Synthesi and NMR characterization of ZSM-35

Article *in* Journal of Chemical Sciences · January 2004

CITATIONS
0

READS
45

1 author:

N. Venkatathri
National Institute of Technology, Warangal
436 PUBLICATIONS **964** CITATIONS

SEE PROFILE

Copy for Au's reference

PC3388 PPP

J. Chem. Sci., Vol. 116, No. 4, July 2004, pp. 1–6. © Indian Academy of Sciences.

Synthesis and NMR characterization of ZSM-35

N VENKATATHRI[a,*] and S GANAPATHY[b]

[a]Catalysis Division and [b]Physical Chemistry Division, National Chemical Laboratory, Pune 411 008, India

e-mail: venkat@cata.ncl.res.in

MS received 7 October 2003; revised 22 December 2003

Abstract. ZSM-35 and ferrierite were synthesized using ethylene diamine and pyrrolidine as templating agents. XRD, SEM, and FT-IR analysis indicate that the synthesized samples are highly crystalline. ^{27}Al MASNMR results show that ZSM-35 and ferrierite contain tetrahedrally coordinated aluminium atoms. This is also supported by ^{27}Al 3Q-MASNMR. ^{29}Si NMR shows that ZSM-35 contains two different silicon species and ferrierite shows the presence of three different silicon species. 3Q-MASNMR of aluminium and sodium atoms in the material shows the presence of four different types of species.

Keywords. ZSM-35; ferrierite; isomorphous; XRD; SEM; FT-IR spectra; MASNMR; 3Q-MASNMR.

1. Introduction

ZSM-35 is a medium-pore molecular sieve, which has extensive applications in the petrochemical industry. Originally patented by Mobil in 1977, this zeolite can be synthesized hydrothermally using pyrrolidine and ethylene diamine templates.[1] Although the complete X-ray structure determination of ZSM-35 is not available, the strikingly similarity of the X-ray diffraction powder spectrum of ZSM-35 to that of ferrierite suggests that its structure is of the ferrierite type. Apart from this, there has been no experimental evidence to show that these two structures are indeed isomorphic. As for ferrierite, for which all the atomic co-ordinates have been determined for the natural mineral, the orthorhombic structure consists of chains of five-membered rings that are parallel to the *c*-axis, and are cross-linked by four-membered rings to the main ten-membered ring channels, lying along [001] with the intersection along [010]. The building units of ferrierite[2–4] contain four unique tetrahedral sites, which in a siliceous material are occupied only by Si. Al occupation of all the four T-sites is however less probable in synthetic ferrierites since Si/Al is typically in the range 8·33 to 17·86[5]. In the case of ZSM-35[6], for which synthetic preparations can yield materials with Si/Al 7·6 and above, one can expect that these T-sites would be occupied by Al when Si/Al is low (≈ 7·6). Similarly, for the as-synthesized zeolite, namely, Na-ZSM-35, the charge on the framework is neutralized by sodium cations, leading to a non-equivalence among sodiums residing in the cationic positions[7]. Thus, a one-to-one mapping of the Al and Na sites in ZSM-35 and a comparison of the experimental results with those obtained on ferrierite, would provide valuable structural insights about ZSM-35.

The present study focuses on delineating the structural features of ZSM-35 using multinuclear solid state MAS/MQ-MAS NMR. MAS (^{29}Si) and 3Q-MAS (^{27}Al) NMR are used to elucidate the framework environments, while ^{23}Na triple quantum experiments are used for the characterization of nonframework cationic positions. Further, a quantification of MAS and 3QMAS results lead to the determination of structurally significant chemical shift (δ_{cs}) and quadrupole interaction (P_Q) parameters.

2. Experimental details

2.1 *Synthesis of ZSM-35 and ferrierite*

In a typical procedure to synthesize ZSM-35, 3·3 g of sodium aluminate (99%, S.D. Fine) was mixed well with 0·7 g of sodium hydroxide (99%, S.D. Fine) and 129 g of distilled water. This mixture was stirred well until all the solid dissolved. This was

*For correspondence

taken as solution A. Another solution, B, was made by thorough mixing of 46·47 g of silica sol (30%, S.D. Fine) and ethylene diamine (18·3 g, 99%, Aldrich, USA). Solutions A and B were mixed well to make a clear solution and charged into a teflon-lined steel autoclave. Crystallization was carried out at 177°C for 10 days. The product was removed and washed with deionised water and the sample was dried at 110°C for 24 h. The zeolite so prepared was subjected to various physicochemical characterizations.

