

²⁹Si and ²⁷Al MAS NMR Study of Zeolite β with Different Si/Al Ratios

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²⁹Si and ²⁷Al MAS NMR and IR spectroscopies have been used to characterize zeolites-β covering a wide range of Si/Al ratios (7.6–110) and to analyze the dealumination process produced during calcination of TEA- or NH₄-exchanged samples. The analyses of samples with low Si/Al ratio has permitted us to differentiate three types of structural sites and to detect some preferential occupation by Al of these sites. In dealuminated samples two new lines associated with SiOH have been identified in ²⁹Si NMR spectra, the first assigned to structural sites, part of them occupied by Al in the starting zeolite, and the second associated with the amorphous material produced during calcination. © 1990 Academic Press, Inc.

INTRODUCTION

The cracking and hydrocracking of large hydrocarbon molecules requires the use of large-pore zeolites in order to reduce diffusional problems; therefore zeolite Y is the most widely used for these two catalytic processes. The benefits of using zeolite Y with a high framework Si/Al ratio as cracking catalyst have been demonstrated (1–3). Unfortunately, it has not been possible up to now to synthesize NaY zeolites with Si/Al ratios higher than about 3.0, and therefore the zeolite must be dealuminated by steam or chemical treatments after synthesis. In addition to the additional cost involved in the dealumination process, the presence of the extraframework Al (EFAL), even if it is catalytically active, can cause some inconvenience due to a less selective cracking performance (4). It is not surprising then that extensive research has been carried out to optimize the dealumination process and EFAL extraction of zeolite Y (5).

Another way of attacking the problem consists of the synthesis of other large-pore, high silica zeolites. One of these is the β zeolite, already synthesized in the sixties

(6) and rediscovered recently (7–10). This material can be obtained in a wide range of Si/Al ratios between 7 and 200 (11, 12) and shows good activity and selectivity for hydroisomerization and hydrocracking (7, 13).

The structure of the β zeolite was reported very recently by two independent research groups (14–16). The first study carried out by Newsam *et al.* (14, 15) showed by high-resolution electron microscopy and electron diffraction that this zeolite is a three-dimensional 12-membered ring zeolite. However, these authors have shown that this zeolite is an intergrowth of tetragonal (A) and monoclinic (B), two related crystalline phases. A very recent report of the Mobil group permitted the identification of a second monoclinic polytype (C) in this group of zeolites (16). A powder X-ray diffraction study of zeolites with Si/Al ratio close to 10 indicated a slight preference (close to 60%) for polymorph B (15). However, structural characteristics associated with Si and Al distribution and dealumination phenomenon, which are essential for a better use of this zeolite in catalysis, are still unknown.

In this work a thorough NMR and IR study of β zeolites with different framework Si/Al ratios and after different activa-

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tion treatments has been carried out. The occupation of different structural positions by Al will be discussed.

EXPERIMENTAL

Tetraethylammonium (TEA)- β samples of different Si/Al ratios were prepared according to the method reported by Pérez-Pariente *et al.* (11, 12). Their chemical compositions are given in Table 1. In order to remove the TEA cation from the zeolite pores the samples were calcined in air at 500°C for 5 h. Then the samples were exchanged with a 2 M NH_4Cl solution at 80°C, dried, and calcined again at 500°C for 5 h. This process was repeated twice to obtain the protonic H- β samples.

High resolution ^{29}Si , ^{27}Al , and ^{13}C NMR spectra were recorded at 59.6, 104.25, and 100.6 MHz, respectively, on a Bruker MSL 400 spectrometer. All measurements were carried out at room temperature. The spinning frequency was in the range 4–4.5 KHz. ^{29}Si and ^{27}Al signals were recorded after 4- and 2- μs pulses. Time intervals of 2 s for Al and 9 s for Si between successive accumulations were chosen in order to avoid saturation effects. Cross-polarized proton-decoupled ^{13}C NMR spectra of TEA molecules retained in the zeolite were obtained with a time contact of 3 ms, a decoupling of 150 ms, and a recycle time of 8 s. $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and tetramethylsilane were used as standard references for the measurement

of aluminum, silicon, and carbon chemical shift (δ in ppm).

X-ray powder diffraction patterns were obtained with a Philips diffractometer equipped with graphite monochromator and using $\text{CuK}\alpha$ radiation.

