Catalysis Today 141 (2009) 215–219

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Effect of acid treatments on physico-chemical properties and isomerization activity of mordenite

Sandeep K. Saxena, Raviraj Kamble, Madhulika Singh, M.O. Garg, N. Viswanadham *

Indian Institute of Petroleum, Dehradun (UA), India

ARTICLE INFO

Article history:
Available online 7 May 2008

Keywords:
Mordenite
Hydroisomerization
Acid leaching
Acid sites

ABSTRACT

A series of mordenite-based catalysts of varying acidity and metal concentrations were prepared and the effect of physico-chemical properties of these catalysts on the *n*-hexane isomerization activity was studied. Acid treatment with nitric acid greatly influenced the nature and amount of aluminum in the zeolite characterized by ^{29}Si and ^{27}Al NMR. The microcalorimerty studies of ammonia adsorption clearly indicated the changes in density and strength of acid sites of mordenite upon acid treatment. At optimum conditions of acid treatment the catalyst exhibited improved properties such as acidity and the catalyst gave enthusiastic results claiming 98% selectivity to isomers in *n*-hexane hydroisomerization reaction. The catalyst and the reaction parameters for activity of Pt/H-mordenite have been discussed in the present paper.

1. Introduction

Light alkanes and preferably the branched ones are indispensable for the production of environment friendly gasoline. The refinery streams produced by hydroisomerization has proved to be excellent for gasoline blending as these components having low sulfur content, no aromatics and olefins, and high octane number. Furthermore, due to their favorable burning properties they produce almost nil or very low concentration of undesired products [1–4]. H-mordenite (HM), a class of zeolite, along with metal Pt has been chosen as catalyst because this zeolite has very strong acid sites, which are necessary for light alkane activation [5]. Hydroisomerization is a chain reaction that occurs by adsorption of reactant molecule on metal sites and acid sites, where, the first step being the alkane dehydrogenation to an alkane on the noble metal, which then gets protonated on the acid site to form carbocation [6,7]. The carbocation undergoes skeletal isomerization on acid site, followed by its hydrogenation to yield a branched alkane. Before deprotonation, the carbocation can undergo another isomerization step forming a di-branched product (with a higher RON) or unwanted cracking products [8,9]. Thus an appropriate catalyst for hydroisomerization should contain acid sites for the formation of carbonium ion and for its skeletal rearrangement, where as metal site is required for the formation of active hydrogen to facilitate dehydrogenation and hydrogenation reactions. Hence, the proton form of mordenite in combination with a noble metal, Pt, was chosen as base for the formation of a series of samples [7,8,10].

In zeolites the framework aluminium is the seat of acidity and dealumination by treatments such as steaming and acid leaching are generally adapted for controlling acidity [11,12]. However, care has to be taken to optimize the acid leaching conditions so as to facilitate dealumination without causing any framework damage [13,14]. The aim of the present study is to investigate the acidity changes occurring in mordenite at different levels of dealumination achieved by acid leaching with nitric acid and their influence on conversion and product selectivity in *n*-hexane hydroisomerization with Pt metal loading on these catalysts.

2. Experimental

2.1. Preparation of catalyst

Commercial mordenite powder obtained from Sud-chemie India Ltd., is used as parent sample. Nitric acid was used for the framework dealumination of the parent H-mordenite, where, the degree of dealumination is varied by varying the concentration on of nitric acid (1N, 2N and 3N) for the treatment of mordenite at 100 °C for 1 h. The conditions used for preparation of the catalysts are shown in Table 1. Loading of Pt was done by incipient wet impregnation method, where the platinum tetra ammonium

---

* Corresponding author at: Catalysis & Conversion Process Division, Indian Institute of Petroleum, Dehradun 248005, India.
E-mail addresses: nvish@iip.res.in, nviswanadham@india.com (N. Viswanadham).

