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Zeolite MCM-22 : Synthesis, Dealumination and Structural Characterization

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Zeolite MCM-22 was synthesized and characterized by selected physico-chemical methods. MAS NMR spectroscopic studies reveal that at least five crystallographically non-equivalent T-sites exist in the structure of MCM-22 and that they are affected to different degrees by dealumination with $SiCl_4$ vapors. From IR and TPDA experiments it can be concluded that the acidic properties of HMCM-22 are very similar to HZSM-5. A Spaciousness Index of ca. 8 is indicative of an effective pore width in the intermediate region between 10- and 12-membered ring zeolites.

1. INTRODUCTION

In the patent literature, zeolite MCM-22 in its acidic form has been claimed to be a useful catalyst for isoalkane/olefin alkylation [1], skeletal and double bond isomerization in olefins [2] and for the conversion of methanol or olefins to higher hydrocarbons [3, 4]. It has been suggested from a comparison of their X-ray powder data [3] that the structures of zeolites MCM-22 and PSH-3 [4] are closely related. However, no further characterization or additional structural data are available so far for either of the two materials. Therefore, a detailed study was initiated in our laboratories with the aim to optimize the synthesis procedure for zeolite MCM-22 and to collect more information on its structural and catalytic properties. Here we report on the synthesis of MCM-22, its dealumination and its characterization by X-ray powder diffraction, ^{27}Al and ^{29}Si MAS NMR spectroscopy, Fourier Transform infrared spectroscopy (FTIR) and temperature programmed desorption of ammonia (TPDA). The effective pore width of zeolite MCM-22 was characterized by the Spaciousness Index [5].

2. EXPERIMENTAL SECTION

In the patent literature [1-4], only hexamethyleneimine is mentioned as a useful template for the synthesis of zeolite MCM-22/PSH-3, and this same template was used throughout this study. For the synthesis experiments, stainless steel autoclaves with a volume of 300 cm^3 were used, which could be rotated with a frequency of ca. 30 min^{-1} in an air oven. For the synthesis of a larger batch of zeolite MCM-22, an optimized recipe was scaled-up to a stirred autoclave with a volume of 5 l. Starting from the synthesis procedures reported in the patent literature, the gel composition, the sources for alumina and silica as well as the synthesis time and temperature were systematically varied. The as-synthesized materials were washed, dried at 393 K and calcined for 48 hours at 813 K in a purge of nitrogen containing 5 vol.-% of oxygen. The Brönsted acid form of zeolite MCM-22 was obtained by fourfold ion exchange of the calcined form at 353 K for 12 hours in a large surplus of a 1 n aqueous solution of NH_4NO_3, followed by a calcination in nitrogen. Dealumination of zeolite MCM-22 was attempted using $SiCl_4$ vapors according to the method of Beyer and Belenykaja [6] or using 0.1 n to 14.5 n nitric acid, as recently described by Bourgeat-Lami et al. for zeolite Beta [7].

The as-synthesized and modified samples were characterized by X-ray powder diffraction (CuKα radiation) and scanning electron microscopy. Their chemical compositions were determined by atomic emission spectroscopy using inductively coupled plasma (AES/ICP) after dissolution of the samples in HF.

The NMR experiments were conducted on a Bruker MSL 400 spectrometer with resonance frequencies of 79.5 MHz for ^{29}Si and 104.3 MHz for ^{27}Al (the MAS frequencies amounted to 4.5 kHz and 10 kHz, respectively). The pulse lengths were adjusted to $\pi/4$ and $\pi/12$ and the repetition times to 10 s and 500 ms, respectively. The chemical shifts are referenced to tetramethylsilane for ^{29}Si and to a 0.1 m aqueous solution of $AlCl_3$ for ^{27}Al. FTIR spectra before and after pyridine adsorption were recorded on a Perkin-Elmer spectrometer model 325 with an ultrahigh vacuum cell. The procedures of the FTIR [8] and TPDA [9] experiments were described previously.

In order to obtain information on its effective pore width, HMCM-22 was loaded with 0.27 wt.-% of Pd by ion exchange with an aqueous solution of $[Pd(NH_3)_4]Cl_2$. On the resulting sample, the Spaciousness Index was determined as described earlier [5]. The partial pressure of butylcyclohexane, the hydrogen pressure and the mass of dry catalyst amounted to 20 kPa, 2.0 MPa and 0.5 g, respectively.