To obtain the IR spectra, self-supporting wafers of 10 $\text{mg} \cdot \text{cm}^{-2}$ were prepared. The samples were introduced in a Pyrex vacuum IR cell and treated at 400°C overnight prior the recording of spectra. The spectra were recorded with a Perkin-Elmer 580B spectrophotometer equipped with data station.

RESULTS

^{29}Si Spectra

^{29}Si MAS NMR spectra of TEA- β , calcined β , and H- β samples with different Si/Al ratios are given in Figs. 1a, 1b, and 1c, respectively. Four different components centered at ≈ -91 , ≈ -104 ppm, -110 ppm, and -115 ppm can be distinguished in ^{29}Si spectra of the TEA- β samples (Fig. 1a).

After the TEA- β samples were calcined (Fig. 1b), several changes can be observed in these spectra. The intensity of the -103 ppm resonance line strongly decreases, in all samples, allowing the detection of peaks at -111 , -105 , and -98 ppm characteristic of Si surrounded by 4 Si, 3 Si 1 Al, and 2 Si 2 Al. On the other hand, as the Al content decreases a shift in the -110 line to -111.5

TABLE 1
Chemical Composition of TEA- β Zeolite Samples

Sample No.	SiO_2	Al_2O_3	Na_2O	K_2O	TEA- β Si/Al (CA)	Calcined Si/Al (NMR)	H- β Si/Al (NMR)
1	85.3	9.4	1.46	3.79	7.6	11.6	13.7
2	93.6	4.3	0.56	1.40	18	16.2	24
3	94.8	2.9	0.62	1.58	29	16.5	—
4	97.8	0.75	0.38	0.91	110	95	>100
5	96.4	0.83	0.89	1.90	100	>100	>100

Note. Si/Al ratios of as-made and calcined samples determined by chemical analysis (CA) and ^{29}Si NMR spectroscopy.

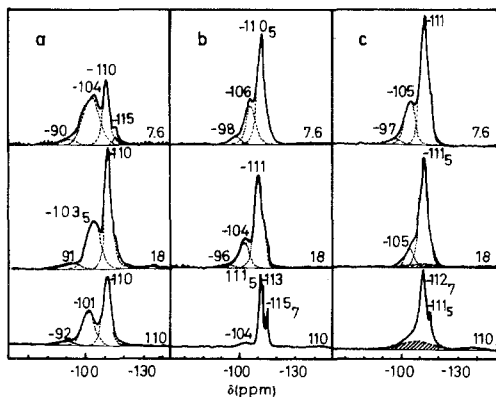


FIG. 1. ^{29}Si MAS NMR spectra of samples 1, 2, and 4; (a) TEA- β , (b) calcined β , (c) H- β . Numbers indicate the Si/Al ratio of the synthesized material (Table 1).

is observed, and new lines centered at ca. -113 and -115 ppm appear. The spectra of samples with Si/Al ratios >100 showed four well-resolved components, centered at -104 , -111.5 , -113 , and -115.7 ppm. The presence of the -104 -ppm line in samples with Si/Al >100 can only be explained by the presence of Si in Si(3 Si, 1 OH) environments. In samples with lower Si/Al ratios the band at -104 ppm would correspond to the superposition of Si (3 Si, 1 Al) (-106 ppm) and Si(3 Si, 1 OH) (-102 ppm) components. The three lines detected above -111 ppm in samples with high Si content could correspond to nonequivalent silicon atoms, with no aluminum in the second coordination sphere (Si surrounded by 4 Si), occupying different structural sites in the zeolite.

In more aluminous samples an additional decrease in the intensity of the -105 -ppm resonance line occurs after the exchange-calcination treatment (sample H- β , Fig. 1c). However, poorly resolved spectra are obtained when the samples were dealuminated by this procedure. Indeed, a very broad signal corresponding to an amorphous material overlaps the other lines present in the spectra (dashed line in Fig. 1c), which suggests a partial destruc-

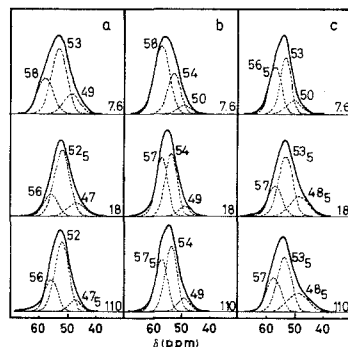


FIG. 2. ^{27}Al MAS NMR spectra (tetrahedral region) of (a) TEA- β , (b) calcined β , (c) H- β . Numbers indicate the Si/Al ratio of the synthesized material (Table 1).

tion of the crystalline structure might have taken place.