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.03.013

Table 1
Description of the preparation of the catalysts

Catalyst	History	Modification
HM	H-mordenite (untreated parent sample)	Nil
HM1	Acid leached sample of HM	Treated with 1N HNO_3 at 100 °C for 1 h
HM2	Acid leached sample of HM	Treated with 2N HNO_3 at 100 °C for 1 h
HM3	Acid leached sample of HM	Treated with 3N HNO_3 at 100 °C for 1 h
Pt/HM	0.3% Pt was loaded on HM1 by incipient wet impregnation method	Pt is loaded on HM
Pt/HM1	0.3% Pt was loaded on HM2 by incipient wet impregnation method	Pt is loaded on HM1
Pt/HM2	0.3% Pt was loaded on HM3 by incipient wet impregnation method	Pt is loaded on HM2
Pt/HM3	0.3% Pt was loaded on HM3 by incipient wet impregnation method	Pt is loaded on HM3

chloride salt $[Pt(NH_3)_4Cl_2]$ equivalent to 0.3 wt% Pt was dissolved in water. H-mordenite as was taken in the extrudates form and the metal chloride solution was added drop-wise with constant stirring. The mixture was kept at room temperature and was allowed to equilibrate over night. The sample was dried at room temperature and 100 °C for 7 and 8 h, respectively. The oxide form of the metal was obtained by calcination of the above mentioned dry mixture at 500 °C temperature for 4 h.

2.2. Physico-chemical characterization

X-ray powder diffraction (XRD) pattern were measured on Rigaku Dmax IIIB equipped with rotating anode and Cu Kα radiations. The measurements were conducted in continuous $\theta/2\theta$ scan refraction mode. The anode was operated at 30 kV and 15 mA the 2θ angles were measured 2–70° at the rate of 2° min^{-1}.

Acidity was characterized on heat flow mircoreactor model Setaram C-80 attached to a volumetric adsorption unit for probe delivery. About 0.1 g of catalyst was outgassed at 723 K under vacuum. The microcalorimetric measurement of ammonia adsorption was carried out at 448 K. Differential heat of ammonia adsorption was determined by introducing small quantity of ammonia on to the outgassed sample, till the neutralization of all acid sites occurred on the catalyst surface. The resulting thermogram for each dose of ammonia gave the heat of adsorption and pressure change gave the amount of ammonia adsorbed [15].

Solid-state magic angle spinning (MAS) ^{29}Si NMR spectra were recorded on a Chemagnetics CMX-300 spectrometer using zirconia rotors of 5 mm in diameter spinning at 3.5 kHz in air. The spectra were acquired at 59.68 MHz by cross-polarization (CP) with a 90° pulse, where contact time was 4 ms and pulse delay was 5 s. The 3000 scans gave good spectra. Chemical shifts (ppm) are referred to external polydimethyl silane (PDMS) standard. Solid-state ^{27}Al MAS NMR spectra were recorded with 78.2 MHz frequencies at a pulse length of 1 μs, which corresponds to $\pi/12$ pulse for non-selective excitation [16].

2.3. Catalyst evaluation studies

The catalyst evaluation was conducted in a fixed bed down flow mircoreactor by loading 2 g catalyst. The catalyst is reduced in situ at 773 K, 5 bar and 12 l/h hydrogen flow for 4 h. Hydroisomerization reaction was carried out at 523 K, 10 bar, 2.3 h^{-1} WHSV, and a H_2/n-hexane molar ratio 2. The product was analyzed by gas chromatograph and the conversion and selectivities of the products were calculated based on the carbon number of the components as defined by the formulae given below

$$\text{selectivity}(C\%) = \frac{\text{product}}{\text{consumed } n\text{-hexane}} \times 100$$

$$\text{yield}(\%) = \text{conversion} \times \text{selectivity}$$

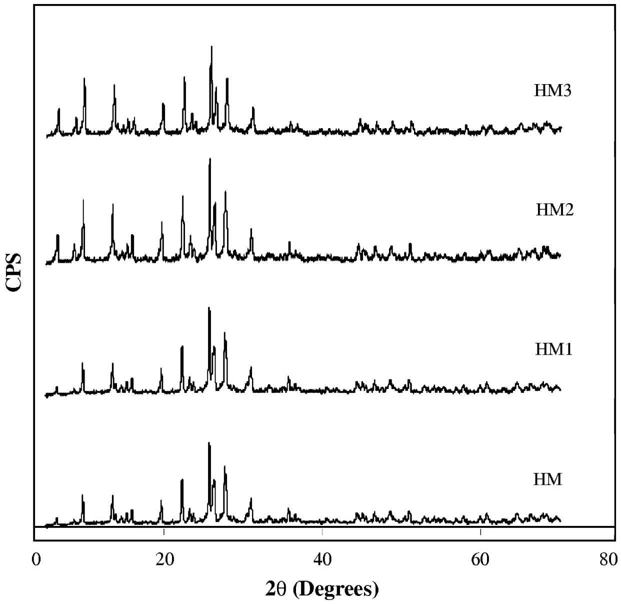

Fig. 1. X-ray diffraction patterns of the zeolite samples.