3. RESULTS AND DISCUSSION

From the synthesis experiments conducted so far, two recipes emerged which reproducibly yield zeolite MCM-22. The first one is based on Mobil's patents [1-3]. In this case, Cab-osil M5 (Fluka, fumed silica) and sodium aluminate (Riedel-de Haën, 54 wt.-% Al_2O_3, 41 wt.-% Na_2O) are used as silica and alumina

sources, respectively. The synthesis gel is prepared as follows: A solution of 0.1 g H_2SO_4 (98 wt.-%) in 5 g H_2O is slowly added under stirring to a solution of 0.53 g NaOH and 0.86 g sodium aluminate in 20 g H_2O. The resulting solution is stirred into a suspension of 8.8 g Cab-osil M5 in 85 g H_2O. Finally, 4.8 g hexamethyleneimine are blended thoroughly into the mixture. The molar composition of the resulting gel amounts to 32.2 SiO_2 : Al_2O_3 : 2.7 Na_2O : 10.6 hexamethyleneimine : 1333 H_2O : 0.22 H_2SO_4. From this gel, MCM-22 with n_{Si}/n_{Al} = 11 (denoted as MCM-22/1) is obtained after 12 days at 423 K under continuous agitation. In the second synthesis route silica sol (30 wt.-% SiO_2 in water, AC 4038, Bayer AG) and $Al_2(SO_4)_3$*18 H_2O (Riedel-de Haën) are used as silica and alumina sources, respectively. The mode of gel preparation resembles the one employed for HMCM-22/1, however, the molar gel composition is now closer to the one typically used in [4], viz. 49.3 SiO_2 : Al_2O_3 : 14.5 Na_2O : 23.7 hexamethyleneimine : 1980 H_2O : 8.8 H_2SO_4. Crystallization of MCM-22 is achieved after 10 days at 423 K under continuous agitation (MCM-22/2, n_{Si}/n_{Al} = 21). This synthesis was succesfully scaled up to a stirred autoclave (stirring rate = 150 min^{-1}) with 5 l volume. The yield of calcined crystalline product obtained from the 5 l autoclave amounted to 250 g as compared to less than 10 g for the small autoclaves. Upon slight variations of the gel composition or the synthesis procedure, several other crystalline phases (mordenite, ZSM-12, ZSM-35) were observed either in physical admixture with MCM-22 or as pure phases.

The X-ray powder pattern of zeolite MCM-22/1 after calcination at 813 K is shown in Fig. 1. Peak positions and relative intensities agree reasonably well with those given in the patent literature [1-4]. The relatively broad peaks could be the result of a very small crystallite size or of structural disorder.

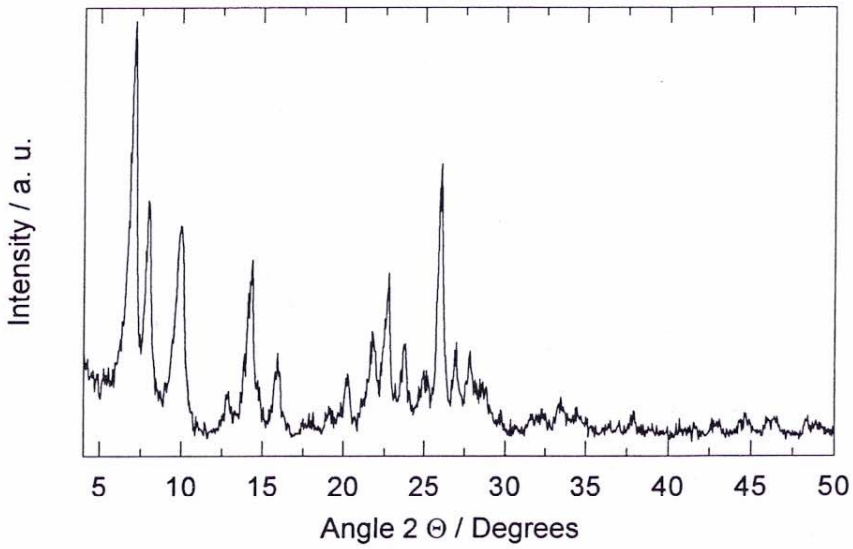


Figure 1. X-ray powder pattern of zeolite MCM-22/1 after calcination at 813 K.

