

A high-resolution solid-state carbon-13 NMR investigation of occluded templates in pentasil-type zeolites : some silicon-29 solid-state NMR characteristics of ZSM-5

Citation for published version (APA):

Boxhoorn, G., Santen, van, R. A., Erp, van, W. A., Hays, G. R., Alma, N. C. M., Huis, R., & Clague, A. D. H. (1983). A high-resolution solid-state carbon-13 NMR investigation of occluded templates in pentasil-type zeolites : some silicon-29 solid-state NMR characteristics of ZSM-5. In G. C. Bond, P. B. Wells, & F. C. Tompkins (Eds.), *Proceedings of the Sixth International Congress on Catalysis (ICC 6) 12 - 16 July, 1976, Imperial College, London* (pp. 694-703). Chemical Society.

Document status and date:

Published: 01/01/1983

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

A HIGH-RESOLUTION SOLID-STATE ^{13}C NMR INVESTIGATION OF OCCLUDED TEMPLATES IN PENTASIL-TYPE ZEOLITES; SOME ^{29}Si SOLID-STATE NMR CHARACTERISTICS OF ZSM-5

G. Boxhoorn, R. A. van Santen, W. A. van Erp, G. R. Hays, N. C. M. Alma, R. Huis and A. D. H. Clague

Koninklijke/Shell-Laboratorium, Amsterdam, (Shell Research B.V.), (The Netherlands)

Using ^{13}C and ^{29}Si solid-state magic angle spinning NMR spectroscopy, we have studied a number of ZSM-5 and ZSM-11 zeolites, prepared with a wide variety of bases. The study has confirmed the presence of occluded organic cations at the intersections of the 10-ring channels in the zeolite. Incorporated tetrapropylammonium cations exhibit a particular splitting of methyl resonances, which is shown to be related to the ZSM-5 channel structure. The nature of ^{29}Si NMR spectra of HZSM-5 strongly depends on the presence of silanol groups in defect positions in the zeolite lattice.

INTRODUCTION

Pentasil-type zeolites such as ZSM-5 and ZSM-11 are synthesized by a hydrothermal treatment (120-180°C) of a mixture containing silica, alumina, an inorganic and an organic base (in the case of ZSM-5 mostly NaOH and tetrapropylammonium hydroxide (TPAH) have been used). ZSM-5 syntheses have been reviewed in the literature (1-3). The TPAH synthesis route is found to be the most flexible route, yielding the fine-crystalline ZSM-5 (up to a few tenths of a μm .) necessary for catalytic application. The composition of the reaction mixture, the concentrations of the reactants, the temperature and duration of the hydrothermal treatment, agitation and in particular the nature of the organic base have a pronounced influence on the structure of the silicate formed. So far little is understood of the role of the organic base in zeolite synthesis; a clathrating/templating role of the organic base has been suggested (2,3).

In an attempt to elucidate the effect of the organic base on the zeolite formation, we have carried out solid-state ^{13}C NMR measurements on the crystallization products ($\text{Na}^+\text{TPA}^+\text{ZSM-5}$) obtained after the hydrothermal synthesis step. In addition, possible effects of the silica/alumina ratio in the zeolite framework and the fate of the occluded organic base during heat treatment have been investigated. These results will be reported in Part 1 of this paper. Some preliminary results have been reported earlier (4).

The use of high-resolution solid-state ^{29}Si in the study of zeolites has also been demonstrated recently (5-8). The existence of five, partially overlapping regions of ^{29}Si chemical shifts of the SiO_4 tetrahedra in aluminosilicates has been shown by Lippmaa (5). The solid-state ^{29}Si spectra of a few ZSM-5 samples have been published (6-8); the ^{29}Si resonances found were assigned to $\text{Si}(1\text{ OH})$ and $\text{Si}(0\text{ Al})$. In ref. (7), the resonances obtained for silicalite were assigned to the crystallographically non-equivalent tetrahedral Si sites.