Ferrierite was synthesized as follows. Sodium silicate (52·5 g in 25 ml of distilled water) was stirred with 10 ml pyrrolidine. To this solution, 2·4 g of aluminium sulphate hexadecahydrate (in 25 ml distilled water) and 1.8 g of sulphuric acid (in 10 ml distilled water) was added. Finally, 30 ml of distilled water was added and the gel (pH = 11·5 ± 0·2) was stirred vigorously for 2 h and autoclaved in a 300 ml stainless steel Parr autoclave (4842, 300 ml) and heated at 160°C for 60 h. The initial gel composition was

$20Na_2O : Al_2O_3 : 37$pyrrolidine $: 66{\cdot}5SiO_2 : 6{\cdot}3H_2SO_4 : 1460H_2O$.

The autoclave was quenched, the residue filtered, and washed, and the product was dried at 110°C for 6–8 h. The resulting material was calcined in air at 550°C for 18–20 h.

2.2 *Characterization*

X-ray diffraction patterns were recorded on a Rigaku (D/MAX III VC) instrument in the 2θ region of 5–45°. Scanning electron microscope pictures were taken using a JEOL JSM 5200 microscope. Chemical analysis was carried out by XRF using a Rigaku 3070 X-ray spectrometer. The framework IR spectra were recorded in the diffuse reflectance mode using 300 : 1 ratio sample in KBr (Nicolet 60SXB).

2.2a *Solid state NMR spectroscopy:* ^{27}Al MAS/3Q-MAS solid state NMR experiments were performed on a Bruker DRX-500 FT-NMR spectrometer, at the resonance frequencies of 130·287 MHz (^{27}Al), 132·256 MHz (^{23}Na) respectively. ^{29}Si MAS NMR experiments were carried out on a Bruker MSL-300 NMR experiments at the resonance frequency 99·3 MHz (^{29}Si). The ^{27}Al, ^{23}Na triple quantum experiments were performed using a three-pulse sequence incorporating a z-filter[8]. The z-filter modification ensured that the echo and anti-echo pathways were symmetrised during the conversion step to get pure absorption-mode 2D spectra with negligible phase distortion. MAS spinning speed of 13·5 kHz was employed along with rotor synchronization during the triple quantum evolution period (t_1) to eliminate spinning side-bands appearing in the isotropic dimension. After shearing, the ^{23}Na and ^{27}Al 3Q-MAS contour plots were analysed by a graphical procedure[9] to extract the chemical shift and quadrupolar interaction parameters.[9] ^{29}Si MAS spectra were acquired using a spinning speed of 4 kHz was employed. The signal positions in ^{29}Si MAS spectra are referenced with respect to TMS (external) while ^{27}Al MAS/3Q-MAS signal positions are referenced with respect to Al^{3+} $(H_2O)_6$.

3. Results and discussion

XRD powder spectra of ZSM-35 and ferrierite are shown in figure 1. The high crystallinity of ferrierite and ZSM-35 is evidenced by sharp peaks in the XRD spectra. ZSM-35 and ferrierite were further characterized by SEM (figure 2), FT-IR (figure 3), carbon and nitrogen analysis. Chemical analysis gives Si/Al = 11 for ZSM-35 and 17 for ferrierite. BET surface areas were determined to be 400 and 360 cm^2/g for ZSM-35 and ferrierite, respectively.

3.1 *^{29}Si MAS NMR*

We show in figure 4, the ^{29}Si MAS spectra of ZSM-35 (a) and ferrierite (b). The increased signal resolution in ferrierite is readily apparent and is attributable to the weaker Si---Al dipolar interactions owing to its higher Si/Al, being removed by MAS. The multiplicity of signals in the –106·97 to –114·83 ppm range is due to crystallographic non-equivalence and the signal assignments follow the earlier report[10]. In the case of ZSM-35, the larger linewidth precludes this distinction. However, signals in the ppm range –114·83 to –112·54, due to Q_4 (4SiOAl) could be identified from the spectral deconvolution. In both ZSM-35 and ferrierite we observe the Si resonance at –106·97 ppm due to Q_3 (3SiAl) environments. The higher intensity for this peak in the case of ZSM-35 is due to lower Si/Al. By deconvolution of ^{29}Si MAS spectra and estimation of the integrated intensities for Q_4 (0Al) and

