Catalysis Letters 14 (1992) 349–357

MAS NMR studies of ZSM-5 zeolites: correlation to para selectivity and SEM observations

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Received 28 January 1992; accepted 16 April 1992

^{27}Al and ^{29}Si MAS NMR studies of various ZSM-5 zeolites of different Si/Al ratio, crystal size synthesized with and without alkali metal salt addition by the hydrothermal technique were carried out. The NMR observations clearly showed that the technique can be employed to differentiate Si/Al ratio, framework tetrahedral content and the crystal size. The last observation has been confirmed by SEM and catalytic activity test for para ethylation of ethylbenzene. A good correlation was found between the catalytic activity and the data from NMR and SEM.

Keywords: Solid state ^{29}Si and ^{27}Al NMR; zeolites; SEM; selectivity

1. Introduction

The crystalline aluminosilicates of ZSM-5 type have a uniform pore system and display fascinating properties such as selective accessibility to sorbates and reactant molecules. Their stupendous success in the petrochemical industry lies in xylene isomerisation, ethylbenzene synthesis, toluene disproportionation and conversion of methanol to gasoline [1,2]. In these zeolites, the catalytic activity is directly related to the composition of framework, the distribution of tetrahedral atoms in the unit cell and the crystal, the cation content, the crystal size and mobility of adsorbed atomic and molecular species. The utility of MAS NMR in determining some of these parameters has been illustrated by several workers [3–5]. However, the aspect of line width broadening, crystal size and para selectivity has not been so far fully studied. In the light of these facts, the present study was aimed at carrying out ^{27}Al and ^{29}Si NMR studies of ZSM-5 zeolite with different Si/Al ratio, crystal size synthesized with and without addition of alkali metal salt, and also to correlate NMR data to SEM observations and para selectivity.

2. Experimental

2.1. MATERIALS

ZSM-5 zeolite samples were synthesized by the well-known hydrothermal technique using tetrapropyl ammonium bromide as template material. The zeolites of different crystal sizes were synthesized with and without addition of alkali metal salts such as LiCl, NaCl, KCl and CsCl. Solutions of aluminium sulfate (A), sodium hydroxide (B), tetrapropyl ammonium bromide (C), Ludox-40 (D) and each of the alkali metal (Li, Na, K and Cs) salts (E) were prepared. Same volumes of A, B, C, D and E (with varying salts) were mixed with stirring and the pH of the gel was adjusted to 10.5 with 0.5 M sulphuric acid. The gel was transferred to a teflon lined vessel and kept for crystallization at 170°C. The synthesized material was finally washed and dried in an oven at 120°C [6–8]. These zeolites were characterized by XRD, IR, SEM and TPD of ammonia. The organic template was removed by calcining at 540°C in air for 5 h and the zeolite was converted to ammonium form by repeated ion exchange with 10% NH_4NO_3 solution. The proton form was obtained by deammoniation at 550°C for 5 h. The zeolite was used in the proton form for ethylbenzene alkylation studies while for NMR and SEM studies it was used in the synthesized form.

2.2. NMR MEASUREMENTS

The solid state MAS NMR spectra were obtained on a Bruker MSL 300 NMR spectrometer. The ^{29}Si and ^{27}Al NMR spectra were recorded at 52.61 MHz and 78.206 MHz, respectively, by taking 500 mg of the sample in the zirconium oxide rotor. ^{29}Si chemical shifts were measured using TMS as reference, while ^{27}Al chemical shifts were obtained with respect to $[Al(H_2O)_6]^{3+}$. The samples were spun at magic angle with rotational speed of 3.3 kHz. Sweep width was 25000 Hz and the number of transients accumulated was 500–2000. Pulse repetition times for ^{29}Si and ^{27}Al NMR spectra were 5 s and 500 ms, respectively.

2.3. SEM MEASUREMENTS

The scanning electron micrographs were recorded in a JEOL JSM 35C microscope at magnification between 1500 and 15000 at an operating voltage of 2.5 kV. Prior to observation the samples were spread on double adhesive tape fixed on to specimen stub and a 5000 Å layer of gold was sputtered on to them.