Since the crystallites (as observed by scanning electron microscopy) possess a disk-like morphology with a diameter below 1 μm and a thickness of only ca. 0.1 μm the former explanation is favored at this moment.

Dealumination of zeolite MCM-22/1 was attempted by treatment with $SiCl_4$ vapors or nitric acid of different concentration. From our experience with the method of Beyer and Belenykaja [6], we selected 523 K as the starting temperature for dealumination. However, upon contacting the zeolite with $SiCl_4$, there was essentially no temperature increase, which indicates that virtually no dealumination occurs at 523 K. Upon raising the temperature to 623 K, an exothermic reaction took place, and the bulk n_{Si}/n_{Al}-ratio of the zeolite increased from 11 to 20. This sample is denoted MCM-22/1 ($SiCl_4$). Attempts to dealuminate MCM-22/2 with nitric acid for 4 hours at 353 K failed so far. Even a treatment in 14.5 n HNO_3 for 30 hours did not result in a significant dealumination.

The ^{27}Al and ^{29}Si MAS NMR spectra of MCM-22/1 with n_{Si}/n_{Al} = 11 and MCM-22/1 ($SiCl_4$) with n_{Si}/n_{Al}= 20 are presented in Fig. 2. In the ^{27}Al MAS NMR spectra of both zeolites, several resonances can be observed in the typical range of chemical shifts for tetrahedrally coordinated aluminum in framework positions. Since it was verified that the resonance positions do not depend on the applied magnetic field strength, it can be assumed that the quadrupolar interactions of the corresponding nuclei are small. Therefore, the observed spectrum could be simulated by gaussian lines. For a suitable fitting of the experimentally recorded spectra, a minimum of four lines is necessary, viz. at about 49 ppm, 53 ppm, 56 ppm and 59 ppm (cf. Fig. 2). Dealumination causes a general decrease in the number or density of tetrahedrally coordinated aluminum atoms (note that the intensity was increased from Fig. 2a to Fig. 2b by a factor of 2). Interestingly, a more than proportional decrease is observed for the species at ca. 56 ppm. This indicates that the latter framework position is particularly prone to dealumination by $SiCl_4$ vapors. In the 0 ppm region (not shown in Fig. 2), no signal of octahedrally coordinated extra-framework aluminum could be observed for MCM-22/1. However, for the dealuminated sample MCM-22/1 ($SiCl_4$) a line at -0.2 ppm (attributed to octahedral aluminum) with an intensity contribution of ca. 5% appeared.

The ^{29}Si MAS NMR spectrum of MCM-22/1 (Fig. 2c) consists of peaks at -104.0 ppm, -110.6 ppm, and -119.3 ppm and a low-field shoulder at approximately -98 ppm. Dealumination causes a splitting of the broad resonance at -110.6 ppm into three lines, viz. at -110.3 ppm, -112.3 ppm, and -115.3 ppm (cf. Fig. 2d).

Due to the relatively high n_{Si}/n_{Al}-ratio of both MCM-22 samples it seems reasonable to assume that their ^{29}Si MAS NMR spectra are mainly composed of Si(1Al) and Si(0Al) lines. Their relative contributions to the total intensity can be estimated from the known n_{Si}/n_{Al}-ratios and the equation given in ref. [10]. Based on the experimental data for MCM-22/1 ($SiCl_4$) (cf. Fig. 2d) it was then assumed that the measured spectra can be simulated by the combination of two sets (one set for Si(0Al) and one for Si(1Al)) of five signals. The difference between the chemical shift of both sets was estimated to ca. 6 ppm from the difference between the chemical shift of the low-field Si(1Al) signal (at

-98 ppm) and the one of the low-field Si(0Al) signal (at -104 ppm). From the reasonably good agreement between the experimentally determined and the simulated spectrum it can be concluded that there are five (or at least five) crystallographically different T-atom positions in the structure of zeolite MCM-22. From the observed range of chemical shifts in the ^{29}Si MAS NMR spectra, mean Si-O-T-angles between 133 ± 4° and 164 ± 4° can be calculated using the correlations recently published by Fyfe et al. [11].