^{27}Al Spectra

^{27}Al spectra of TEA- β , calcined- β , and H- β are given in Figs. 2 and 3. The TEA- β sample with the highest Al content shows two broad resonance lines at ca. 56–58 and 52–53 ppm (Fig. 2a). The intensity of the first line decreases as the Al content decreases, while both lines shift to lower ppm. After removing the organic material by calcination in air (Fig. 2b), the spectra of

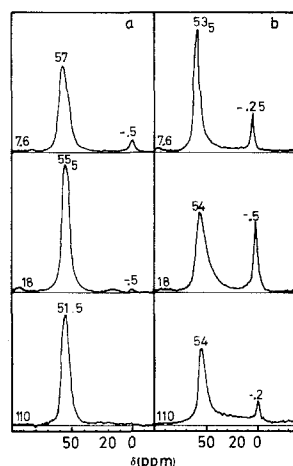


FIG. 3. ^{27}Al MAS NMR spectra; (a) calcined β , (b) H- β . Numbers indicate the Si/Al ratio of the synthesized material (Table 1).



FIG. 4. ^{13}C NMR spectra of TEA- β (samples 1 and 4).

the samples show two broad resonance lines at ≈ 58 and 54 ppm, the relative intensity of the latter increasing with decreasing Al content. The deconvolution of these spectra has permitted, as in the case of Si spectra, the detection of another less intense component at ≈ 49 ppm. However, the important halfwidth of the three components reduces considerably their resolution in these signals. After the exchange-calcination treatment (Fig. 2c) the intensity of the 57-ppm line decreases and becomes smaller than the 54-ppm line, resulting in the relative intensity of the two lines being similar in all analyzed samples. A resonance line at ≈ 0 ppm corresponding to octahedral Al is visible when exchanged samples were subsequently calcined, its relative intensity decreasing in general in samples with lower Al content (Fig. 3). The amount of octahedral Al produced during TEA decomposition is in all cases clearly lower than that obtained during heating of exchanged samples.

^{13}C Spectra

^{13}C spectra of TEA- β samples of Si/Al ratios 7.6 and 110 are shown in Fig. 4. Two

narrow resonance lines centered at 8.3 and 53.8 ppm corresponding, respectively, to carbon atoms of methyl and methylene groups can be observed in both spectra. This result indicates that the tetraethylammonium species are very similar and the interaction with the zeolite framework is not intense enough to produce the differentiation of the organic charge-compensating "cation" from the "occluded" ones which are present as hydroxide species in zeolite (10, 11).

IR Spectroscopy

The IR spectra of calcined and H- β zeolites or different Si/Al ratios in the 4000- to 3000- cm^{-1} region are shown in Fig. 5a and 5b, respectively. A band at 3745 cm^{-1} assigned to terminal or external silanol groups is visible in all the calcined samples. The large half-width and asymmetry of this band suggest the presence in the sample of internal silanol groups, appearing between 3600 and 3500 cm^{-1} (17, 18).

After NH_4^+ exchange and subsequent calcination a new band at 3615 cm^{-1} is detected, which has been assigned to acidic hydroxyl groups in the framework (10). The intensity of this band decreases with Al content, supporting that assignment (Fig. 5b). During this treatment no large changes were observed in the band corresponding to the silanol groups, except in the case of the sample with the highest Si/Al ratio, whose

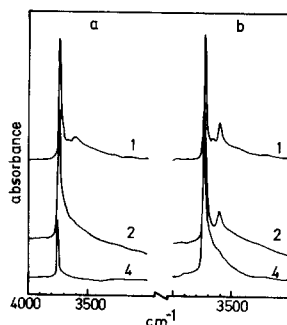


FIG. 5. IR spectra (hydroxyl region) of samples 1, 2, and 4; (a) calcined β (b) H- β .

intensity increases strongly. In some cases (sample 5), the amount of internal silanol groups increases strongly after calcination (Fig. 7).

DISCUSSION

The assignment of ^{29}Si and ^{29}Al NMR components in the spectra of TEA- β zeolites to specific environment is difficult due to interaction of organic molecules with the tetrahedral network. The removal by calcination of the organic molecules (TEA) from the zeolite clarifies the NMR spectra and permits the detection on ^{29}Si spectra of peaks associated with Si surrounded by 4 Si, 3 Si 1 Al, and 2 Si 2 Al in samples with Si/Al ratio ranging from 7.6 to 110.