2.4. ACTIVITY TESTS

The catalytic activity test was carried out in a plug flow, fixed bed glass reactor at atmospheric pressure. The proton form of the zeolite powder (1 g)

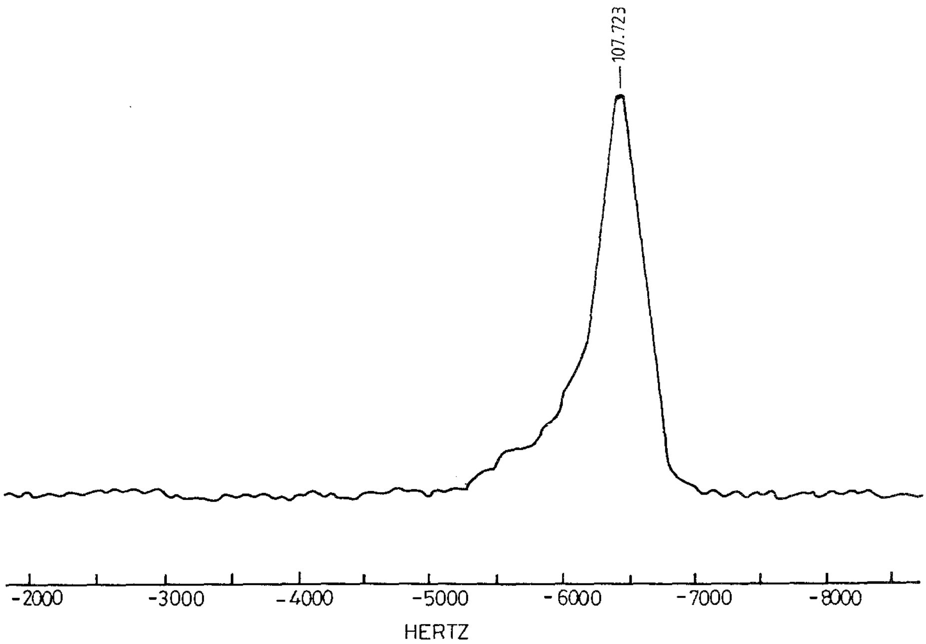


Fig. 1. ^{29}Si MAS NMR spectrum of ZSM-5 zeolite (Si/Al = 100).

was used for carrying out ethylation of ethylbenzene using hydrogen as a carrier gas. The details of experimental setup are reported in our earlier work [9]. The reactants and products were analysed by a Varian Vista 6000 gas chromatograph using a 50 m LB-550 capillary column.

3. Results and discussion

Fig. 1 depicts ^{29}Si NMR spectrum of ZSM-5 zeolite with Si/Al = 100. Evidently in such a high silicious zeolite a strong signal corresponding to Si(4Si) at high field side is observed. However, other types of silicons like silicons attached to one, two, three or four aluminium atoms through oxygens are observed as shoulders. Fyfe et al. [10] have shown that by the deconvolution of the ^{29}Si NMR of high silica zeolite responses in terms of Gaussian curves it is possible to obtain the peak areas of shoulders and approximate estimation of Si/Al ratios. The peak width at half height for ZSM-5 samples is also given in table 1. In the case of ZSM-5 zeolites synthesized without any salt addition the line width decreases with increase in cation size in the salt. However, the magnitude of line width values is higher for the zeolites synthesized with alkali salt addition, which is due to the fact that these zeolites contain more of monoclinic unit cells than the zeolites synthesized without any salt addition. This observation is in concurrence with the observations made by Jacobs et al.

Table 1
Si/Al ratio and line width of peak at half height from ^{29}Si NMR for various ZSM-5 samples

Sr. No.	Sample	Approximate Si/Al ratio	Line width of ^{29}Si NMR (Hz)
1.	ZSM-5 (1)	39	350
2.	ZSM-5 (2)	77	333
3.	ZSM-5 (3)	166	320
4.	ZSM-5 (Li)	54	435
5.	ZSM-5 (Na)	34	430
6.	ZSM-5 (K)	27	425
7.	ZSM-5 (Cs)	25	415

[11]. In other words, with increase in Si/Al ratio in ZSM-5 samples synthesized without any salt addition the crystallite sizes increase. They are also found to increase with the change in cation from Li to Cs in zeolites synthesized with the addition of alkali metal salt.

Figs. 2 and 3 show the ^{27}Al NMR spectra of ZSM-5 zeolites with Si/Al ratio nearly 100, synthesized with and without LiCl addition. The delay time between successive pulses was longer than the longitudinal relaxation time in order to achieve quantitative data from ^{27}Al NMR signal. In fig. 2 a peak which appears at 60 ppm is generally interpreted as due to four-coordinated (tetrahedral) framework aluminium, whereas non-framework octahedral aluminium is usually