3. Results and discussions

3.1. Physico-chemical properties of catalyst

X-ray diffraction patterns of the four acid leached mordenite samples are given in Fig. 1. Dealumination is known to expel aluminium from the zeolite framework, but care has to be taken to optimize the severity of dealumination as very severe dealumination may lead to structural collapse. All the samples exhibited similar X-ray diffraction patterns indicating structural integrity of the mordenite even after dealumination. However, a gradual increase in the intensities of low angle X-ray diffraction peaks ($2\theta = 0$–20) was observed with increasing severity of acid leaching, i.e., from HM to HM3. As the framework aluminium is known to influence the hydrophilicity and the intensity of low angle peak of zeolites, the increased intensity of low angle peaks of dealuminated mordenite can be ascribed to increased hydrophobicity of the mordenite on dealumination [12,17].

Acidity and strength distribution of the H-mordenite and acid treated mordenite samples (HM1, HM2 and HM3) were measured by micro-calorimetric ammonia adsorption method and Table 2 compares their acidity pattern. The acidity has been categorized in three classes, namely, strong, medium and weak based on the heat of adsorption of ammonia. The acid sites showing the heat of adsorption value greater than 100 kJ/mol are considered strong acid sites while the ones having the value between 100 and 75 kJ/mol are medium and the ones having even less than this value are weak acid sites. Thus it is evident from the table that the total acidity is decreased from 1.48 to 1.26 m mol of ammonia adsorbed per gram of catalyst upon acid leaching. However it is interesting that the strong acidity is increased from 0.36 to 0.81 m mol after

Table 2
Effect of acid treatment on the acidity of the catalyst

Catalyst	Acidity (m mol/g cat.)			
	Total	Strong	Medium	Weak
HM	1.48	0.36	0.65	0.47
HM1	1.40	0.49	0.58	0.33
HM2	1.35	0.74	0.45	0.16
HM3	1.26	0.81	0.41	0.04

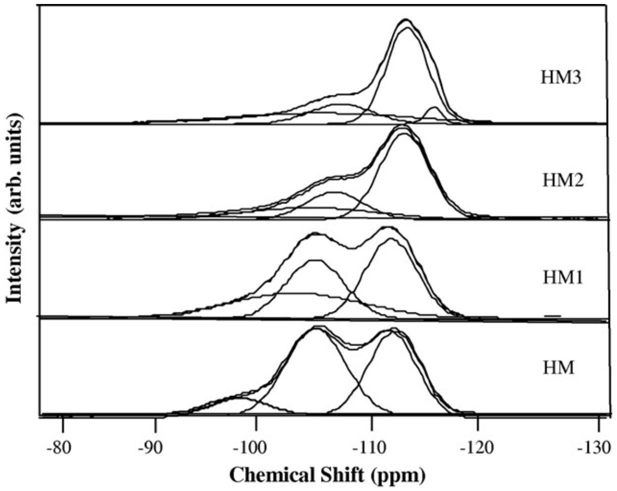

Fig. 2. ^{29}Si NMR spectra of catalyst samples.

acid leaching. This is very much advantageous, as we need strong acid sites for low temperature activation of *n*-hexane for isomerization reaction. This can be attributed to the removal of some of the aluminum from the zeolite framework of H-mordenite.

The deconvulated ^{29}Si MAS NMR spectra for all acid treated samples are given in Fig. 2. Untreated sample HM exhibits three peaks at about −102, −109.4 and −116.1 ppm and these represent three different Si environments viz. Si(2Al), Si(1Al) and Si(0Al), respectively [18]. With increasing dealumination from HM1 to HM3, the intensity of Si(2Al) and Si(1Al) is decreased whereas that of Si(0Al) is increased. At high severity dealumination, i.e., HM2 and HM3 samples exhibited two new Si(0Al) environments at −119 ppm and −117.2 ppm. These changes clearly indicate framework dealumination of mordenite. This is further confirmed from ^{27}Al NMR spectrum where untreated mordenite (HM) exhibits a peak near 53 ppm indicating the presence of tetrahedral (framework) Al. There is a change in the intensity and position of this peak as it becomes broad and is shifted to 55 ppm on dealumination. With further dealumination the intensity of this peak goes on decreasing indicating the removal of framework aluminium and this trend is again maximum upto HM3 (Fig. 3).