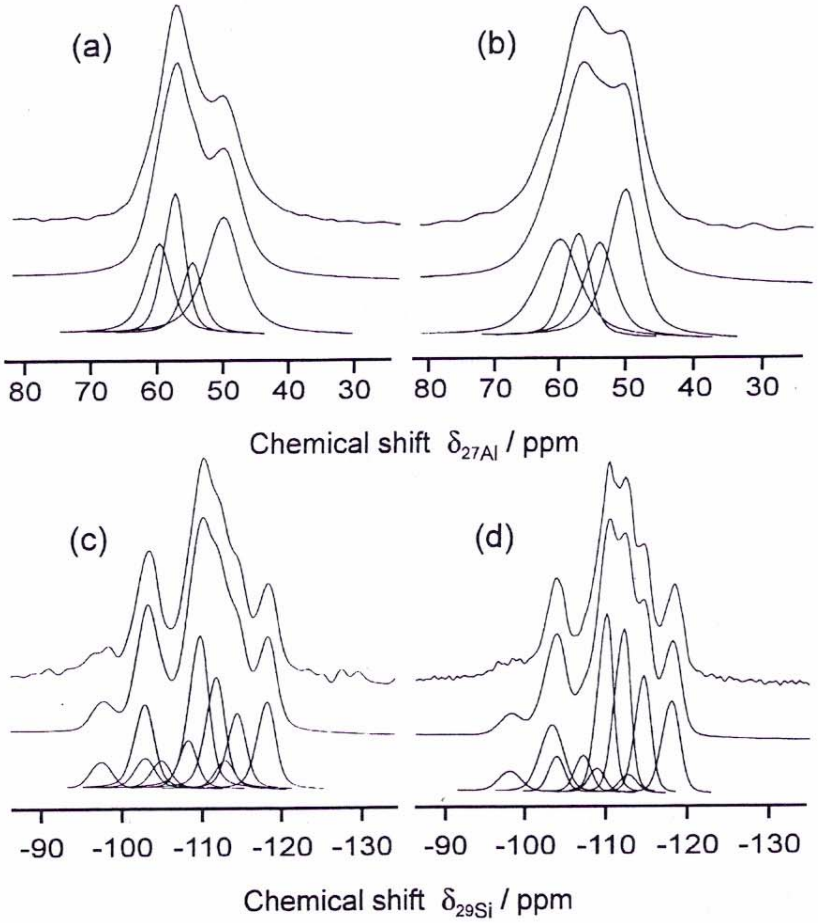


Figure 2. ^{27}Al MAS NMR (a and b) and ^{29}Si MAS NMR (c and d) spectra of zeolites MCM-22/1 (a and c) and MCM-22/1 ($SiCl_4$), (b and d). Upper curves: experimentally recorded; lower curves: deconvoluted spectrum; middle curves: simulated spectrum. The intensity was increased from (a) to (b) by a factor of 2 to account for the reduced aluminum content.

Typical IR spectra obtained for zeolite HMCM-22/2 are depicted in Fig. 3. After activation in vacuum for 2 hours at 675 K, three bands can be observed in the range of the OH-stretching frequencies, resulting from strongly acidic Brönsted OH-groups (centered around 3628 cm^{-1}), weakly acidic OH-groups (at ca. 3670 cm^{-1}) probably resulting from OH-groups associated with extra-framework aluminum species, and terminal silanol groups (at ca. 3750 cm^{-1}). Upon adsorption of pyridine at 475 K for 2 hours and desorption of physisorbed pyridine at the same temperature for 1 hour in high vacuum, the two bands at higher wavelengths disappear whereas the 3750 cm^{-1} band is still present (cf. Fig. 3). Simultaneously, peaks indicative of both Brönsted (at ca. 1545 cm^{-1}) and Lewis acid sites (at ca. 1455 cm^{-1}) appear in the region from 1400 to 1700 cm^{-1}. Increasing the activation temperature to 1075 K results in a reduction of the number of Brönsted acid sites by ca. 50 % due to dehydroxylation. As a result, the number of Lewis acid sites increases, hence the strongly increased intensity of the band at ca. 1455 cm^{-1}.