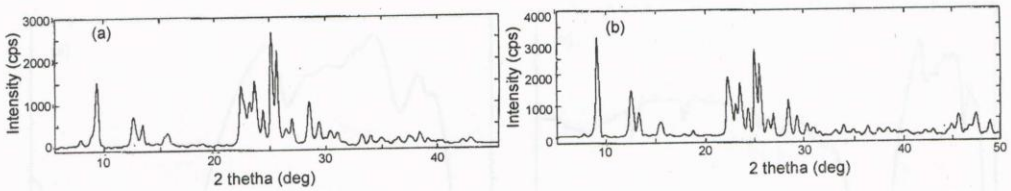

Figure 1. X-ray diffraction pattern of (**a**) ZSM-35 and (**b**) ferrierite.

Figure 2. Scanning electron micrograph of (**a**) ZSM-35 and (**b**) ferrierite.

Table 1. Graphical analysis results for ^{23}Na in ZSM-35

Species	δ_{iso} (ppm)	P_Q (MHz)
Td1	–26·74	3·26
Td2	–29·21	3·09
Td3	–31·26	2·91
Td4	–34·01	2·49

Table 2. Graphical analysis results of ^{27}Al in ZSM-35

Species	δ_{iso} (ppm)	P_Q (MHz)
Td1	58·52	1·54
Td2	57·64	1·51
Td3	56·50	1·65
Td4	54·79	1·72

Q_3(1Al) silicon resonances, the framework Si/Al is found to be 8·06 and 8·36 for ferrierite and ZSM-35 respectively.

3.2 *^{27}Al MAS/3Q-MAS NMR*

Figure 5 shows the comparison of ^{27}Al MAS spectra of ZSM-35 (a) and ferrierite (b). These spectra depict Al purely in tetrahedral co-ordination due to the appearance of signals in the 6·411 to 51·0 ppm region. However, no clues are provided about signal multiplicity due to crystallographic nonequivalence. This is due to residual second order quadrupolar broadening, which is not eliminated under MAS. The residual second-order quadrupolar broadening is eliminated in the triple quantum MAS experiment (figures 6 and 7). This is achieved by a two-dimensional correlation of orientation-dependent triple quantum frequencies with the corresponding single quantum frequencies detected during the acquisition period (t_2). After scaling, the centre of gravity of the contour is located at (54, 56) and (54, 56) and the chemical shift (δ_{cs}) and the second-order quadrupole shift (P_Q) parameters are readily determined for 3Q-MAS spectra.[9] Four different splitting patterns in the 3QMAS NMR appear for non-equivalent tetrahedrally coordinated aluminium. The δ_{iso} values for ZSM-35, *Td1* to *Td4* species, decrease from 58·52 to 54·79 ppm. The same molecular sieve increase for P_Q went up from 1·54 to 1·72 mHz. The contour in ZSM-35 and ferrierite are situated in the same position, which shows that in both zeolites, aluminium is located in the same environment. This is in similar to the ^{27}Al MASNMR result.

3.3 *^{23}Na 3Q-MAS NMR*

Figures 6 and 7 show the comparison of ^{23}Na 3Q-MASNMR spectrum of ZSM-35 and ferrierite. The residual second-order quadrupolar broadening is eliminated in the triple quantum MAS experiment. This is achieved by a two-dimensional correlation of orientation-dependent triple quantum frequencies with the corresponding single quantum frequencies detected during the acquisition period. After scaling the centre of gravity of the contour is located at (12, 32) and (8, 5) and the chemical shift (δ_{cs}) and the second-order quaadrupole shift (PQ) parameters are

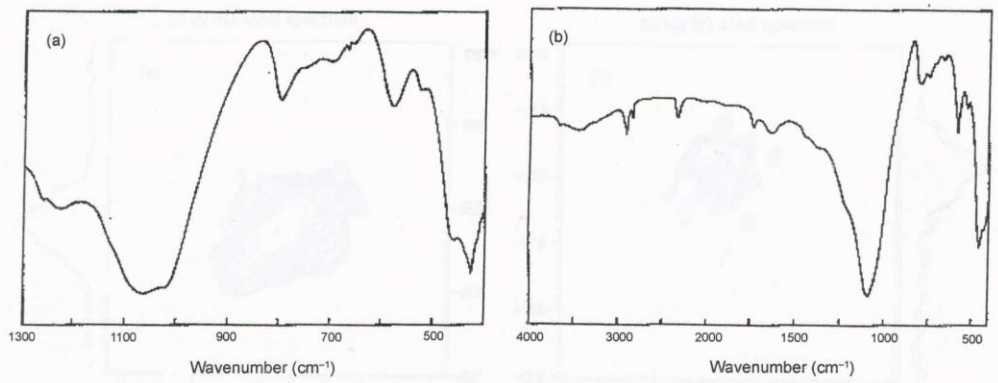

Figure 3. FT-IR spectrum of (**a**) ZSM-35 and (**b**) ferrierite.