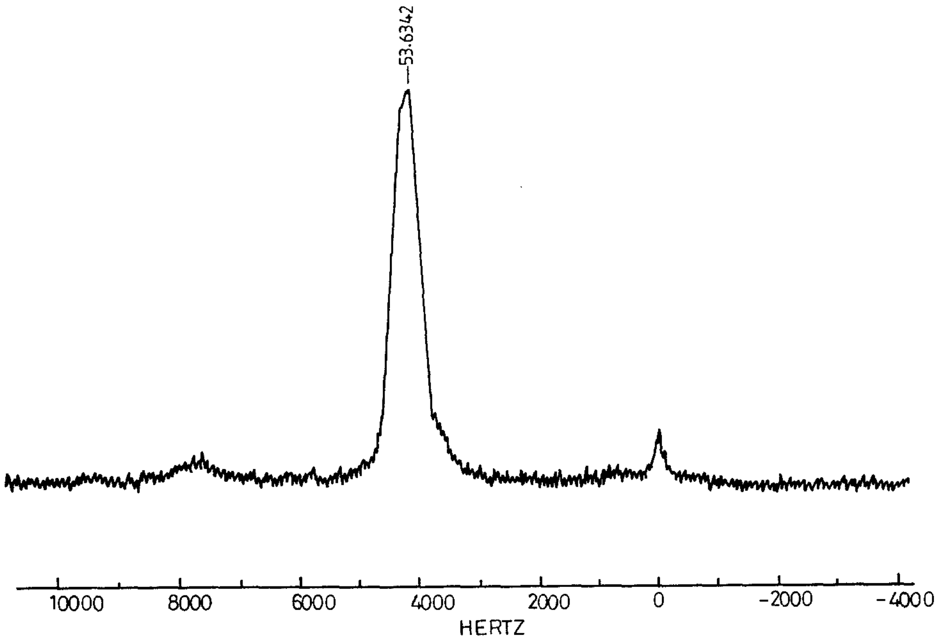


Fig. 2. ^{27}Al MAS NMR spectrum of ZSM-5 zeolite (Si/Al = 100).

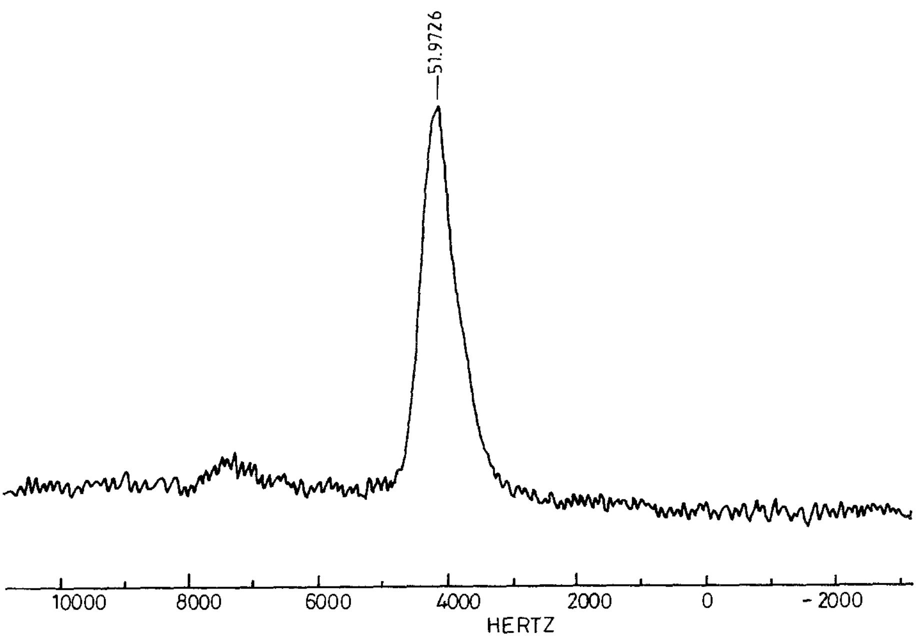


Fig. 3. ^{27}Al NMR spectrum of ZSM-5 zeolite (LiCl).

observed at 0 ppm [12]. Table 2 shows the quantitative data for the types of aluminium present in various zeolites samples.