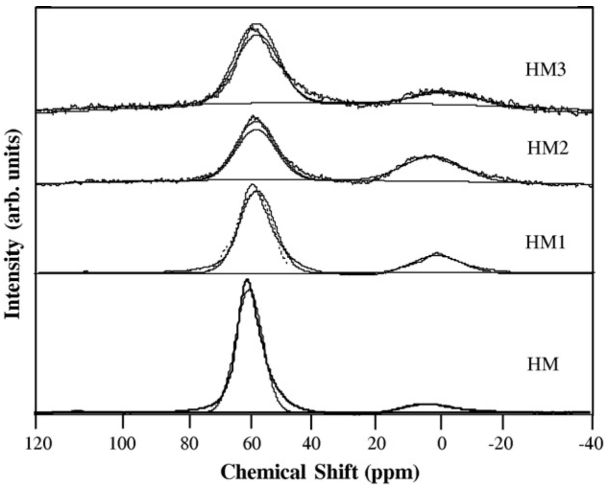

Fig. 3. ^{27}Al NMR spectra of catalyst samples.

3.2. *Effect of dealumination controlled structural changes on n-hexane isomerization performance of H-mordenite*

Performances of four catalysts HM, HM1, HM2 and HM3 for *n*-hexane hydroisomerization are compared in Table 3. Effect of acid

Table 3
Catalyst performance on hydroisomerization of *n*-hexane

Catalyst	HM	HM1	HM2	HM3	Pt/HM	Pt/HM1	Pt/HM2	Pt/HM3
Conversion (wt%)	6.2	3.7	9.8	4.7	21.1	36.9	31.0	43.1
Product yields (wt%)								
∑Cracking	5.1	0.7	1.4	1.2	10.0	0.6	0.5	1.1
C_1	0.1	0.0	0.0	0.0	0.5	0.0	0.0	0.0
C2	0.2	0.0	0.0	0.0	0.9	0.0	0.0	0.0
C3	1.3	0.0	0.1	0.2	1.8	0.1	0.1	0.1
C4	1.8	0.2	0.4	0.5	3.6	0.2	0.2	0.5
C5	1.7	0.5	0.9	0.5	3.2	0.3	0.2	0.5
∑Isomers	1.1	2.7	7.1	3.4	11.0	36.2	30.4	41.8
2-MP	0.5	1.2	3.3	1.7	5.1	18.3	14.5	19.5
3-MP	0.3	0.8	2.0	1.0	3.8	11.7	9.6	13.2
2,2-DMB	0.1	0.3	0.9	0.3	0.9	2.7	2.4	4.0
2,3-DMB+CP	0.2	0.4	0.9	0.4	1.2	3.5	3.9	5.1
∑Others	0.0	0.3	1.3	0.1	0.1	0.1	0.1	0.2
Selectivity								
Cracking	82.3	18.9	14.3	25.6	47.0	1.6	1.6	2.5
Isomers	17.7	73.0	72.4	72.3	52.0	98.1	98.1	97.0
Mono-branched	12.9	54.1	54.1	57.4	42.0	81.3	77.7	75.9
Di-branched	4.8	18.9	18.3	14.9	10.0	16.8	20.3	21.1
Undesired product	0.0	8.1	13.3	2.1	1.0	0.3	0.3	0.5
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

