a secondary pore system in the zeolite crystal although they related its formation only to the removal of aluminum species.

The oxalic acid solution, on the other hand, had a higher pH (pH = 0.5) which prevented the hydrolysis of the silicon bonds and lacked the ability of chelating silicon ions as well.

Comparison of the micropore volumes of M-HN-20 and M-Ox-4 in Tab. 5.1.
shows that the nitric acid dealuminated mordenite has a volume which is in agreement with the theoretical one (calculated to be $0.210 \, \text{cm}^3/\text{g}$ by Breck and Grose [15]). M-Ox-4, on the other hand, had an even higher micropore volume. This showed, not only that the samples were crystalline after dealumination but also that the aluminum extraction with oxalic acid led to the formation of additional micropores due to a deeper removal of aluminum from the framework [16].

A confirmation that the investigated samples were still crystalline after dealumination came from XRD analysis reported in Fig. 5.6. The crystallinity of M-HN-20 and M-Ox-4 were unaffected by the treatment when compared to NaM, as indicated by the well–resolved diffractograms.

![XRD diffractograms](image)

Fig. 5.6: XRD diffractograms of: a) NaM, b) M-HN-20, and M-Ox-4

The analysis of the pore volume distribution calculated with the method of Barret, Joyner and Halenda [17] of the meso– and macropores region ($20 - 1000 \, \text{Å}$) in Fig. 5.7 showed that the texture of the sample treated with oxalic acid remained unchanged, while the sample leached with nitric acid had additional
Dealumination of mordenite

Fig. 5.7: Pore volume distribution of: a) HM, b) M-Ox-4, and c) M-HN-20 volume in pores between 100 and 600 Å, accordingly mainly mesopores (comprised in the 20 – 500 Å region) and some macropores (pore diameter > 500 Å) were formed.

The sharp peaks at around 40 Å do not represent pore volume. In fact Broekhoff and van Beek [18] observed that the desorption branch of systems exhibiting B–type hysteresis [19], as is the case here, commonly becomes very steep at or near the critical relative pressure due to the sudden emptying of the capillaries. This behavior only depends on the physical properties of the adsorbate, i.e. from its surface tension, rather than from the pore size distribution in the system. This means that the sharp peaks at about 40 Å calculated from the desorption branch of the isotherm are artefacts of the method and that the method gives no information on pore size below this critical point.
Fig. 5.8: SEM pictures of M-HN-20 (top) and M-Ox-4
The formation of additional pores was further confirmed by scanning electron microscope pictures of M-HN-20 and M-Ox-4 in Fig. 5.8 which show that the surface of M-HN-20 was strongly corroded and contained many cracks bigger than 3 nm, the thickness of the platinum layer, whereas the surface of M-Ox-4 was essentially unchanged and very smooth.

5.2.3 NMR analyses

To establish the effects of the treatments on the framework composition, NMR analyses were performed on the samples. $^{27}\text{Al}$ MAS NMR was used to investigate the coordination number of the aluminum atoms, $^1\text{H}$ MAS NMR to characterize the nature of the hydroxyl groups, while $^{29}\text{Si}$ MAS NMR was used to determine the number of Si and Al atoms attached to the silicon unit considered.

5.2.3.1 $^{27}\text{Al MAS NMR}$

According to the literature cited in Chapter 3.2.2.1, the signal at around 55 ppm was ascribed to tetrahedral framework aluminum, the one at 30 ppm to penta-coordinated aluminum, and the one at 0 ppm to octahedral aluminum, i.e extra-framework aluminum (EFAI).

Spectra in Fig. 5.9 disclosed that even the exchange step, without any further calcination, was sufficient to extract some aluminum from the framework, in fact, while NaM contained only framework aluminum, zeolite HN-nc showed a peak at 0 ppm and a broad shoulder from 50 to 20 ppm. This was explained with the use of hydrochloric acid during dealumination of NaM: even a mildly acidic solution of it (1 M) succeeded in removing some framework aluminum.

As mentioned in the discussion of the nitrogen adsorption data, calcination
of HM-nc led to extraction of aluminum from the framework as can be seen in the increased intensity of the peak at 0 ppm. In addition, the signal attributed to pentacoordinated aluminum was clearly enhanced as well. Extra-framework aluminum was removed more easily than the tetrahedral species by acid leaching with 6 M nitric acid, in fact after only 2 h treatment a decrease of the non-framework aluminum peaks was observed. The peak of tetrahedral aluminum also decreased, especially after 20 h treatment, thus showing that the treatment with nitric acid affected the framework aluminum content of the zeolite.

![Al NMR spectra](image)

**Fig. 5.9:** $^{27}$Al NMR spectra of: a) NaM, b) HM-nc, c) HM, d) M-HN-2, and e) M-HN-20

The effect of oxalic acid on the aluminum content is reported in Fig. 5.10. The main difference compared to the nitric acid treatment was that the framework aluminum content strongly decreased, even after only 2 h treatment.
Comparison of M-HN-20 and M-Ox-4 in Fig. 5.11 showed that, while nitric acid was able to extract practically all EFAl, the sample leached with oxalic acid still contained a large amount of extra-framework aluminum as indicated by the broad peak at around 0 ppm.
The results of the quantitative analyses reported in Tab. 5.2 show a framework (Si/Al)$_A$ ratio of 161 for the M-Ox-4 sample, well above the bulk value of 79, thus confirming that about half of the aluminum was out of the framework. M-HN-20 on the other hand, had a barely visible EFAl peak and the framework (Si/Al)$_A$ ratio of 86 proved that in this case there is a lower aluminum loss from the framework since the bulk Si/Al ratios of both samples were similar.

<table>
<thead>
<tr>
<th></th>
<th>M-HN-20</th>
<th>M-Ox-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Si/Al)$_b$</td>
<td>77</td>
<td>79</td>
</tr>
<tr>
<td>(Si/Al)$_A$</td>
<td>86</td>
<td>161</td>
</tr>
<tr>
<td>(% Al in framework)$_A$</td>
<td>89</td>
<td>49</td>
</tr>
</tbody>
</table>

Accuracy: ±10 %

Tab. 5.2: Bulk and framework aluminum content of M-HN-20 and M-Ox-4 as determined by AAS and $^{27}$Al NMR

The extensive removal of aluminum from the framework by oxalic acid is due to the nature of this acid which both hydrolyses aluminum from the lattice and forms an aluminum complex in solution. This complexation is the driving force of the deeper aluminum extraction by this acid. In contrast with Apelian et al. [7] who did not observe any octahedral aluminum when dealuminating zeolite Beta with oxalic acid, we always found a relatively large amount in our mordenite samples. We suppose that the migration of the aluminum oxalato complex out of the zeolite is difficult in the one-dimensional pores of mordenite which have an
opening of 6.5 x 7.0 Å. No EFAI species were found in oxalic acid treated zeolite Beta, in which, because of its wider tridimensional pore system (opening of 6.5 x 7.4 Å [20]) the aluminum oxalato complex has a higher diffusivity.

5.2.3.2 $^1$H MAS NMR

$^1$H MAS NMR analyses were performed on M-HN-20 and M-Ox-4, the spectra are reported in Fig. 5.12. The spectra were analyzed according to literature as described in Chapter 3.2.2.3. The signal attributed to silanol groups in the 1.2 – 2.0 ppm region was found to be split in three different signals: an intense peak at around 2 ppm with a shoulder at higher field and a signal at about 1.2 ppm. The latter was assigned to isolated silanol groups by Gay [21] by comparison with a pure amorphous SiO$_2$ phase (silica gel).

It was also observed that in M-HN-20 the two signals at 4.9 and 3.9 ppm belonging to Brønsted protons are more intense, compared to the one that belongs to EFAI at 2.4 ppm. In M-Ox-4 however, the Brønsted signal at 5.1 and 4.2 ppm are weaker which pointed to a higher extraction of framework aluminum. The signal at around 5 ppm could also originate from water adsorbed or not fully removed from the samples. However, because of the sample pre–treatment described in Chapter 4, it is unlikely that this signal belongs to water.

Other differences between the two spectra are the large amount of bridging silanol groups in M-Ox-4 at 3.0 ppm, which indicated a high number of defects in the sample and the high number of acidic groups interacting with the oxygen atom of the framework at 4.9 ppm in M-HN-20.
Fig. 5.12: $^1$H MAS NMR spectra of M-HN-20 (top) and M-Ox-4 (bottom)
Since for every Brønsted hydroxyl group there must be an aluminum atom in the framework, the signals belonging to the isolated Brønsted protons and belonging to interacting Brønsted protons were used to calculate the framework \((\text{Si/Al})_\text{H}\) ratio as explained in Chapter 4.2.2.3.

The quantitative analysis of the spectra gave the results summarized in Tab. 5.3. As expected, the aluminum extraction from the framework is larger in the case of oxalic acid, with a framework \((\text{Si/Al})_\text{H}\) ratio of 150 in the case of M-Ox-4, thus leaving a large amount of extra-framework aluminum species in the sample (only about 50 % of its aluminum was tetrahedrally coordinated), whereas with nitric acid practically no EFAl was found, nearly 100 % of the aluminum was in framework position.