A comparison of the framework Si/Al ratios, deduced from NMR spectra on the basis of compliance with Loewenstein's rule, with those obtained by chemical analysis (Table 1) shows that the framework aluminum content of the zeolites, as determined from the NMR, is overestimated. These results can be explained by considering that the line at 104 ppm corresponds in all cases not only to Si (3 Si 1 Al) but also to Si (3 Si 1 OH) species produced during calcination. This conclusion is confirmed by IR spectroscopy, which shows that during calcination of these zeolites a considerable number of silanol groups are created.

This observation is also supported by the increase in the $\text{Al}^{\text{VI}}/\text{Al}^{\text{IV}}$ ratio, which indicates that β zeolite becomes dealuminated mainly by deep-bed calcination of exchanged samples. The dealumination is accompanied by a decrease in the number of the hydroxyl groups appearing at 3615 cm^{-1} in the IR spectrum. However, following the evolution of the intensity of this band with the Al content of the H- β samples (Fig. 6), it becomes clear that the Al is more easily removed from samples with a higher Al content. In exchanged samples dealumination is parallel with the partial destruction of zeolite framework and the formation of the amorphous phase detected by ^{29}Si NMR spectra.

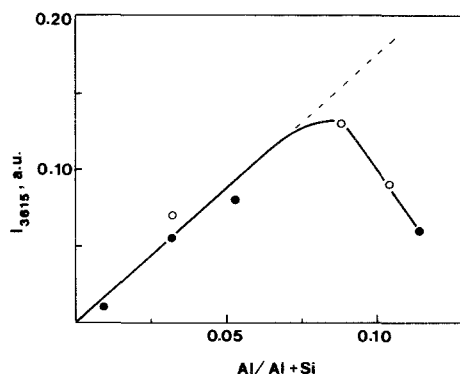


Fig. 6. Intensity of the 3615-cm^{-1} band as a function of the aluminum content of H- β zeolites. (●) Samples 1 to 4; (○) data from Ref. (10).

In order to assign the components detected in the ^{29}Si and ^{27}Al spectra to ions in different crystallographic sites, it is interesting to remark that the position of the line for silicon and aluminum atoms has the same variation with TOT angle (either Si or Al), i.e., the higher the TOT angle, the more negative is the chemical shift of both lines (19–21). ^{29}Si NMR spectra of calcinated samples are formed by three components at -115 , -113 , and -111 ppm, their detection being favored when the aluminum content of the sample is very low. In the same samples three components at 57, 54, and 49 ppm with intensities similar to those of ^{29}Si spectra were detected in the ^{27}Al NMR spectra. However, the presence of second-order quadrupolar effects seems to decrease the spectral resolution in relation to that of ^{29}Si NMR spectra. The ^{27}Al NMR spectra of calcined samples show that the ratio of the intensity of the high and low field lines, i.e., 54 and 57 ppm, increases when the Si/Al ratio of the zeolite is increased. These results support the existence of preferential occupation of certain sites by Al in zeolite β .

In the process of thermal dealumination of the zeolite, the aluminum is not equally removed from the different sites, and those corresponding to the 54-ppm resonance signal are more resistant toward dealumina-

tion than those associated with the 57-ppm line. After NH_4^+ exchange and calcination, no large differences in Al occupancy of the two sites were observed in any of the analyzed samples.

Analysis of the ^{29}Si NMR spectra of calcined samples in the region of chemical shift corresponding to Si(4 Si) indicates the existence of three lines corresponding to Si in different crystallographic sites. In a previous work, Fyfe *et al.* (22) showed that the ^{29}Si NMR spectrum of highly dealuminated zeolite β has nine peaks, supporting the existence of nine nonequivalent tetrahedral sites in the unit cell of this material. This fact has been recently confirmed by the structural analysis carried out by Newsam *et al.* using X-ray and high-resolution TEM techniques (15). In the ^{29}Si NMR spectra reported by Fyfe *et al.*, three sets of lines were detected around -111 , -113 , and -115 ppm, and the relative integrated intensities of these groups of lines were, respectively, 47, 29, and 23%. In our case, only three lines could be resolved, and their relative intensity was 50, 27, and 23%, which is in very good agreement with the results of Fyfe *et al.* The lower resolution observed in our spectrum can be due to the existence of a higher concentration of stacking faults or defects in the sample. Calcination of zeolites with very low Al content ($\text{Si}/\text{Al} > 100$) would increase the number of structural defects. Figure 7 shows that the higher the amount of silanol groups created by calcination, the lower is the resolution of three components in the ^{29}Si NMR spectra.