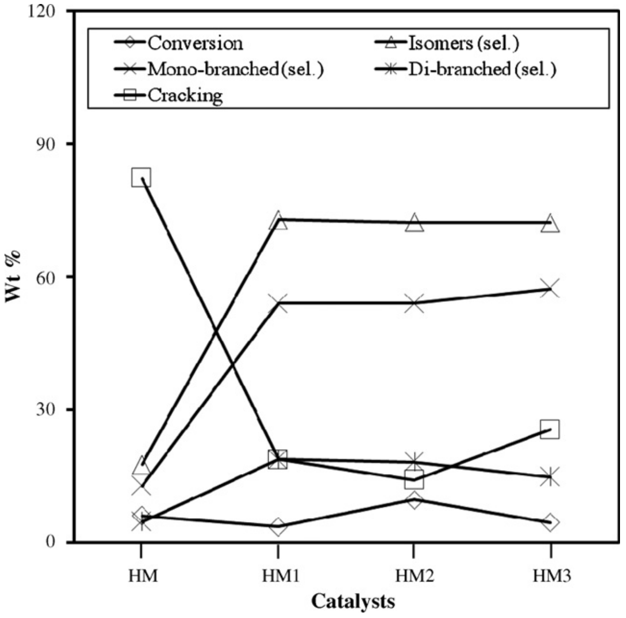

Fig. 4. Effect of acid leaching on n-hexane hydroisomerization.

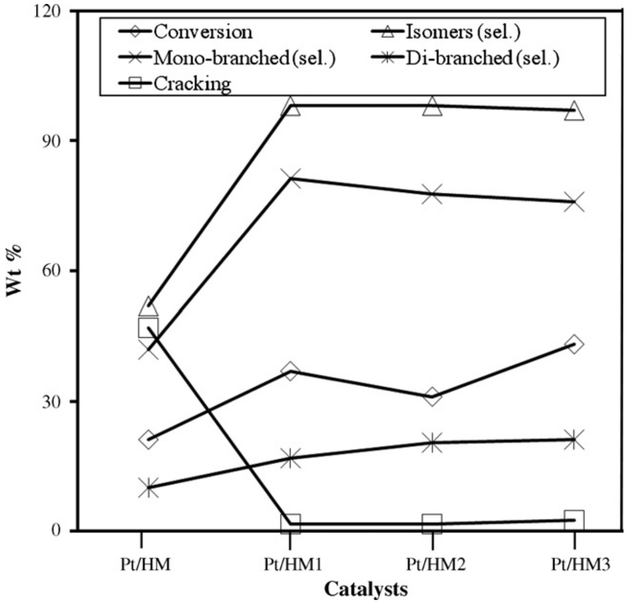

Fig. 5. Effect of Pt on n-hexane hydroisomerization.

leaching on the catalyst performance is evident from the data. Based on the nature of the product obtained, the entire product is classified into (1) cracking product (C1–C5) and (2) isomer product. It is observed from Table 3 that the conversion of *n*-hexane as well as cracking yields have decreased from HM to HM1 (conversion from 6.2% to 3.7% and cracking yield from 5.1% to 0.7%). But the isomers yield has increased from 1.1% to 2.7%. Though there is a decrease in the conversion levels, the increasing isomer yield with simultaneous decrease of cracking yield clearly shows that acid leaching is an effective method for tailor making of acidity of mordenite to improve isomer yield. The mono and di-branched isomer yields have also increased from HM to HM1. Through there is a deviation in conversion trend, all the acid leached samples, i.e., HM1, HM2 and HM3 exhibited higher isomerization and lower cracking activities when compared to HM. Such an amazing performance of the catalyst towards hydroisomerization selectivity can be further visualized from selectivity values which have increased from 17.7% to72.3% and also there is an 80% decrease in the cracking selectivity. These spectacular changes in selectivities are also evident from Fig. 4, where, the selectivities towards various isomers obtained in parent and acid-leached catalysts are plotted. The figure shows a decrease in trend of cracking selectivities of the catalysts with progressive acid leaching which is favorable to control the undesired products. The catalysts also exhibited the increasing trend of isomerization selectivity after acid leaching.

3.3. *Effect of Pt-impregnation*

Effect of Pt on the isomerization activity can be understood by comparing the performance data of all the Pt/HM samples given in Table 3. Loading of Pt on HM increased the conversion that is reflected in increase in selectivities of both cracking and isomer yields. Different from this, loading of Pt on HM1 caused preferential increase in isomer yield (from 73% to 98.1%) with decrease in cracking yields (18.9–1.6 wt%). That means, the framework dealumination of mordenite is contributing to the controlled cracking reactions in Pt/HM1. Trends in product pattern of further dealuminated samples (Fig. 5) also suggest the positive role of dealumination on controlling cracking. It indicates that the Pt impregnation alone cannot increase the conversion and isomer formation, and hence, there should be a balance between the acid sites and Pt sites to obtain maximum isomers. The selectivities towards mono and di-branched products were increased after Pt loading (HM to Pt/HM) and also increased with dealumination (Pt/HM to Pt/HM3).