<table>
<thead>
<tr>
<th></th>
<th>M-HN-20</th>
<th>M-Ox-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{Si/Al})_\text{b})</td>
<td>77</td>
<td>79</td>
</tr>
<tr>
<td>((\text{Si/Al})_\text{H})</td>
<td>79</td>
<td>150</td>
</tr>
<tr>
<td>((% \text{ Al in framework})_\text{H})</td>
<td>97</td>
<td>52</td>
</tr>
</tbody>
</table>

Tab. 5.3: Bulk and framework aluminum content of M-HN-20 and M-Ox-4 as determined by AAS and \(^1\text{H} \) NMR

Comparison of the framework silicon–to–aluminium ratio \((\text{Si/Al})_\text{H}\) found by integrating the \(^1\text{H} \) MAS NMR spectrum with the \((\text{Si/Al})_\text{AI}\) ratio for both samples, showed that the two methods, considering their accuracies, gave the same values, confirming our assumption that under the experimental conditions reported in Chapter 4.2.1 all framework aluminum is visible.

5.2.3.3 \(^{29}\text{Si MAS NMR}\)

The \(^{29}\text{Si MAS NMR} \) spectra in Fig. 5.13 show only the signals at -114 and -104 ppm, assigned to Si(0Al) and Si(1Al), respectively [22].
Fig. 5.13: $^{29}$Si MAS NMR spectra of M-HN-20 (top) and M-Ox-4 (bottom)
The silicon–to–aluminium ratios of the samples may be calculated from the intensities of the signals using the following equation [23]:

\[
\left( \frac{\text{Si}}{\text{Al}} \right)_\text{Si} = \frac{N_{\text{Si}}}{N_{\text{Al}}} = \frac{\sum_{n=0}^{4} \frac{n}{4} I_{\text{Si}(n\text{Al})}}{\sum_{n=0}^{4} I_{\text{Si}(n\text{Al})}}
\]

As explained in Chapter 3.2.2.2 since the Si(1Al) signal has the same shift as Si(1OH) [22], the calculated (Si/Al)\text{Si} will be lower for a sample having many defects. We took, however, advantage of this feature in order to quantify the defect formation in the samples by comparing the framework Si/Al ratios obtained with Al and Si NMR analyses. The Si(1Al) signal of M-Ox-4 was bigger than that of M-HN-20 and deconvolution of the spectra showed that M-HN-20 had a (Si/Al)\text{Si} = 70, comparable with the value found from the \text{27}Al NMR, while M-Ox-4 had a (Si/Al)\text{Si} = 33, well below the (Si/Al)\text{Al} value of 161 (see Tab. 5.4). This is an indication that M-Ox-4 has more defects than M-HN-20.

<table>
<thead>
<tr>
<th></th>
<th>M-HN-20</th>
<th>M-Ox-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Si/Al)\text{b}</td>
<td>77</td>
<td>79</td>
</tr>
<tr>
<td>(Si/Al)\text{Si}</td>
<td>70</td>
<td>33</td>
</tr>
<tr>
<td>(SiOH/Si)\text{Si} (x 10^3)</td>
<td>3</td>
<td>24</td>
</tr>
<tr>
<td>(EFAI/Si)\text{Si} (x 10^3)</td>
<td>1.4</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Accuracy: ± 10 %

Tab. 5.4: Bulk and framework aluminum content of M-HN-20 and M-Ox-4 as determined by AAS and \text{29}Si NMR. In addition, silanol content was calculated by comparison of (Al/Si)\text{Al} with (Al/Si)\text{Si}.

The quantitative evaluation of these defects was possible by comparing the framework (Al/Si)\text{Al} with the (Al/Si)\text{Si} ratios. This way we could actually verify that M-Ox-4 contained more silanol groups than M-HN-20: (SiOH/Si) = 0.024 for M-Ox-4, compared to 0.003 for M-HN-20. This was also confirmed by the cross polarization \text{29}Si MAS NMR of both samples, where the signal intensities of sili-
con atoms bearing hydroxyl groups were enhanced. Unfortunately, due to the non linear intensity enhancements of structurally different silicon centers, a quantitative evaluation of the spectra is not possible [24]. This technique proved, however, to be useful in a qualitative identification of the silanol groups present. As can be seen in Fig. 5.14, the oxalic acid treated sample contained more defects because the Si(1OH) signal was, relatively to the Si(0OH), bigger; moreover, the Si(2OH) signal was clearly recognizable. In M-HN-20, not only was the Si(1OH) peak smaller, but also the Si(2OH) was hardly visible, thus confirming that oxalic acid left more defects in the zeolite structure after dealumination.

We suggest that the reason that M-Ox-4 contains more silanol groups than M-HN-20 is firstly the enhanced elimination of framework aluminum by oxalic acid as shown by $^{27}$Al NMR, leaving four OH–groups for every Al atom, and secondly an elimination of silica units from the framework in M-HN-20 hence reducing the number of defects in this sample and leaving additional pores in agreement with nitrogen adsorption data.

In the $^{29}$Si NMR spectra of Fig. 5.13 the Si(0Al) signal of M-HN-20 was split and three peaks belonging to different crystallographically inequivalent Si sites [25] T1, T4 and (T2 + T3) at -112, -113 and -115 ppm, respectively, were observed whereas in M-Ox-4 there was only one broad peak centered at -112 ppm with a shoulder at around -114 ppm, due to the enlargement of the single signals. Fyfe et al. [25] ascribed the broadening of the Si(0Al)–signal to the presence of aluminum in the lattice: the less aluminum the more resolved the peaks. This explanation alone, however, could not explain the broadening in M-Ox-4: since this sample had a higher framework Si/Al, it should even have had better resolved peaks and not a broad signal. Since according to Bertea et al. [26] both tetrahedrally and octahedrally coordinated Al affect the splitting, the differences between M-HN-20 and M-Ox-4 may be due to the presence of EFAI in
Fig. 5.14: cp $^{29}$Si MAS NMR spectra of M-HN-20 (top) and M-Ox-4 (bottom)
M-Ox-4. The silanol groups which create disorder in the framework could also interfere with the resolution of the Si(0Al) peak. Accordingly we analyzed a sample (M-Ox-8) treated 8 h with 2 M oxalic acid; its $^{29}\text{Si}$ NMR is reported in Fig. 5.15, whereas the results of its analysis are summarized in Tab. 5.1 and Tab. 5.5.

<table>
<thead>
<tr>
<th></th>
<th>M-Ox-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{Si/Al})_b$</td>
<td>119</td>
</tr>
<tr>
<td>$(\text{Si/Al})_{\text{Al}}$</td>
<td>216</td>
</tr>
<tr>
<td>$(% \text{ Al in framework})_{\text{Al}}$</td>
<td>55</td>
</tr>
<tr>
<td>$(\text{Si/Al})_{\text{Si}}$</td>
<td>32</td>
</tr>
<tr>
<td>$(\text{SiOH/}{\text{Si}})_{\text{Si}} (x \times 10^3)$</td>
<td>27</td>
</tr>
<tr>
<td>$(\text{EFAI/}{\text{Si}})_{\text{Si}} (x \times 10^3)$</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Accuracy: ± 10 %

Tab. 5.5: Analyses of M-Ox-8

![Fig. 5.15: $^{29}\text{Si}$ MAS NMR spectra of M-Ox-8](image-url)
The Si(0Al) peak of M-Ox-8 showed some resolution, not as good as that of M-HN-20 but better than that of M-Ox-4, although the number of defects in M-Ox-8 was somewhat higher than in M-Ox-4 and ten times as much as in M-HN-20. The main difference here was the lower EFAl content, which was about half of that in M-Ox-4. For this reason we assume that the splitting of the Si(0Al) peak is not affected by lattice defects but only by framework and extra-framework aluminum species.

### 5.2.4 XRD and IR

Unit cell parameters and dimensions in the a, b and c direction for HM, M-HN-20 and M-Ox-4 are summarized in Tab. 5.6. As can be seen, the dealumination process causes a contraction of the unit cell volume [27,28] as is expected for the removal of aluminum atoms whose T–O–T bond length is longer than that of silicon: 1.75 vs. 1.62 Å [29]. The cell constants are smallest for M-Ox-4 in agreement with its deeper removal of aluminum from the framework thus leaving hydroxyl groups in its place. Although a substitution of aluminum by silicon can not be ruled out completely, this seems unlikely since this substitution usually takes place in the presence of water vapor. This was not the case here since, before calcination, all samples were dried at 120°C during 10 h.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>vol (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HM</td>
<td>18.14</td>
<td>20.33</td>
<td>7.49</td>
<td>2762 ± 2</td>
</tr>
<tr>
<td>M-HN-20</td>
<td>18.05</td>
<td>20.26</td>
<td>7.47</td>
<td>2732 ± 1</td>
</tr>
<tr>
<td>M-Ox-4</td>
<td>18.01</td>
<td>20.19</td>
<td>7.44</td>
<td>2705 ± 2</td>
</tr>
</tbody>
</table>

Tab. 5.6: Unit cell dimensions

The changes in the unit cell dimensions are anisotropic, the strongest contraction occurring in the a and b direction, due to the selective removal of alu-
minum atoms from different inequivalent sites [28].