^{27}Al NMR line width at half height is mainly dependent on crystallinity of the sample and the quadrupolar coupling constants e^2Qq/h. The quadrupolar coupling constant, which increases the peak width, is inversely proportional to r^{-6} (r is the average Al–Al distance). In the present set of samples the r^{-6} values when estimated were found to be in the narrow range 1.2×10^{-7}–4.0×10^{-3}, thereby not varying the quadrupolar coupling constants significantly. It indicates a change in the Si/Al ratios had not changed the quadrupolar

Table 2
Framework/extra framework aluminium content and line width at half height from ^{27}Al NMR for different ZSM-5 samples

Sr. No.	Sample	Frame work/ tetrahedral	Extra-framework/ octahedral	Line width ^{27}Al NMR (tetrahedral) (Hz)
1.	ZSM-5 (1)	94	6	1500
2.	ZSM-5 (2)	96	4	1450
3.	ZSM-5 (3)	100	0	1450
4.	ZSM-5 (Li)	100	0	1800
5.	ZSM-5 (Na)	98	2	1700
6.	ZSM-5 (K)	97	3	1640
7.	ZSM-5 (Cs)	97	3	1580

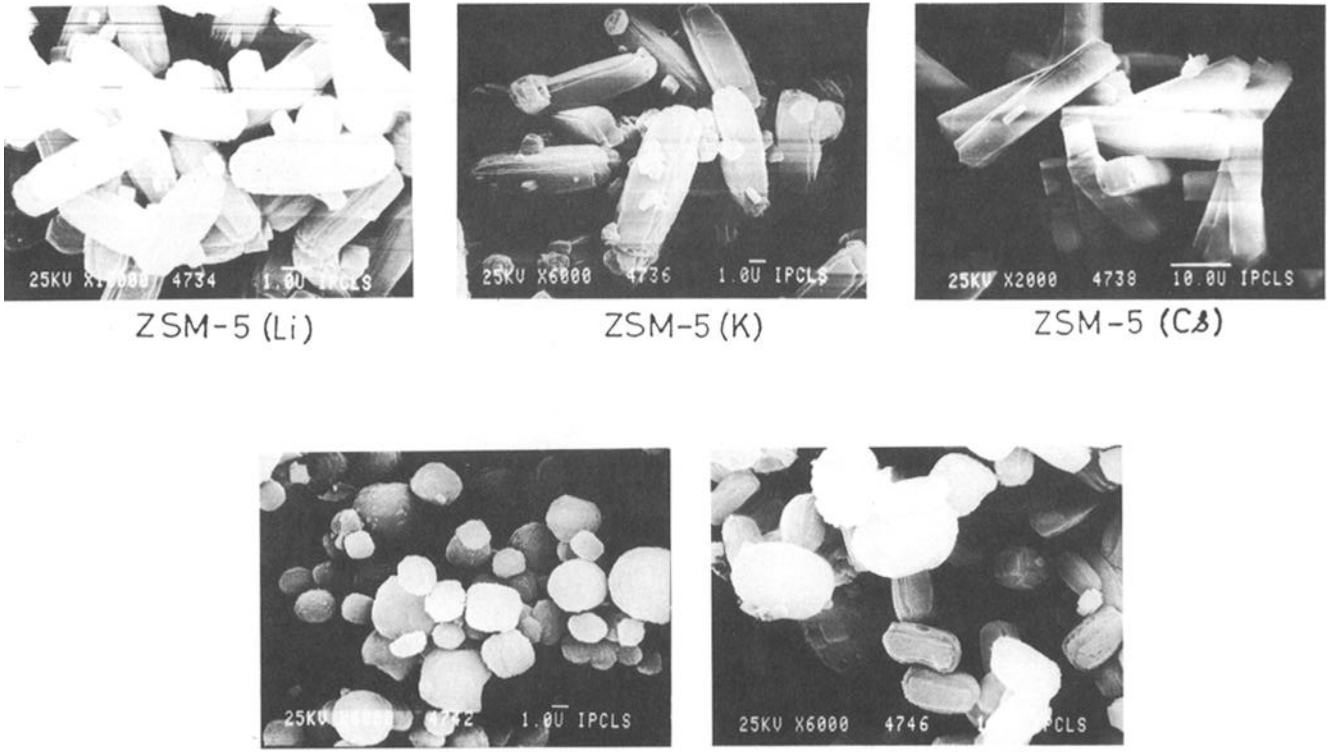
coupling constants contributing to the line widths. Hence, any change in the line width has been attributed only to the crystallinities. Nagy et al. [13] have also shown that even in samples with large variations in Si/Al ratios, the mutual influence of Al atoms does not dominate the ^{27}Al NMR line width. Table 2 also shows the line widths measured at half height of ^{27}Al (framework) NMR signal for all the samples. Results show an increase in crystalline domains with increase in Si/Al ratio for zeolites synthesized without addition of alkali metal cations. However, in the case of zeolites synthesized with alkali metal salt addition line width decreases and crystalline domain increases with change in cation from Li to Cs.