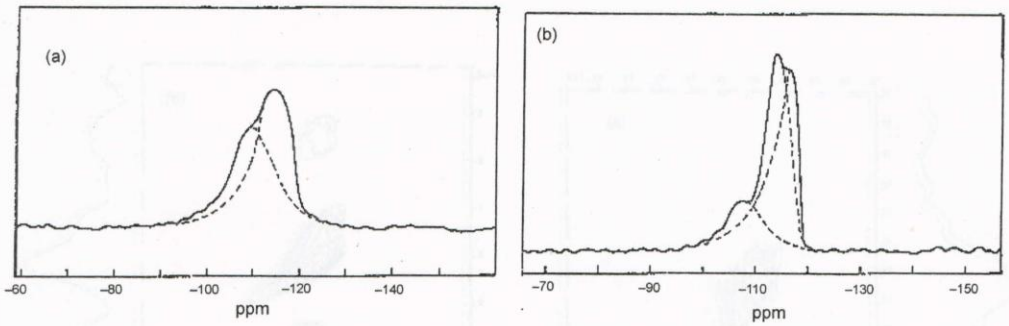

Figure 4. ^{29}Si MAS NMR spectrum of (**a**) ZSM-35 and (**b**) ferrierite.

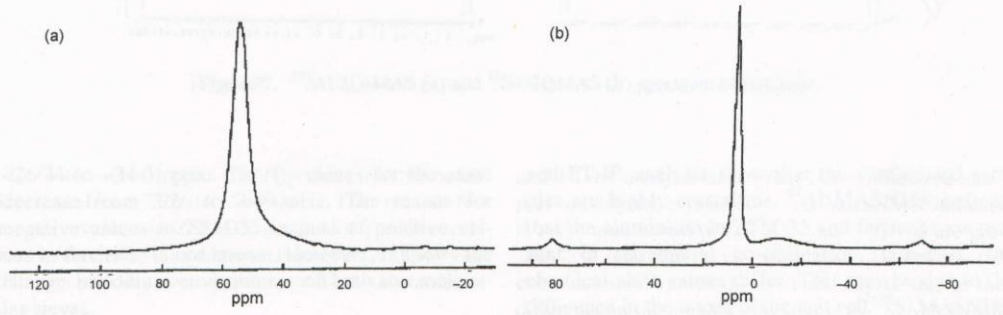

Figure 5. ^{27}Al MAS NMR spectrum of (**a**) ZSM-35 and (**b**) ferrierite.

readily determined for 3Q-MAS spectra.[9] Four different splitting patterns appear in 3Q-MAS for environmentally different sodium. The δ_{iso} values for ZSM-35, *Td1* to *Td4* species, decrease from

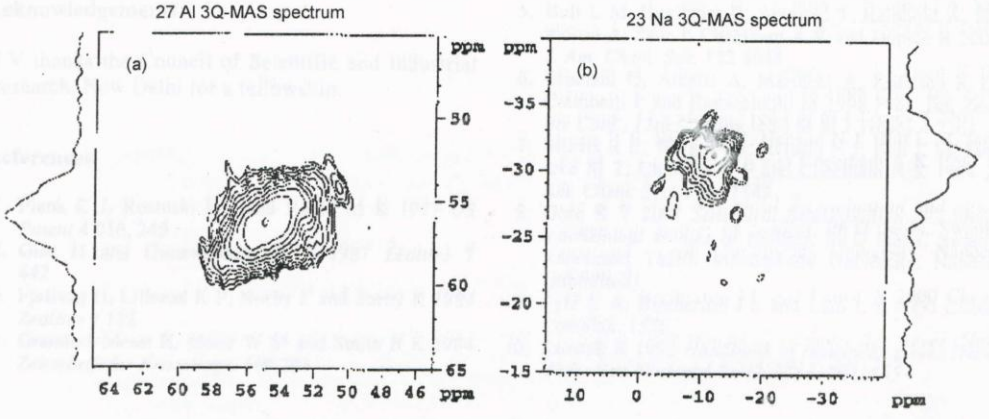

Figure 6. ^{27}Al 3Q-MAS (**a**) and ^{23}Na 3Q-MAS (**b**) spectrum of ZSM-35.