As a complement of $^1$H NMR, infrared analyses were also performed on HM, M-HN-20 and M-Ox-4, whose spectra of the hydroxyl region are given in Fig. 5.16.

![Infrared spectra](image)

**Fig. 5.16:** Infrared spectra of the hydroxyl region of: a) HM, b) M-HN-20, and M-Ox-4.

The samples contained many bridged hydroxyl groups, caused either by defects in the framework as in the case of the oxalic acid treated sample or by acidic hydroxyl groups interacting with the oxygen atoms of the framework, as in the case of M-HN-20. These interacting hydroxyl groups caused a broadening and a shift of the characteristic bands [30] thus rendering an unambiguous interpretation of the spectra impossible. In addition to this a quantitative evaluation of the spectra is generally not possible since a calibration to determine the extinction coefficient is hardly feasible.
5.2.5 Identification of the oxalate species

During dealumination with oxalic acid the presence of an oxalato complex was postulated. In order to confirm the presence of an oxalato complex in the zeolite pores and to identify its nature, mordenite dealuminated with oxalic was analyzed before and after calcination. The results were compared to those of the self-synthesized aluminum tris-oxalato and aluminum bi-oxalato reference compounds.

5.2.5.1 Equilibrium distribution

In order to identify the kind of species that took part in the equilibrium, MINEQL+, a program for chemical equilibrium modeling in aqueous solution from Environmental Research Software was employed. Starting concentration of

<table>
<thead>
<tr>
<th>Species</th>
<th>$\log K^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Al(C}_2\text{O}_4)_3]^2^+$</td>
<td>15.12</td>
</tr>
<tr>
<td>$[\text{Al(C}_2\text{O}_4)_2]^+$</td>
<td>11.09</td>
</tr>
<tr>
<td>$[\text{Al(C}_2\text{O}_4)]^{1+}$</td>
<td>6.00</td>
</tr>
<tr>
<td>$\text{H}_2\text{C}_2\text{O}_4$</td>
<td>4.22$^2$</td>
</tr>
<tr>
<td>$\text{HC}_2\text{O}_4^-$</td>
<td>1.12$^2$</td>
</tr>
<tr>
<td>$\text{OH}^-$</td>
<td>-14$^2$</td>
</tr>
<tr>
<td>$\text{Al(OH)}^{2+}$</td>
<td>-4.99$^2$</td>
</tr>
<tr>
<td>$\text{Al(OH)}_2^{2+}$</td>
<td>-10$^2$</td>
</tr>
<tr>
<td>$\text{Al(OH)}_3^{(aq)}$</td>
<td>-16.00$^2$</td>
</tr>
<tr>
<td>$\text{Al(OH)}_3^{-}$</td>
<td>-10.38</td>
</tr>
<tr>
<td>$\text{Al(OH)}_4^{-}$</td>
<td>-23</td>
</tr>
</tbody>
</table>

Tab. 5.7: Equilibrium constants of the species considered during equilibrium calculations

$^1$ Equilibrium constants of hydroxy species refer to the following equilibrium reaction:
$\text{Al(OH)}_{n}^{x^m} + n \text{H}^+ \rightarrow \text{Al}^{x^m} + n \text{H}_2\text{O}$. Therefore $\log K = \log \beta_{x^m} / \log (K_w)^n$

$^2$ These species were not found at equilibrium
[Al$^{3+}$] and [C$_2$O$_4^{2-}$] were 0.2 and 2 M, respectively. The species considered during the calculation and their equilibrium constants can be found in Tab. 5.7.

Fig. 5.17: Aluminum distribution calculated with MINEQL+. O: Al(ox)$_3^{3+}$; □: Al(ox)$_2$; ◊: Al(ox); △: Al(OH)$_4$; ♦: Al(OH)$_3$.5

The relative equilibrium concentrations, referred to aluminum, in the pH range 0 to 14 are plotted in Fig. 5.17. The pH of the 2 M oxalic acid solution employed during dealumination was 0.5. At this pH free aluminum ions do not exist, they form either a bi- or a tris-oxalato complex. The mono-oxalato species is only present at pH below 0.5 and at very low concentration (below 5 %). It will therefore not be considered a likely candidate. Aluminum forms a stable [Al(C$_2$O$_4$_3)$_5$] complex over a wide pH range, above pH 8, however, this complex quickly decomposes to Al(OH)$_3$ (s) and Al(OH)$_4^-$. From these preliminary results it was concluded that the existence of aluminum oxalato complexes in the zeolite pores was chemically feasible.
5.2.5.2 Sample synthesis

a) Aluminum tris-oxalato complex
Sodium aluminum tris-oxalate was prepared by adding 0.1 mol aluminum nitrate nonahydrate \( \text{Al(NO}_3\text{)}_3 \cdot 9 \text{H}_2\text{O} \) (Fluka, puriss p.a.) to a water solution containing 0.3 mol sodium oxalate \( \text{Na}_2\text{C}_2\text{O}_4 \) (Fluka, puriss, p.a.). The pH of the solution was regulated to \( \text{pH} = 4 \) by addition of nitric acid and sodium hydroxid. \( \text{Na}_3[\text{Al(C}_2\text{O}_4\text{)}_3] \) was obtained by evaporating the liquid phase. The product was finally purified by recrystallization.

b) Aluminum bis-oxalato complex
Aluminum bis-oxalate was prepared according to [31]. 0.05 mol aluminum ethoxide \( \text{Al(C}_2\text{H}_5\text{O)}_3 \) (Fluka, pract.) dissolved in 150 ml ethanol were added to 0.1 mol oxalic acid (Fluka, purum) dissolved in 150 ml ethanol. \( \text{Na[Al(C}_2\text{O}_4\text{)}_2] \cdot \text{EtOH} \) was precipitated by slowly adding 0.05 mol sodium ethoxide \( \text{NaC}_2\text{H}_5\text{O} \) (Fluka, pract.) dissolved in 200 ml ethanol to the alcoholic solution of aluminum-dioxalic acid. It was reported that the salt could not be recrystallized [31].

c) Zeolite containing an aluminum-complex
The dealumination procedure was the same as described in Chapter 4. Dealumination was carried out with 2 M oxalic acid for 1 h. The thus obtained sample was thoroughly washed and analyzed before and after calcination.
5.2.5.3 Analysis of the aluminum complex

$^{13}$C NMR

$^{13}$C NMR spectra of the two aluminum complexes and of the mordenite samples are reported in Fig. 5.18.

All samples, except the calcined mordenite, showed a peak at 168 ppm typical of oxalate species. This unambiguously shows that an aluminum oxalato complex was present within the mordenite pores. However, it was not possible to discriminate between the two complexes since they had the same shift.
UV–Vis

UV–Vis spectra were recorded on a Perkin Elmer Lambda16 spectrometer equipped with an integration sphere that allowed measurements in the reflection mode. BaSO₄ was used as a reference. The spectra were collected on powdered samples and represented through the Kubelka–Munk function, which is defined as [32]:

\[
F(R_m) = \frac{(1 - R_m)^2}{2 \cdot R_m}
\]

where \( R_m \) is the transmittance (0 ≤ \( R_m \) ≤ 1), i.e. the ratio between adsorption and reflection coefficient of the analyzed sample.

![UV–Vis spectra](image)

**Fig. 5.19:** UV–Vis spectra of: a) aluminum tri–oxalate, b) aluminum bi–oxalate, c) uncalcined mordenite, and d) calcined mordenite

The spectra in Fig. 5.19 showed that the uncalcined zeolite had a sharp band at around 200 nm and a weak one at 250 nm. Since both bands disappeared upon calcination and are in the same range as the characteristic bands of the
two aluminum complexes, it was suggested that they are due to the aluminum oxalato complexes in the zeolite pores. However, even these analyses were not sufficiently accurate to discriminate between the two aluminum complexes.

**Raman spectroscopy**

Raman measurements were performed with a FRA 106/s FT–Raman accessory mounted on an EQUINOX 55 Bruker in emission mode. The spectra of the two aluminum complexes and the calcined and uncalcined mordenite can be seen in Fig. 5.20.

![Raman spectra of: a) aluminum tri-oxalate, b) aluminum bi-oxalate, c) uncalcined mordenite, and d) calcined mordenite. The spectra are not scaled. In particular, spectra c) and d) were enlarged.](image)

The uncalcined mordenite samples showed three bands at around 1000 – 875, 1540 – 1400, and 1760 – 1640 cm⁻¹ which disappeared upon calcination. Comparison with the aluminum oxalate spectra identified these bands as belonging to an oxalato complex. The most characteristic feature of aluminum tris–
oxalate is the presence of a very sharp peak at 1050 cm\(^{-1}\) and a weaker one at 700 cm\(^{-1}\) which were neither present in aluminum bis-oxalate nor in the uncalcined mordenite sample, thus suggesting that the complex present in the mordenite pores was not aluminum trioxalate.