Thus, the studies indicate the importance of two factors namely, (1) framework dealumination and (2) Pt loading on achieving the proper balance between acidity and metal sites in mordenite-based isomerization catalyst. The Pt/HM catalyst exhibited low selectivity towards isomers, but the selectivity was increased after dealumination, i.e. from Pt/HM1 to Pt/HM3. This situation suggests the importance of controlling acidity to minimize cracking and to increase the isomer yields. Among the dealuminated mordenite samples, Pt/HM3 could exhibit maximum isomer yield (41.8 wt%).

4. Conclusion

The acid leaching and Pt impregnation of mordenite to an optimum extent has contributed to increase in isomerization activity of the catalysts. NMR acted as an excellent probe to estimate the extent of dealumination. The acid leaching decreases the density of acid sites on one hand and increases the strong acid sites on the other, which favors the isomerization reaction. The dealumination caused by acid leaching has also decreased the cracking activity of the catalyst, which decreased the formation of undesired product. The impregnation of Pt on the acid leached samples also greatly influences the isomerization reaction by increasing isomer selectivity. Overall, the two catalyst modification methods, namely, acid leaching and Pt impregnation, both helped in tailor making of catalyst properties. Thus finally taking all the factors related to isomerization reaction viz. high conversion, high isomerization selectivity and lower cracking selectivity into account, it can be concluded that Pt/HM3 is the best catalyst among the ones prepared in this study in achieving as high as 97% isomerization selectivity at 43.1% conversion levels (41.8 wt% isomer yield).

Acknowledgements

Authors are thankful to GC analysis lab at IIP and NMR analysis lab at the University of Tokyo, Japan for analytical support.

References

[1] A. Hollo, J. Hancsok, D. Callo, Appl. Catal. A: Gen. 229 (2002) 93.
[2] J. Bousquet, M. Valais, Appl. Catal. A: Gen. 8 (1996) 134.
[3] J. Hancsok, Petrol. Coal 40 (1998) 33.
[4] P.J. Kuchar, Hydrocarbon Eng. 4 (1999) 50.
[5] J.-K. Lee, H.-K. Rhee, Catal. Today 38 (1997) 235.
[6] K.J. Chao, H.C. Wu, Appl. Catal. 143 (1996) 223.
[7] H.W. Kouwenhoven, Molecular Sieves ACS Advances in Chemistry Series, vol. 121, Am. Chem. Society, Washington, 1973, p. 529.
[8] N. Essayem, Y. Ben Taarti, J. Catal. 219 (2003) 97.
[9] A. Chica, A. Corma, J. Catal. 187 (1) (1999) 167.
[10] T. Yashima, A. Kamo, T. Yoneda, Catal. Today 29 (1–4) (1996) 279.
[11] M. Guisnet, G. Perot, in: F. Ramoca Ribeiro, A.E. Rodoringues, L.D. Rollmann, C. Naccache (Eds.), Zeolite Science and Technology, NATO ASJ Series, The Hauge, 1984, pp. 397–420.
[12] M. Guisnet, V. Fouche, M. Bellon, J.P. Bournville, C. Traves, Appl. Catal. 71 (1991) 283.
[13] Z.C. Shi, A. Aurox, Y. Ben Taarit, Can. J. Chem. 66 (1998) 1013.
[14] P.B. Koriada, J.R. Kiovsky, M.Y. Asim, J. Catal. 178 (1980) 290.
[15] N. Viswanadham, L. Dixit, J.K. Gupta, M.O. Garg, J. Mol. Catal. A: Chem. 258 (2006) 15.
[16] N. Viswanadham, T. Shido, T. Sasaki, Y. Iwaswa, J. Phys. Chem. B 106 (2002) 10955.
[17] T.A.G. Hardenberg, L. Martens, P. Mesman, H.C. Muller, C.P. Nicoliades, Zeolites 12 (1992) 685.
[18] G. Engelhardt, D. Michel, High Resolution Solid State NMR of Silicates and Zeolites, John Wiley and Sons, 1987.