Fig. 4 shows the micrographs of well defined crystallites of ZSM-5 with Si/Al ratio 50, 200 and samples prepared with Li, K, Cs salt addition during synthesis. Table 3 shows the dimensions of the crystallites which are the average of 20 crystallites at two different magnifications. Apparently an increase in the crystallite size with the change of cation size from Li to Cs, supported both ^{27}Al and ^{29}Si NMR observations. Further with increase in Si/Al ratio the crystallite sizes increased. However, their spherical morphology changed to oblong. Addition of alkali salts led to larger crystallite sizes of oblong nature and with sharper edges.

The catalytic activity for ethylbenzene ethylation with ethanol was studied over all ZSM-5 samples. Table 4 presents the results for ZSM-5 zeolites of different crystallite sizes. It has been demonstrated earlier that para product selectivity in alkylation of alkylbenzene can be enhanced by using zeolites of larger crystallite sizes [4]. There is a direct relationship between the crystallite size and para product selectivity. The alkylbenzene alkylation normally produces para alkylated product within the zeolite channel due to its shape selectivity features. However, the para product is isomerised to ortho and meta isomers on the external surface and pore mouth sites, resulting in lower external surface area, hence less possibility of para isomer getting converted to isomeric products. From table 4 it is quite evident that para diethylbenzene selectivity increases from 47 to 70% with the change in crystallite size from 2.2 (l/b) to 4.5 (l/b). In all the zeolites, formation of *o*-diethylbenzene in negligible quantity is due to steric factors. In other words, the activity/selectivity studies confirmed MAS NMR and SEM observations indicating that there is an increase in crystallite size of zeolite by the change in the addition of metal cation salt from LiCl to CsCl.

4. Conclusions

By deconvolution of the ^{29}Si MAS NMR signal it is possible to obtain an approximate value of Si/Al ratio in high silica containing zeolites. ^{27}Al MAS NMR can be efficiently used to determine framework (tetrahedral) and non-framework (octahedral) aluminium content. The line width of peak at half



ZSM-5 (Li) ZSM-5 (K) ZSM-5 (Cs)

ZSM-5(SI/Al :50) ZSM-5 (Si/Al:200)

Fig. 4. Micrographs of various zeolites. (The magnifications as published are: Li 6500, K 3900, Cs 1300, Si/Al:50 3900, Si/Al:200 3900.)

Table 3
Dimensions of crystallites in various zeolite samples measured by SEM

Sr. No.	Sample	Dimensions and particles (μm)		l/b
		length l	breadth b	
1.	ZSM-5 (LiCl)	4.0 ± 0.7	1.8 ± 0.5	2.2
2.	ZSM-5 (KCl)	8.4 ± 0.8	2.9 ± 0.6	2.9
3.	ZSM-5 (CsCl)	24.1 ± 2.5	5.3 ± 0.7	4.5
4.	ZSM-5 (Si/Al = 50)	2.7 ± 0.8	2.7 ± 0.8	1
5.	ZSM-5 (Si/Al = 100)	4.7 ± 0.7	2.5 ± 0.9	1.7

Table 4
Ethylbenzene ethylation on different ZSM-5 zeolites. Reaction conditions: temperature = 350°C, ethylbenzene/ethylalcohol mol ratio = 5, H_2/alkylation mix mol ratio = 3, pressure = 1 atm

Performance	ZSM-5 [a]	Zeolite			
		ZSM-5 [b] (LiCl)	ZSM-5 [c] (NaCl)	ZSM-5 [d] (KCl)	ZSM-5 [e] (CsCl)
ethylbenzene conversion (wt%)	23.90	21.92	24.30	22.50	23.55
selectivity to products (%)					
para-diethylbenzene	47.34	51.87	56.00	60.99	70.45
meta-diethylbenzene	51.56	47.24	43.28	38.64	29.55
ortho-diethylbenzene	1.10	0.89	0.72	0.37	0.00

[a] 6 ml/h. [b] 5 ml/h. [c] 4 ml/h. [d] 3 ml/h. [e] 2 ml/h.

height of both ^{29}Si and ^{27}Al showed a good indication of crystallite size of the zeolite. MAS NMR observations were further confirmed by SEM and para product selectivity test. MAS NMR is a good tool to obtain information regarding crystalline domain of high silica pentasil zeolites.

Acknowledgement

The authors gratefully acknowledge to Dr. N. Suryaprakash of I.I. Sc., Bangalore for rendering experimental assistance and also thank Professor C.L. Khetrapal for helpful discussions. They are grateful to Dr. I.S. Bhardwaj, Director (R&D) for this continuous encouragement and permission to publish the paper.

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