**Molecular modelling**

The framework of mordenite and aluminum tri- and bi-oxalato complexes were modelled using the Cerius\(^2\), version 3.5, program.

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Fig. 5.21: Simulation of aluminum bi-oxalate in the mordenite channels

The tri-oxalato complex was found to be too bulky to enter the mordenite pores (figure not shown). The slimmer aluminum dioxalate however, did fit in the
pores, as shown in Fig. 5.21.

Considering the preceding analyses of the samples which pointed to the presence of an aluminum complex in the mordenite pores, it is now suggested that the complex formed in mordenite is aluminum dioxalate. The presence of a mono-oxalato complex was ruled out since chemical equilibrium calculation showed that its concentration at the prevailing pH was negligible.

5.3 Conclusions

The effects of nitric and oxalic acid during the dealumination of mordenite were investigated. It was found that oxalic acid was more effective than nitric acid in dissolving framework aluminum. The resulting product contains many structural defects (silanol groups) and a fair amount of octahedrally coordinated aluminum in the zeolite channels. Nitric acid, on the other hand, dissolves almost all extra-framework aluminum and removes silica units which in turn leads to the formation of a secondary pore structure in the zeolite crystal.

The splitting of the Si(0Al) in the $^{29}$Si NMR is inhibited by the presence of both framework and extra-framework aluminum; silanol groups do not influence the resolution of the signal.

Due to the broadening and shifting of the bands, infrared spectroscopy is not a suitable technique for the characterization of samples with a high content of defects; relevant information can, however, be obtained from $^1$H NMR.

An oxalato species was found in the mordenite pores; molecular modeling indentified it as aluminum dioxalate.
5.4 References


6. Mordenite extrudates

6.1 Introduction

Whittemore described the preparation of mordenite extrudates using kaolin [1]. The first part of this chapter is dedicated to the study of this reaction, in particular the factors governing the synthesis will be investigated.

Using the knowledge about mordenite dealumination gathered in the previous chapter, methods for the dealumination of mordenite extrudates will be described. Differences in the dealumination behavior will be examined.

Finally mordenite extrudates will be employed for the adsorption of a solvent mixture. Their behavior will be compared to that of mordenite powder.

6.2 Synthesis of mordenite extrudates

6.2.1 Reaction temperature and time

Mordenite extrudates were prepared as described in Chapter 4.1.1. A factor influencing the reaction is the reaction time: by using high reaction temperature

<table>
<thead>
<tr>
<th>Run</th>
<th>T [°C]</th>
<th>t [h]</th>
<th>% crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>185</td>
<td>16</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>185</td>
<td>65</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>18</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>220</td>
<td>18</td>
<td>81</td>
</tr>
</tbody>
</table>

Tab. 6.1: Influence of temperature and reaction time.
Precursor molar composition: 1 Al: 0.95 Na: 4.9 Si; molar composition during reaction: 1 Al: 2.5 Na: 7.5 Si.
the time for the formation of the zeolites can be considerably shortened.

Tab. 6.1 shows that the reaction temperature played a central role in the crystallization of mordenite extrudates. In fact, it was found that the reaction was extremely slow at 185°C, reaching 50% crystallinity after 65 h reaction but could be accelerated by raising the temperature to 200°C. 18 h were then sufficient to achieve 80% conversion. A further raise to 220°C did not have any measurable influence on the crystallinity.

![Crystallization curve](image)

Fig. 6.1: Crystallization curves of mordenite extrudates (O) and of a mordenite powder synthesized with a conventional method ( ). Reaction temperature in O was 220°C, molar compositions were the same as in Tab. 6.1. Reaction conditions in were as follow: 2.6 Na : 1 Al : 7.7 Si : 235 H₂O – 0.7% seed; T = 195°C.

The time–crystallization curve depicted in Fig. 6.1 shows that 81% was the maximum achievable crystallinity for mordenite extrudates at 220°C, a prolonged reaction time did not raise the crystallinity any further.

The crystallization curves of mordenite extrudates and of powder have a dif-

104
ferent shape. The shape of these curves is related to the crystallization mechanism. In fact, a sigmoidal curve, as is the case for mordenite powder, is indicative of an induction period followed by rapid crystallization [2]. The crystallization curve of mordenite extrudates on the other hand, did not show a sharp knee. This points to a slower nucleation and growth rate since the reactants are bound together and diffusion of reactants is hindered.

Reaction of kaolin to zeolite was described by Akolekar et al. [3]. Their proposed mechanism involves three steps:

- the first step is the conversion of metakaolin to a gel type aluminosilicate phase due to the alkalinity of the solution;
- the second stage is nucleation: zeolite crystals begin to grow utilizing the matrix material and the volume available within the extrudates. Rees and Chandrasekhar [4] suggested that zeolite crystallization commenced before complete conversion of metakaolin to gel. This is in agreement with the gradual increase of the mordenite-yield reported in Fig. 6.1;
- the matrix steadily disappears, but the crystals are sufficiently bound together to retain the extrudate morphology.

Transformation of extrudates into crystalline mordenite extrudates was also followed by scanning electron microscopy and $^{27}$Al MAS NMR.
Fig. 6.2: SEM picture of unreacted precursor (top) and mordenite extrudates
No mordenite crystal could be recognized on the precursor surface. The surface is fairly smooth (Fig. 6.2). Many crystals were, however, visible in mordenite extrudates. In the same picture there were also small debris particles (< 500 nm), probably unreacted material.

$^{27}$Al MAS NMR of a calcined unreacted precursor and as-synthesized mordenite extrudates are reported in Fig. 6.3.

Fig. 6.3: $^{27}$Al MAS NMR of as-synthesized mordenite extrudates (top) and unreacted precursor.
As can be seen, both the unreacted precursors and the mordenite extrudates have a peak at around 55 ppm meaning that aluminum was tetrahedrally coordinated. This meant that NMR analysis could not be employed to calculate the framework silicon to aluminum ratio since a differentiation between framework aluminum and aluminum that belonged to the precursor matrix was not possible.

### 6.2.2 Variation of the calcination temperature

In order to establish whether the calcination temperature of the precursor had an effect on the crystallization of the mordenite extrudates, reactions with precursors calcined at 600, 700, and 800°C were carried out at normalized conditions. Higher calcination temperatures were not investigated because of the transformation of metakaolin into spinel at around 900°C.

<table>
<thead>
<tr>
<th>Run</th>
<th>Calc. temperature [°C]</th>
<th>% crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>700</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>800</td>
<td>79</td>
</tr>
</tbody>
</table>

Tab. 6.2: Influence of the calcination temperature on the reaction yield. The reactions were carried out at 220°C during 18 h. Molar composition were the same as in Tab. 6.1.

Results in Tab. 6.2 show that the calcination temperature did not affect the rate of crystallization. In order to clarify the role of the calcination temperature, the transition of kaolin to metakaolin was investigated by thermal analysis. Thermogravimetric analysis combined with single differential scanning analysis was performed on a TGA/SDTA 851° Mettler Toledo instrument under air/nitrogen flow (1:1) in the temperature range 25 – 800°C with a heating rate of 10°C/min. The results are reported in Fig. 6.4.
6.2.3 Presence of quartz after transformation to mordenite

Transformation into mordenite was followed with XRD. Typical diffractograms of mordenite extrudates, unreacted precursors, and metakaolin are reported in Fig. 6.5.
Fig. 6.5: XRD diffractograms of a) metakaolin; b) unreacted precursors; c) mordenite extrudates. The thick peak at 2 Theta = 27 degree was attributed to quartz.

The transformation yielded a highly crystalline mordenite: no peaks attributed to mordenite were found in the precursor, whereas the final material was highly crystalline. Analcime, a by-product often found when synthesizing mordenite over a long time [5], was not present in the final product. However, at 2 Theta = 27 degree a peak attributed to quartz was noticed. Although quartz is sometimes a by-product of zeolite synthesis [6], in this case it was not generated during the synthesis since it was already present in the calcined precursor and in the metakaolin phase. Quartz probably originates from the rearrangement of the kaolin structure during calcination. A consequence of this is that the presence of a small amount of quartz is unavoidable and has to be taken in account.
6.2.4 Variation of reactant composition

Another parameter that could influence the synthesis is the composition of the precursor and of the reaction mixture. For this purpose precursors with different kaolin, silica, and waterglass content were prepared. Their composition and the effect on the achieved crystallinity are reported in Tab. 6.3. Run 0 refers to the usual reaction conditions, in Runs 1–4 the amount of kaolin was successively decreased, in Runs 5–6 the amount of silica was decreased, whereas Run 7 was carried out using extrudates prepared with less sodium silicate solution.