The acid strength distribution of HMCM-22/2 after activation at 675 K was characterized by temperature programmed desorption of ammonia (TPDA). The measured TPDA curve was deconvoluted into three relatively broad peaks with maxima around 518 K, 627 K and 834 K (cf. Fig. 4). These three peaks can be tentatively attributed to weakly acidic Lewis sites, strongly acidic Brönsted

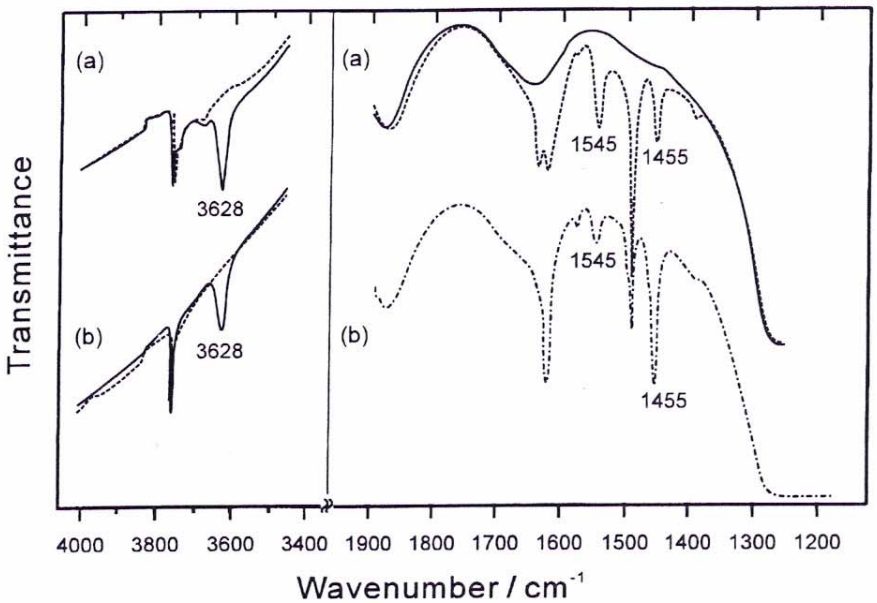


Figure 3. IR spectra of zeolite HMCM-22/2 after activation at 675 K (a) and 1075 K (b); solid lines: base spectra; broken lines: after pyridine adsorption (about 600 Pa, 475 K, 2 h) and desorption of excess pyridine (10^{-5} Pa, 475 K, 1 h).

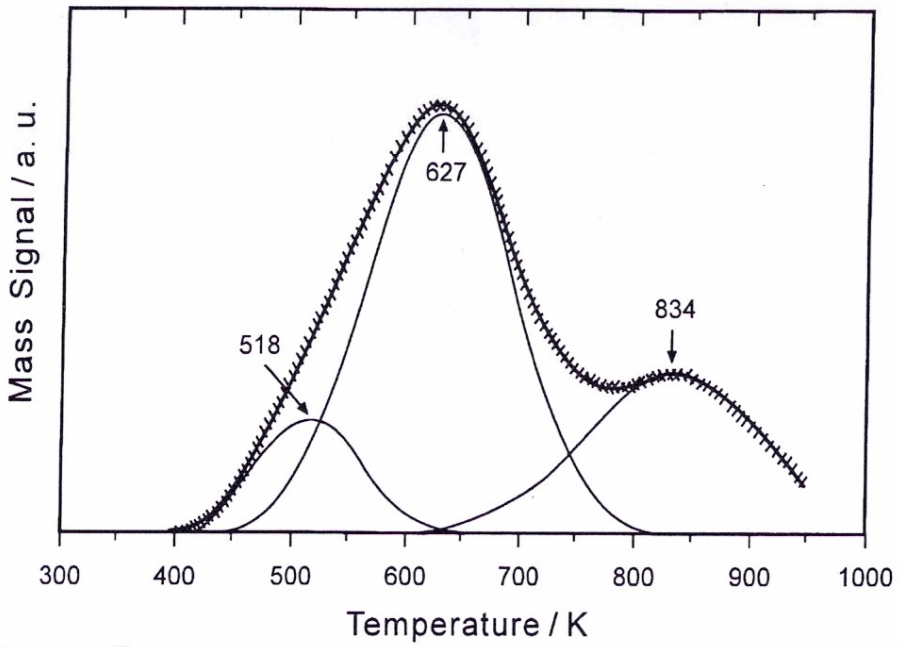


Figure 4. Temperature-programmed desorption of ammonia from zeolite HMCM-22/2 at a rate of 10 K/min, after activation at 675 K, loading with NH_3 under 120 Pa (0.5 h) at 395 K and pre-degassing at 395 K (1 h).