In order to identify which types of structural sites correspond to different lines we have computed the atom coordinates of the unit cell, the mean TOT angles, and T - T distances for each tetrahedral site in the two types of structures (monoclinic and tetragonal) proposed by Newsam *et al.* ^{29}Si chemical shifts associated with each site were deduced by use of the correlation between TOT angle and silicon chemical shift proposed by Thomas *et al.* (19). It can be seen that only the spectrum corresponding to the tetragonal structure gives lines in the

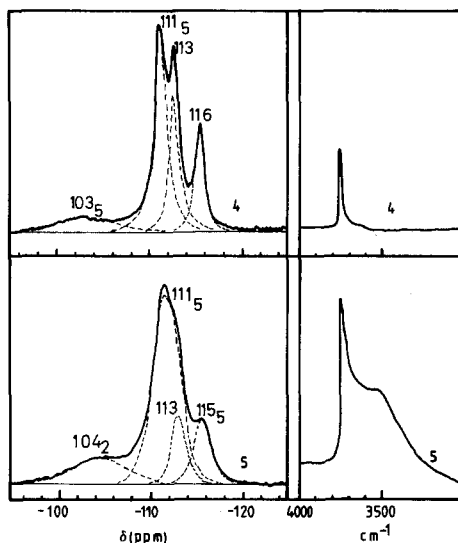


FIG. 7. ^{29}Si NMR and IR (hydroxyl region) spectra of samples 4 and 5 (H- β samples).

three regions where components are detected (Fig. 8); however, relative intensities do not correspond to those observed in the NMR spectra. In the case of the structures proposed by Higgins *et al.* (16), the calculated ^{29}Si chemical shifts are always lower than those corresponding to the experimental ones. These results indicate that a better refinement of proposed structures would be desirable in order to obtain a more reliable correlation between both methods.

CONCLUSIONS

^{29}Si and ^{27}Al MAS NMR study shows that the synthesized TEA-zeolite β produces a low dealumination during calcination in air. However, NH_4^+ exchange followed by calcination increases considerably the fraction of aluminum removed from the lattice, this fraction being higher for samples with high aluminum content. NMR analysis has also shown that the aluminum is not completely randomly distributed in the framework of asynthesized material but has some preference in the occupation of certain tetrahedral positions, their occupancy changing as a function of the aluminum content of the material. The aluminum is less easily removed by calcination from preferential

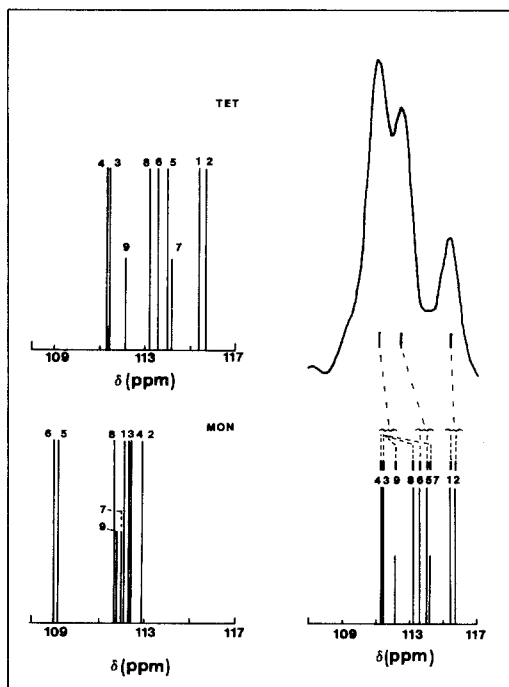


FIG. 8. Predicted chemical shifts in the silicon sites for the tetragonal (TET) and monoclinic (MON) structures. Comparison with the experimental spectrum of sample 4 calcined. The structural data have been taken from Ref. (15). The height of lines indicates the relative population of each tetrahedral site.

sites and the ^{27}Al NMR spectra of all samples are similar after calcination of exchanged samples.

During dealumination, acid OH groups of the structure are removed, as shown by IR spectroscopy, while external (3745 cm^{-1}) and internal ($3000\text{--}3500\text{ cm}^{-1}$ broad band) silanol groups are created. In the same process, the tetrahedral network breaks down and additional broad bands are detected in NMR spectra.

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