<table>
<thead>
<tr>
<th>Run</th>
<th>Prec</th>
<th>Al</th>
<th>Na</th>
<th>Si</th>
<th>Cryst. [%]</th>
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<td>prec.</td>
<td>1.0</td>
<td>0.95</td>
<td>4.9</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>react.</td>
<td>1.0</td>
<td>2.5</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>prec.</td>
<td>1.0</td>
<td>1.1</td>
<td>5.3</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>react.</td>
<td>1.0</td>
<td>2.4</td>
<td>7.7</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>prec.</td>
<td>1.0</td>
<td>1.2</td>
<td>5.8</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>react.</td>
<td>1.0</td>
<td>2.7</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>prec.</td>
<td>1.0</td>
<td>1.6</td>
<td>7.4</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>react.</td>
<td>1.0</td>
<td>3.1</td>
<td>9.9</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>prec.</td>
<td>1.0</td>
<td>2.4</td>
<td>10.6</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>react.</td>
<td>1.0</td>
<td>3.4</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>prec.</td>
<td>1.0</td>
<td>0.96</td>
<td>4.3</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>react.</td>
<td>1.0</td>
<td>2.5</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>prec.</td>
<td>1.0</td>
<td>0.96</td>
<td>3.9</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>react.</td>
<td>1.0</td>
<td>2.5</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>prec.</td>
<td>1.0</td>
<td>0.81</td>
<td>4.6</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>react.</td>
<td>1.0</td>
<td>2.5</td>
<td>7.5</td>
<td></td>
</tr>
</tbody>
</table>

Tab. 6.3: Achieved crystallinity with precursors of different composition. Prec.: precursor composition; react.: composition during reaction to mordenite, i.e. precursors and waterglass.

All reactions were carried out at 220°C during 18 h.
These results show that there is an optimal composition range for the transformation to mordenite. As already reported by Bajpai [5] for the synthesis of mordenite powder, the initial composition of the mixture, and in particular the Si/Al ratio, is of paramount importance in governing the crystallization to mordenite. Barrer and White [6] noticed that by increasing the Si/Al ratio, the product formation was in the direction analcime (Si/Al = 2 - 2.5) to mordenite (Si/Al = 4 - 6) to quartz (Si/Al > 6). From the results reported in Tab. 6.3 it seems that the crystallization of mordenite required higher silicon to aluminum ratios. However, this is understandable since a part of silicon is added in the autoclave during the transformation to mordenite as sodium silicate solution: only a part of this silicon is effectively incorporated in the mordenite phase, in fact the Si/Al ratio of the as-synthesized mordenite extrudates is 5.7 in Run 0. These reaction experiments showed that, in order to obtain a highly crystalline material, the Si/Al ratio of the precursor had to be increased by diminishing the amount of kaolin added during precursor preparation. In fact, by adding 20 % less kaolin (Run 2) a crystallinity of 87 % was obtained. A further decrease of kaolin led to lower crystallinity. The reason was that in this case the Si/Al ratio was above the optimal limit.

As expected, decreasing the amount of silica (Runs 5 and 6) lowered the quality of the product.

Comparison of Runs 0 and 7 showed that, although the molar composition during the reaction was the same, a lower crystallinity was achieved. The difference between the two runs was that Run 7 had a different precursor composition, in fact its sodium and silicon content were lower compared to Run 0. This implies that the precursor composition is a critical factor in the synthesis of mordenite and that the building units come preferentially from the precursor matrix; the role of the sodium silicate solution is to facilitate its conversion to a zeolite.
In addition to this, reaction experiments varying the amount of waterglass during the synthesis were carried out as well.

<table>
<thead>
<tr>
<th>Run</th>
<th>Al</th>
<th>Na</th>
<th>Si</th>
<th>Cryst. [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>2.0</td>
<td>6.6</td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2.5</td>
<td>7.5</td>
<td>81</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>3.3</td>
<td>8.3</td>
<td>80</td>
</tr>
</tbody>
</table>

Tab. 6.4: Molar composition during conversion to mordenite. Molar composition of the unreacted precursors is the same as in Run 0 in Tab. 6.3. Reaction temperature and time were 220°C and 18 h, respectively.

A confirmation that the amount of silicate solution added during the transformation to mordenite was not a critical factor, came from the data reported in Tab. 6.4. In fact, decreasing (Run 1) or increasing (Run 3) the amount added, compared to the standard synthesis method (Run 2), did not significantly affect the synthesis.

6.2.5 Effect of different silica and kaolin sources

Other factors that could affect the quality of the synthesis were the silica and kaolin sources. As silica sources, three different samples were used: two precipitated silica’s, i.e. FK320 (Degussa) and Hi-Sil (PPG), and a pyrogenic silica, i.e. Cab–osil M–5 (Fluka). Data on nitrogen adsorption and weight loss upon calcination are collected in Tab. 6.5.
<table>
<thead>
<tr>
<th>Silica sample</th>
<th>MSA [m$^2$/g]</th>
<th>ESA [m$^2$/g]</th>
<th>weight loss [%]</th>
<th>weight loss [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>at 200°C</td>
<td>at 800°C</td>
<td></td>
</tr>
<tr>
<td>FK320</td>
<td>50</td>
<td>130</td>
<td>4.5</td>
<td>7.0</td>
</tr>
<tr>
<td>Hi-Sil</td>
<td>46</td>
<td>130</td>
<td>4.5</td>
<td>7.0</td>
</tr>
<tr>
<td>Cab-osil M-5</td>
<td>43</td>
<td>157</td>
<td>0.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Tab. 6.5: Micropore surface area (MSA), external surface area (ESA), and weight loss upon calcination of the three silica samples.

The precipitated and pyrogenic silica's differ in their method of synthesis. As the name suggests, precipitated silica, which consists of aggregates of colloidal silica particles, is obtained by precipitation from an alkaline silicate solution, such as sodium silicate, by addition of an acid, usually sulfuric acid. Pyrogenic silica, also called fumed silica, a highly-disperse, fluffy powder, is produced by flame hydrolysis of silicon tetrachloride mixed with dry air and hydrogen at around 2000°C. The resulting SiO$_2$ and hydrochloric acid have then to be separated. These two methods of preparation result in materials with different characteristics: pyrogenic silica typically consists of non-porous, extremely fine particles (7–40 nm) with a high external surface area having a silanol group concentration of 2.5 to 3.5 SiOH/nm$^2$. Precipitated silica, on the other hand, consists generally of larger aggregates possessing a smaller external surface area but showing some pore volume; the surface has 5–6 silanols per nm$^2$, thus being more hydrophilic than the previous silica. The weight loss by calcination confirmed that Cab–osil M–5 was less hydrophilic (0.5 % loss at 200°C compared to 4.5 % for the other silica samples) and contained less silanols (a further 0.5 % weight loss at 800°C compared to 2.5 % for FK320 and Hi–Sil).

The results of the syntheses of mordenite extrudates are reported in Tab. 6.6
Tab. 6.6: Crystallization yields when using different silica sources. Reaction temperature and time were 220°C and 18 h, respectively. Molar composition were the same as in Tab. 6.1.

The silica source was found not to play a significant role in the synthesis of mordenite extrudates.

Beside kaolin from Fluka, three other kaolin samples were investigated, i.e. one from ICN and two samples from Acros. Their chemical analyses can be found in Tab. 6.7, whereas the results of the syntheses are reported in Tab. 6.8.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂ [%]</th>
<th>Al₂O₃ [%]</th>
<th>Na₂O [%]</th>
<th>Fe₂O₃ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Fluka</td>
<td>45.1</td>
<td>54.7</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td>2 ICN</td>
<td>36.8</td>
<td>62.9</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>3 Acros</td>
<td>34.8</td>
<td>64.9</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>4 Acros</td>
<td>51.4</td>
<td>48.3</td>
<td>0.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Tab. 6.7: Relative molar composition of the different kaolin samples as determined by AAS.

<table>
<thead>
<tr>
<th>Run</th>
<th>Kaolin source</th>
<th>Crystallinity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fluka</td>
<td>81</td>
</tr>
<tr>
<td>2</td>
<td>ICN</td>
<td>72</td>
</tr>
<tr>
<td>3</td>
<td>Acros 1</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>Acros 2</td>
<td>91</td>
</tr>
</tbody>
</table>

Tab. 6.8: Achieved crystallinity using different kaolin sources. Reactions were carried out at 220°C for 18 h.

The change of kaolin source had a greater influence on the obtained crystallinity than the change of the silica source. An improvement in the crystal-
linity of more than 10 % compared with Run 1 was observed in Run 4.

The kaolin composition in Tab. 6.8 showed that Samples 1 and 4, from which the best results were obtained, had a higher silica content than the others. In 6.2.4 a higher silica content in precursors has already been linked to an improvement of the synthesis quality. It is therefore suggested that the increase of the crystallinity when using Samples 1 and 4 is due to the different composition of kaolin with regard to the silica and alumina content.

In contrast with Murat et al. [7,8] who, for the synthesis of zeolite 4A, found that the lower the iron content of the kaolin sample, the better the synthesis (see also [9]), it was found that the best results were obtained using the two samples with the highest iron content. However, the kaolin samples used here (maximum iron content 0.7 %) had a lower iron content than the one used by Murat et al. which did not give satisfactory results (iron content 1.3 %). This would indicate that iron exhibits an inhibitory activity on the synthesis of zeolite only at higher concentration than the one used here.