centers and relatively large amounts of very strongly acidic Lewis sites, respectively. The presence of Brönsted acid sites and the occurrence of strong Lewis sites is in principal agreement with the results of the IR spectroscopic characterization.

It has been reported in the patent literature (e. g., example 1 of ref. [3]) that HMCM-22 adsorbs up to 14.6 wt.-% of cyclohexane. This indicates the presence of 10-membered ring or larger pores. To collect further information on the effective pore width, the Spaciousness Index (SI) of HMCM-22/2 loaded with 0.27 wt.-% Pd was determined. An SI value of 8 clearly ranks MCM-22 among the large pore zeolites with a pore size intermediate between the strongly puckered 12-membered ring systems (e. g., ZSM-12 or mordenite) and the more open structures like zeolite L or Beta. From the currently available data, no conclusions with respect to the dimensionality of the pore system of MCM-22 can be drawn.

4. CONCLUSIONS

Zeolite MCM-22 can be reproducibly synthesized from specific gel compositions containing hexamethyleneimine as organic template. Typically, n_{Si}/n_{Al}-ratios

from 11 to 21 are obtained. Post-synthesis dealumination using $SiCl_4$ vapors or nitric acid appears to be difficult. Possible reasons are steric restrictions for $SiCl_4$ in the relatively narrow pores of MCM-22, and the high stability of the latter against acid attack. ^{29}Si MAS NMR spectroscopy reveals that there are at least five crystallographically non-equivalent T-sites in the structure of zeolite MCM-22. FTIR spectroscopy and TPDA show that HMCM-22 contains both strong Brönsted and strong Lewis acid sites after activation at 675 K. In general, the acid properties of this material resemble those of zeolite HZSM-5. A Spaciousness Index of 8 indicates that the effective pore size of zeolite MCM-22 is between the one of strongly puckered 12-membered ring materials (e. g., ZSM-12) and the one of more open structures (e. g., zeolite Beta). Therefore, MCM-22 is a most attractive material for the shape selective conversion of bulkier molecules.

5. ACKNOWLEDGEMENTS

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REFERENCES

1. A. Huss, Jr., G. W. Kirker, K. M. Keville and R.T. Thomson, US Patent 4 992 615, 1991 (assigned to Mobil Oil Corp.).
2. K. J. Del Rossi and A. Huss, Jr., US Patent 5 107 047, 1992 (assigned to Mobil Oil Corp.).
3. C. T.-W. Chu, US Patent 4 956 514, 1990 (assigned to Mobil Oil Corp.).
4. L. Puppe and J. Weißer, DE 3 117 135, 1982 (assigned to Bayer AG).
5. J. Weitkamp, S. Ernst and R. Kumar, Appl. Catal. **27** (1986) 207-210.
6. H. K. Beyer and I. Belenykaja in: "Catalysis by Zeolites", B. Imelik et al. (eds.), Studies in Surface Science and Catalysis, Vol. **5,** 1980, pp. 203-210.
7. E. Bourgeat-Lami, F. Fajula, D. Anglerot and T. Des Courieres, Microporous Materials **1** (1993) 237-245.
8. H. G. Karge, Z. Phys. Chem. (NF) **95** (1975) 241-254.
9. H. G. Karge and V. Dondur, J. Phys. Chem. **94** (1990) 765-772.
10. G. Engelhardt and D. Michel: "High-Resolution Solid-State NMR of Silicates and Zeolites", John Wiley & Sons, Chichester, New York, 1987, p. 212.
11. C. A. Fyfe, Y. Feng and H. Grondey, Microporous Materials **1** (1993) 393-400.