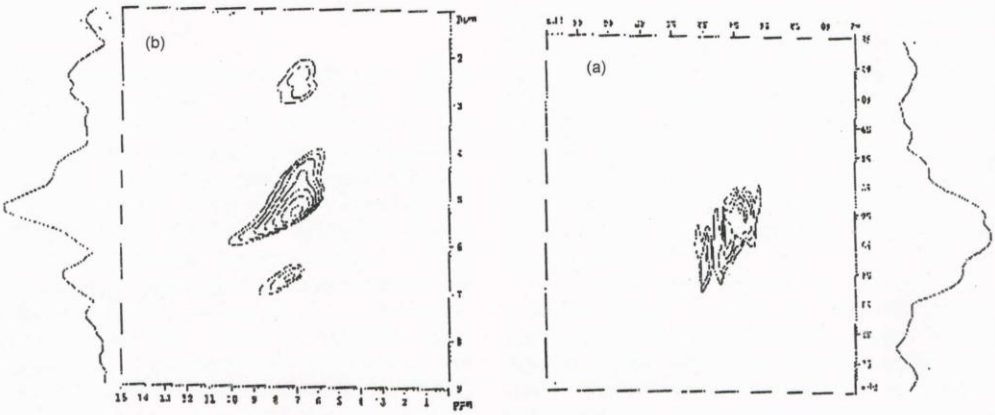

Figure 7. ^{27}Al 3Q-MAS (**a**) and ^{23}Na 3QMAS (**b**) spectrum of ferrierite.

–26·74 to –34·01 ppm. The P_Q values for the same decrease from 3·26 to 2·49 mHz. The reason for negative values in ZSM-35 instead of positive values in ferrierite is not known. However, it shows the change in sodium environment of both the molecular sieves.

4. Conclusions

ZSM-35 and ferrierite were synthesized using ethylene diamine and pyrrolidine templates. XRD, SEM and FT-IR analysis show that the synthesized samples are highly crystalline. ^{27}Al MASNMR indicate that the aluminium in ZSM-35 and ferrierite are present in tetrahedral co-ordination. However, the chemical shift values differ. This may be due to the difference in the *a*-axis of the unit cell. ^{29}Si MASNMR shows the presence of two different species in ZSM-35 and three different species in ferrierite samples. ^{27}Al and ^{23}Na 3Q-MAS NMR of ZSM-35 and ferrierite show the presence of four crystallographically distinct species.

Acknowledgements

N V thanks the Council of Scientific and Industrial Research, New Delhi for a fellowship.

References

1. Plank C J, Rosinski E J and Rubin M K 1977 *US Patent* **4** 016, 245
2. Gies H and Gunawardane R P 1987 *Zeolites* **7** 442
3. Fjellvag H, Lillerud K P, Norby P and Sorby K 1989 *Zeolites* **9** 152
4. Gramlich-Meier R, Meier W M and Smith B K 1984 *Zeitschrift fur Kristallogr.* **169** 201
5. Bull L M, Bussemer B, Anupold T, Reinhold A, Samoson A, Saur J, Cheetham A K and Dupree R 2000 *J. Am. Chem. Soc.* **122** 4948
6. Cruciani G, Alberti A, Martucci A, Knudsen K D, Ciambelli P and Rapacciuolo M 1998 *Proc. Int. Zeolite Conf., 12th Meeting* (ed.) M M J Treacy **4** 2361
7. Morris R E, Weigel S J, Henson N J, Bull L M, Janicke M T, Chmelka B F and Cheetham A K 1994 *J. Am. Chem. Soc.* **116** 11849
8. Gore K V 2001 *Structural determination and physicochemical studies of zeolites*, Ph D thesis, Swamy Ramanand Teerth Marathwada University, Nanded (submitted)
9. Fyfe C A, Bretherton J L and Lam L Y 2000 *Chem. Commun.* 1575
10. Szostak R 1992 *Handbook of molecular sieves* (New York: Van Nostrand Reinhold) p. 201, 545