6.3 Dealumination of mordenite extrudates

6.3.1 Preliminary results

Mordenite extrudates were exchanged using 1 M hydrochloric acid followed by 1 M ammonium nitrate, calcined 2 h at 750°C, and dealuminated using 6 M nitric acid or 2 M oxalic acid during 18 h, as described in Chapter 4.1.2; their analyses are reported in Tab. 6.9.
Mordenite extrudates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al</th>
<th>MSA [m²/g]</th>
<th>ESA [m²/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-MOR-Extr</td>
<td>5.7</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>H-MOR-Extr</td>
<td>6.3</td>
<td>377</td>
<td>2</td>
</tr>
<tr>
<td>HN-MOR-Extr</td>
<td>7.2</td>
<td>400</td>
<td>5</td>
</tr>
<tr>
<td>Ox-MOR-Extr</td>
<td>23</td>
<td>486</td>
<td>5</td>
</tr>
</tbody>
</table>

Tab. 6.9: Bulk Si/Al ratio and nitrogen adsorption results of mordenite extrudates. Na-MOR-Extr: as-synthesized; H-MOR-Extr: exchanged using 1 M HCl followed by 1M NH₄NO₃; HN-MOR-Extr: dealuminated with 6 M nitric acid; Ox-MOR-Extr: dealuminated using 2 M oxalic acid.

Comparison of these results with those of the mordenite powder (Chapter 5) showed that the exchange and dealumination behaviors are quite different:

- as-synthesized extrudates did not possess any surface area. However, a highly porous material is obtained after sodium exchange;
- dealumination with nitric acid was much less effective than with oxalic acid: while aluminum removal with oxalic acid amounted to 73 %, with nitric acid only 12 % of the aluminum could be leached;
- dealumination of mordenite extrudates was lower than with mordenite powder (final Si/Al of 77 and > 100 when using nitric and oxalic acid, respectively).

As with mordenite powder, oxalic acid was found to be the better dealuminating agent. This was correlated with the fact that it can act both as hydrolizing and as chelating agent.

6.3.2 Effect of sodium exchange

The strong increase in the micropore and, partially, in the external surface area observed upon ion exchange, can not only be attributed to the removal of sodium acting as a counterion. Some debris particle also contributed to the pore blockage.
In order to identify the nature of this debris, the zeolite extrudates were weighed and analyzed by AAS before and after sodium exchange. The concentration of silicon, aluminum, and sodium was determined in the aqueous solution as well. The amount of dissolved species was found by subtracting the amount of species in the aqueous solution found by AAS from the amount of the same species in the as-synthesized mordenite extrudates. The accuracy of this method was crosschecked with the composition of the exchanged mordenite, as determined by AAS.

This procedure was applied to mordenite extrudates exchanged with two different methods. The first involved a three-step sodium exchange using 1 M ammonium nitrate, the second an exchange with 1 M hydrochloric acid followed by 1 M ammonium nitrate. The results are reported in Tab. 6.10.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al</th>
<th>Na/Al</th>
<th>MSA [m²/g]</th>
<th>ESA [m²/g]</th>
<th>dissolved species [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-MOR-Extr</td>
<td>5.7</td>
<td>0.94</td>
<td>3</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>H1-MOR-Extr</td>
<td>5.7</td>
<td>0.18</td>
<td>401</td>
<td>1</td>
<td>0.13 0.01 80.48</td>
</tr>
<tr>
<td>H2-MOR-Extr</td>
<td>6.3</td>
<td>0.09</td>
<td>377</td>
<td>2</td>
<td>0.77 10.91 90.83</td>
</tr>
</tbody>
</table>

Tab. 6.10: Identification of the dissolved species during sodium exchange. H1-MOR-Extr: three-fold exchange using 1 M NH₄NO₃; H2-MOR-Extr: exchange using 1 M HCl followed by 1 M NH₄NO₃.

The exchange with ammonium nitrate (H1-MOR-Extr) dissolved mainly sodium and some silicon. This suggests that the pore blockage is due to sodium acting as a counterion and to sodium silicate species left after hydrothermal transformation to mordenite. Dissolution of other species did not play a significant role in the increase of the extrudate surface area, in fact H2-MOR-Extr had similar textural properties even though there was a fair removal of aluminum.

The surface area did not change significantly when the exchange was car-

---

1 Amount of dissolved species relative to Na-MOR-Extr (in weight %)
ried out using a combination of hydrochloric acid and ammonium nitrate, the material composition, however, was different: while the first exchange procedure affected only the sodium to aluminum ratio, the second exchange procedure resulted in a material having significantly less aluminum owing to the dealuminating capacity of the 1 M hydrochloric acid solution. This method was also more effective in removing sodium: more than 90% of it could be exchanged.

Since one of the goals of this research was to obtain a highly dealuminated material, exchange procedure 2 was employed.

6.3.3 Effect of high temperature calcination

As already mentioned in Chapter 5, a calcination step before acid leaching is necessary in order to facilitate the removal of aluminum. The high temperature calcination of a zeolite leads to a migration of aluminum from a framework to an

![Graph showing the effect of high temperature calcination on the Si/Al ratio.](image)

Fig. 6.6: Obtained silicon-to-aluminum ratio vs. calcination temperature after dealumination with 2 M oxalic acid.
extra-framework position, where it is more easily dissolved. It was therefore checked if, by varying the calcination temperature of the exchanged extrudates, a higher dealumination degree could be achieved.

The results of the dealumination experiments using 2 M oxalic acid during 18 h on H-MOR-Extr are reported in Fig. 6.6.

As can be seen, the Si/Al ratio after dealumination resulted in a curve showing a maximum of dealumination at 700°C, where a Si/Al ratio up to 27 could be reached. Below that temperature, aluminum leaching was lower. This is related to the fact that the calcination temperature was too low to allow an appreciable migration of aluminum in extra-framework position.

Aluminum removal from mordenite extrudates calcined at temperatures higher than 700°C was also lower, in spite of the increased formation of extra-framework aluminum hydroxide species which should facilitate aluminum leaching. However, the increased availability of aluminum hydroxides species combined with the high calcination temperature led to the transformation of them into an insoluble aluminum oxide phase.

6.3.4 Steam calcination

Instead of a shallow bed calcination, mordenite extrudates were subjected to a steam calcination before each leaching with 2 M oxalic acid. Extrudates in the ammonium form, i.e. not subjected to high temperature calcination after ion exchange, were placed inside a cylindrical reactor that was heated to 500°C. Steam dealumination was then carried out for 6 h at 500°C by flowing water vapor through the reactor. The product was finally dried at 500°C for 1 h.

Acid leaching was carried out using the conventional procedure described in Chapter 4.1.2, by stirring the extrudates with 2 M acid at reflux temperature. The whole procedure, i.e. steam dealumination and acid leaching, was repeated.
Fig. 6.7: Si/Al ratio after each leaching step. Step 0 was Ox-MOR-Extr, as described in Tab. 6.9.

Comparison of the Si/Al ratios obtained after each step with the mordenite extrudates, dry–calcined and dealuminated using 2 M oxalic acid (Run 0 in Fig. 6.7) showed that steam calcination was better than shallow bed calcination. Whereas a Si/Al ratio of 23 was reached with a dry calcination followed by acid leaching (Step 0), a Si/Al ratio up to 30 was reached after the first calcination–leaching step when applying steam calcination, i.e. there was a 23 % increase in aluminum removal. After three steps a Si/Al ratio of 47 was attained. This indicated that 88 % of the aluminum, compared to the exchanged extrudates which had Si/Al = 5.6, could be leached out of the zeolite and a 51 % improvement compared to Run 0 was attained.

This indicates that steam calcination is able to extract more aluminum form the framework and that the resulting extra–framework aluminum species were
more soluble.

### 6.3.5 Comparison of powder and extrudate dealumination

In order to find out if diffusion of acid into, or of aluminum out of the zeolite pore had an influence on the dealumination behavior, experiments using whole and finely crushed mordenite extrudates were carried out using 6 M nitric acid or 2 M oxalic acid, after dealumination with 1 M hydrochloric acid and 1 M NH₄NO₃; the results are reported in Tab. 6.11.

<table>
<thead>
<tr>
<th>Run</th>
<th>Treatment</th>
<th>Si/Al</th>
<th>Al extraction [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole extrudates</td>
<td>H exchange</td>
<td>6.5</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>6 M nitric acid</td>
<td>21</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>2 M oxalic acid</td>
<td>32</td>
<td>80</td>
</tr>
<tr>
<td>Crushed extrudates</td>
<td>H exchange</td>
<td>7.5</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>6 M nitric acid</td>
<td>26</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>2 M oxalic acid</td>
<td>37</td>
<td>80</td>
</tr>
</tbody>
</table>

Tab. 6.11: Aluminum removal after dealumination relative to the aluminum content of exchanged extrudates.

These results show that diffusion did not hinder the dealumination of the extrudates. In fact the relative aluminum extraction, referred to the exchanged extrudates in the same Run, was exactly the same, regardless of the fact if whole or crushed extrudates were employed. Only the exchange step was influenced by the smaller particle size; comparison of whole and crushed extrudates revealed that when using crushed extrudates there was a 13 % increase in the aluminum removal. This diffusion limitation, however, was not sufficient to explain the lower dealumination degree compared to mordenite powder.

Variation of some parameters during dealumination permitted to improve the aluminum removal, in particular the use of a steam calcination instead of a dry
Mordenite extrudates

one, even though the reached Si/Al ratios were always much lower compared to mordenite powder.

In order to explain the lower dealumination of mordenite extrudates an exchanged unreacted precursor was dealuminated using 2 M oxalic acid for 18 h, and its results compared with those of mordenite powder and mordenite extrudates exchanged and dealuminated under the same conditions, as reported in Tab. 6.12.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(Si/Al)$_{exch}$</th>
<th>(Si/Al)$_{deal}$</th>
<th>Al removal [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder</td>
<td>6.7</td>
<td>120</td>
<td>94</td>
</tr>
<tr>
<td>Extrudates</td>
<td>6.3</td>
<td>23</td>
<td>73</td>
</tr>
<tr>
<td>Precursor</td>
<td>5.8</td>
<td>8.6</td>
<td>32</td>
</tr>
</tbody>
</table>

Tab. 6.12: Si/Al ratios of mordenite powder, mordenite extrudates, and unreacted precursors after dealumination with 2 M oxalic acid for 18 h. Aluminum removal is relative to the aluminum content of the exchanged material.

Dealumination of the unreacted precursors was very low. Only about 32 % of the aluminum could be removed, while aluminum removal of mordenite powder was 94 %.

As found earlier in this chapter, mordenite extrudates are 80 % crystalline, i.e. they contain 20 % unreacted precursor acting as a matrix holding the extrudates together. From the data presented here it seems that the reason for the low dealumination of the extrudates is the presence of a hard-to-dealuminate unreacted precursor phase. To clarify this, and in particular to exclude the possibility that the unreacted precursor phase somehow blocked the dealumination of the zeolite phase, as for instance by partially preventing the contact with the acid phase, unit cell dimensions of sodium extrudates (as-synthesized) and of extrudates dealuminated with 2 M oxalic acid were measured. These results were compared with the unit cell dimension of a zeolite powder dealuminated with
2 M oxalic acid having a Si/Al = 55, i.e. a value near the hypothetical Si/Al of the zeolite phase, supposing that the dealuminated mordenite extrudates (Si/Al = 23) are composed of 20 % unreacted precursor (Si/Al = 8.6) and 80 % zeolite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>vol (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na extrudates</td>
<td>5.7</td>
<td>18.10</td>
<td>20.47</td>
<td>7.52</td>
<td>2785 ± 1</td>
</tr>
<tr>
<td>Deal. extrudates</td>
<td>6.3</td>
<td>18.03</td>
<td>20.20</td>
<td>7.44</td>
<td>2709 ± 2</td>
</tr>
<tr>
<td>Mord. powder</td>
<td>55</td>
<td>18.04</td>
<td>20.23</td>
<td>7.45</td>
<td>2719 ± 1</td>
</tr>
</tbody>
</table>

Tab. 6.13: Comparison of unit cell dimensions of as-synthesized and exchanged mordenite extrudates with dealuminated mordenite powder.

Removal of aluminum tetrahedra from the zeolite framework causes a contraction of the unit cell volume because the presence of aluminum ions causes an expansion of the lattice due to the negative charge and larger size of the aluminum ion, compared to silicon tetrahedra.

Olsson and Rollmann [10] quantitatively correlated the unit cell dimension of dealuminated mordenites with their aluminum content. The scope of our analysis was not to quantify the aluminum content of the extrudates, which would have required the analyses of many extrudates with different Si/Al ratios in order to establish a reliable trend, but rather to qualitatively estimate the Si/Al ratio of the zeolite phase in the dealuminated extrudates.

The data reported in Tab. 6.13 show that the unit cell of the zeolite phase contained in the dealuminated extrudates underwent a great contraction, nearly 3 %, comparable to the one of mordenite powder. This suggests that the zeolite phase is dealuminated to a high extent, thus supporting the assumption that the reason for the lower dealumination of the mordenite extrudates is not the difficulty of dealumination of the zeolite itself, but rather the presence of a phase that is hard to dealuminate.

Moreover, these results combined with the one gathered in Chapter 6.3.5
that showed that there is only a slight influence of diffusion, permitted to exclude the possibility that the unreacted precursor phase prevented the dealumination of the zeolite.

6.4 Adsorption experiments

6.4.1 Introduction

The main purpose of this project was to find a viable method for the preparation of zeolite adsorbens to be employed in the abatement of VOC in exhaust gas.

For this reason the adsorption capacity of the extrudates prepared as described before was tested. Their behavior was then compared with that of pelletized mordenite.
6.4.2 Experimental

6.4.2.1 Adsorption unit

Fig. 6.8: Setup of the adsorption unit

The adsorption unit used during the measurements comprised five parts (see Fig. 6.8):

- solvents and water were injected with the help of two precision pumps in a helium stream that acted as a carrier gas;
- a mixer was necessary in order to level variations in the solvent concentration;
- the reactor consisted of a steel cylinder that enclosed an adsorption chamber containing the zeolitic material. Two thermocouples, one in the chamber, the other around it, controlled the temperature;
- a Shimadzu GC14A gaschromatograph analyzed solvent and water concentration;
- a heater and a thermostatic bath kept a constant temperature throughout the adsorption process.

### 6.4.2.2 The adsorption process

Before every adsorption experiment, 1 – 1.5 g zeolitic adsorbents were calcined in situ at 500°C under helium flow; the reactor was then cooled to 26°C and kept at that temperature during adsorption.

The adsorption behavior will be explained by commenting Fig. 6.9 which shows the ideal profile of an adsorption experiment using one solvent. In this figure five different regions can be recognized.

![Fig. 6.9: Ideal profile of an adsorption experiment using one solvent.](image)
Initial concentrations had to be kept as constant as possible; for this reason a mixer was built in and the unit was kept running overnight, by-passing the reactor, before every experiment (region 1). When solvent concentrations were found to be constant, the solvent flow was diverted to the reactor and the outgoing concentrations monitored by gas chromatography. This diversion caused the concentration to suddenly drop to zero, meaning that the solvent was completely adsorbed in the zeolite (region 2). When the amount of solvent exceeded the adsorption capacity of the zeolite, a sudden breakthrough was observed and the outgoing concentration equaled the incoming one (region 3). The breakthrough can be accelerated or retarded by other solvents. When the relative concentration \( c/c_0 \) reached 1, the solvent flow through the reactor was replaced by pure helium and an isothermic desorption was carried out (region 4). At its completion a temperature programmed desorption to 500°C (heating rate 25°C/min) completed the adsorbens regeneration (region 5).

A full description of the reactor and the adsorption procedure can be found in [11].

6.4.2.3 Solvents employed

Five different solvents, i.e. methanol, methyl ethyl ketone, \( n \)-pentane, \( p \)-xylene, and toluene plus water were employed during the adsorption study (Fig. 6.10).
These molecules were chosen because they have different characteristics with respect to polarity, vapor pressure, and dimensions, as summarized in Tab. 6.14.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Polarity $\epsilon^0$ (Al$_2$O$_3$)</th>
<th>Vapor pressure [kPa]</th>
<th>Van der Waals volume [m$^3$/kmol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>1.00</td>
<td>3.41</td>
<td>0.01237</td>
</tr>
<tr>
<td>methanol</td>
<td>0.95</td>
<td>17.4</td>
<td>0.02171</td>
</tr>
<tr>
<td>MEK</td>
<td>0.51</td>
<td>14.1</td>
<td>0.04927</td>
</tr>
<tr>
<td>n-pentane</td>
<td>0</td>
<td>71.8</td>
<td>0.05803</td>
</tr>
<tr>
<td>toluene</td>
<td>0.29</td>
<td>4.03</td>
<td>0.05951</td>
</tr>
<tr>
<td>p-xylene</td>
<td>0.26</td>
<td>1.26</td>
<td>0.07066</td>
</tr>
</tbody>
</table>

Tab. 6.14: Physical properties of the solvents used during the adsorption experiments

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1 $\epsilon^0$ values refers to the adsorbent alumina and are relative to the solvent n-pentane, for which $\epsilon^0$ is defined equal to zero [12].
2 Calculated from the Antoine equation $\log p = A - B/(T + C)$. A, B, and C values from [13]
3 Data from [14]; they were calculated from experimental data, namely, from covalent bond distances and van der Waals radii [15].
Chapter 6

Water and a solution containing all the solvents were injected in an helium stream. The solution composition and pump speed were chosen so as to have an initial concentration of 1000 ppm (vol/vol) for each solvent, only water had an initial concentration of 14250 ppm (vol/vol), corresponding to 60 % relative humidity.

Measurements were carried out with and without water addition.

6.4.2.4 Adsorbents properties

The properties of the employed adsorbents are summarized in Tab. 6.15

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al</th>
<th>MSA [m$^2$/g]</th>
<th>ESA [m$^2$/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-HN-20</td>
<td>77</td>
<td>467</td>
<td>32</td>
</tr>
<tr>
<td>M-Ox-4</td>
<td>79</td>
<td>597</td>
<td>13</td>
</tr>
<tr>
<td>H-MOR-Extr</td>
<td>6.3</td>
<td>377</td>
<td>2</td>
</tr>
<tr>
<td>HN-MOR-Extr</td>
<td>20.5</td>
<td>485</td>
<td>8</td>
</tr>
<tr>
<td>Ox-MOR-Extr</td>
<td>31</td>
<td>494</td>
<td>7</td>
</tr>
</tbody>
</table>

Tab. 6.15: Silicon-to-aluminum ratios and textural properties of the adsorbents employed during the adsorption studies.

6.4.3 Results and discussion

6.4.3.1 Adsorption on mordenite powder

Before analyzing results of solvents adsorption on extrudates, the behavior of mordenite powder in the adsorption of the solvent mixture will be explained by commenting the adsorption profiles of M-HN-20 in Fig. 6.11 and M-Ox-4 in Fig. 6.12. These results will then be used to interpret the adsorption profiles of mordenite extrudates.
Comparison of the ideal adsorption profile in Fig. 6.9 with those experimentally found shows that the behavior at breakthrough was very different. In fact the relative concentration $c/c_0$ of the first components was remarkably higher than 1; this is due to the fact that some solvents are displaced by others and are literally pushed out of the zeolite pores.

As depicted in Fig. 6.11, the first molecules to desorb are n-pentane, followed by toluene and p-xylene, i.e. the molecules that only weakly interact with the zeolite framework due to their lack of polarity. Although p-xylene is slightly less polar than toluene it desorbed later because of its dimensions: diffusion of smaller molecules, such as toluene, from the zeolite pores is favored.

Water, methanol, and methyl ethyl ketone, on the other hand, are able to interact with Brønsted hydroxyl groups of the zeolite framework, as well as with silanols groups and with Lewis acid centers associated with extra-framework aluminum and desorbed therefore later.
The adsorption behavior of M-Ox-4 in Fig. 6.12 was different from that of M-HN-20, in particular for the polar molecules. As already observed in Chapter 5, dealumination with oxalic acid leaves a fair amount of extra-framework aluminum in the zeolite pores and leads to the formation of a large number of defects, i.e. silanol groups.

n-Pentane, toluene, and p-xylene broke through in the same order as with M-HN-20. Toluene and p-xylene, however, desorbed significantly later and this is explained with differences in the textural properties of the material: As reported in Tab. 6.15, M-Ox-4 has more micropore and less external surface area than M-HN-20. This hindered the diffusion of adsorbed molecules, in particular the bulkier ones, as toluene and p-xylene, out of the zeolite pores. Water desorbed a little earlier probably because of the diminished aluminum content in the framework that reduced the amount of hydrophilic Brønsted hydroxyls. The most striking difference was the retarded desorption of methyl ethyl ketone.
This implies that extra-framework aluminum species and silanol groups have a great influence on the adsorption of methyl ethyl ketone.

### 6.4.3.2 Adsorption on exchanged mordenite extrudates

Preliminary adsorption experiments were carried out using H-MOR-Extr. This will permit to gain a better understanding of the adsorption process on dealuminated extrudates. The adsorption in Fig. 6.13 was carried out in the presence of water, while the one depicted in Fig. 6.15 was carried out in its absence.

![Graph](image)

Fig. 6.13: Adsorption results of H-MOR-Extr. Experiment carried out in the presence of water.

Adsorption on H-MOR-Extr with or without water was not selective, all solvent broke through at the same time, only water and methanol had a delayed desorption. This showed that only these two molecules were able to interact with acidic hydroxyl groups. Methyl ethyl ketone, as found in the previous sec-
tion, is preferentially adsorbed on extra-framework aluminum species and silanol groups and does not show a good affinity for acidic protons.

The possible interactions of water and methanol with the zeolite framework are shown in Fig. 6.14.

![Interactions of water and methanol molecules with acidic hydroxyl groups of the zeolite framework.](image)

Fig. 6.14: Interactions of water and methanol molecules with acidic hydroxyl groups of the zeolite framework.

![Adsorption profile of H-MOR-Extr, without addition of water.](image)

Fig. 6.15: Adsorption profile of H-MOR-Extr, without addition of water.
An adsorption experiment carried out without water addition, as depicted in Fig. 6.15, showed that no solvent but methanol was influenced by the absence of water: hydrophilic centers that were previously occupied by water are now occupied by methanol. Despite the increased availability of acid centers, methyl ethyl ketone was not affected, again indicating that it did not have a high affinity for these sites.

6.4.3.3 Adsorption on extrudates dealuminated with nitric acid

The following adsorption experiments were carried out using HN-MOR-Extr.

![Graph](image)

Fig. 6.16: Adsorption results of HN-MOR-Extr in the presence of water.

The adsorption in Fig. 6.16 was carried out in the presence of water. Comparison with Fig. 6.11 shows that HN-MOR-Extr adsorbed slightly less solvents than M-HN-20. The explanation for this behavior is that mordenite extrudates were less crystalline than mordenite powder and their adsorption capacity was therefore lowered. The desorption order was similar to HN-HN-20, only water
desorbed significantly earlier. This was rather surprising since, considering the higher aluminum content ratio of the extrudates which pointed to a higher affinity with water, a retarded desorption, compared to M-HN-20, was expected. An explanation could be that, as mentioned in Chapter 6.3.5, the zeolite phase underwent a high dealumination, thus reducing the amount of acidic hydroxyls. A similar effect was also observed for methanol.

![Adsorption experiment without water](image)

Fig. 6.17: Adsorption of solvents on HN-MOR-Extr without water addition.

The adsorption experiment without water in Fig. 6.17 showed that, as expected, the solvents which were most influenced by the absence of water were the more polar methyl ethyl ketone and methanol. One reason for the increased uptake of methanol has been explained in the previous section, i.e. the absence of water molecules that compete for the same adsorption sites.

A factor that also influences the adsorption of methanol and methyl ethyl ketone is the presence of hydroxyl groups left in the zeolite framework after
Mordenite extrudates dealumination. It is certainly conceivable that water can interact with these hydroxyls. As a consequence, in the absence of water these groups can bind to other polar molecules such as methanol and methyl ethyl ketone.

6.4.3.4 Adsorption on extrudates dealuminated with oxalic acid

Comparison of the adsorption on Ox-MOR-Extr, shown in Fig. 6.18, with the one on M-Ox-4 in Fig. 6.12 showed again that mordenite extrudates had a lower adsorption capacity due to their decreased micropore volume. Moreover, the desorption rate of methanol and methyl ethyl ketone is slower compared to M-Ox-4. This is probably due to the presence of the aluminum-rich unreacted precursor phase that showed some affinity toward these molecules. In addition to this, the macroporosity of Ox-MOR-Extr is also reduced compared with M-Ox-4, which pointed to a slower diffusion.

Comparison of adsorption on HN-MOR-Extr in Fig. 6.16 and on

![Graph: Adsorption profile of Ox-MOR-Extr in the presence of water.](image)

Fig. 6.18: Adsorption profile of Ox-MOR-Extr in the presence of water.
Ox-MOR-Extr in Fig. 6.18 shows that desorption of methanol and methyl ethyl ketone was also slower in the latter case. This is probably due to the increased availability of silanol groups and extra-framework aluminum species left after dealumination with oxalic acid that were able to interact with these molecules.

Adsorption in the absence of water, as reported in Fig. 6.19, showed the same trend as in Fig. 6.17: there was an increased uptake of methanol and methyl ethyl ketone.

![Fig. 6.19: Solvent adsorption on Ox-MOR-Extr without water addition](image)

**6.5 Conclusions**

The synthesis of mordenite extrudates was found to be mainly influenced by the reaction temperature and the composition of the precursor. By choosing an optimum temperature range and precursor composition, highly crystalline mordenite extrudate can be synthesized. The small amount of quartz present in
the mordenite extrudates originates from the calcination of kaolin.

Debris particles left after transformation to mordenite that, together with the counterion sodium, completely blocked the pore structure of mordenite extrudates were identified as sodium silicate species. The inferior dealumination of mordenite extrudates, compared to mordenite powder, is attributed to the presence of a hard-to-dealuminate unreacted precursor phase. The use of a steam calcination instead of a dry calcination, followed by leaching with oxalic acid, improved the removal of aluminum.

Mordenite extrudates are good adsorbents, their adsorption behavior is comparable to that of mordenite powder. Apolar solvents desorbed earlier because they are not able to interact with the zeolite framework. Their desorption order is governed by the molecular dimensions: small molecules desorb earlier than bulky one. Among the polar molecules, methyl ethyl ketone is preferentially adsorbed on extra-framework aluminum species and silanol groups. Water and methanol adsorb preferentially on acidic hydroxyl groups. Water also competes with methanol and methyl ethyl ketone for adsorption on silanol groups; its absence induces an increased uptake of methanol and methyl ethyl ketone. The presence of the unreacted precursor phase slows the desorption of methanol and methyl ethyl ketone.
6.6 References

Curriculum Vitae

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Education

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