In Part 2 of this paper we will report the ^{29}Si solid-state NMR spectra of $\text{Na}^+\text{TPA}^+\text{ZSM-5}$; $\text{Na}^+\text{H}^+\text{ZSM-5}$; $\text{NH}_4^+\text{H}^+\text{ZSM-5}$ and $\text{H}^+\text{ZSM-5}$. Additionally, we have measured the cross-polarization spectra in order to identify the silanol groups.

EXPERIMENTAL

1. Synthesis

The zeolites were prepared according to ref. 9 starting from slurries containing amorphous silica, NaAlO_2 , NaOH , the organic template and water. The mixture was hydrothermally treated for one to six days at 150°C . The product was separated by filtration, washed with water and dried at 120°C . The products were characterized by XRD and elemental analysis.

2. NMR Measurements

The high-resolution solid-state ^{13}C spectra were recorded at room temperature using either a Bruker CXP 300 NMR spectrometer (7.05 T magnetic field, ^{13}C frequency 75.45 MHz) or a Bruker CXP 200 NMR spectrometer (4.7 T, 50.3 MHz). The hollow sample rotors used in this investigation were fashioned from coated boron nitride (10), which yields no background signals in the spectrum. For the experiments described here, we used rotors containing about 200 mg of sample; rotation rates of between 3 and 5 kHz were achieved. Single cross-polarization contacts with contact times of 5 ms were employed. Recycle times between acquisitions were usually 5 s; B_1 field strengths were 1.1 and 4.4 mT for the proton and carbon channels, respectively. Chemical shifts are given with respect to an external sample of liquid TMS.

59.6 MHz ^{29}Si solid-state MAS NMR spectra were recorded on the Bruker CXP-300 NMR spectrometer. Samples were contained in Beams-Andrew mushroom rotors, fashioned from Delrin and spinning at a frequency of 3.2 kHz. Typically 2000 FIDs were accumulated with a repetition time of 30 s. In cross-polarization experiments single contacts were employed using the flip-back sequence (11) with spin temperature inversion (12). Contact times of 1 ms were used to selectively enhance the SiOH signals. Chemical shifts are given in ppm with respect to tetramethylsilane, taking the signal of Na_2SiO_3 as a secondary external reference (-68.7 ppm). Upfield shifts are taken to be negative.

RESULTS AND DISCUSSION

Part 1. ^{13}C NMR of TPA ions in ZSM-5

1. TPAH ZSM-5

Figure 1A shows the solid-state ^{13}C NMR spectrum of TPAH ZSM-5. The assignments of the three distinct resonances are indicated in the figure; for comparison the spectrum of solid TPAH is given in Figure 1B. There are two points to be made: firstly, the ^{13}C NMR spectrum of TPAH ZSM-5 is generally in agreement with that of solid TPAH, and the overall intensities remain the same. The observed differences in ^{13}C chemical shifts (see Table 1) may be caused by a distortion of the symmetry around the positively charged nitrogen atom and/or a different interaction with the counterion, which might be the zeolite lattice. Secondly, there is a remarkable splitting of the CH_3 group signal. The origin of this splitting will be discussed below. From the spectrum of TPAH ZSM-5 it seems that the TPA ion has remained intact during the ZSM-5 synthesis.

We studied separately the ^{13}C NMR spectra of TPABr and TPACl. The symmetrical structure of TPABr is clearly reflected in the NMR spectrum of TPABr (13) and no CH_3 group splitting is observed (Table 1). By contrast, TPACl shows several CH_3 resonances, which indicates a significantly different arrangement of TPA^+ and Cl^- ions in solid TPACl. For ZSM-5 prepared via TPABr and TPACl, spectra identical to that of TPAH ZSM-5 have been obtained, which might indicate that the nature of the counterion (i.e., OH^- , Br^- or Cl^-) has no influence on the ^{13}C NMR

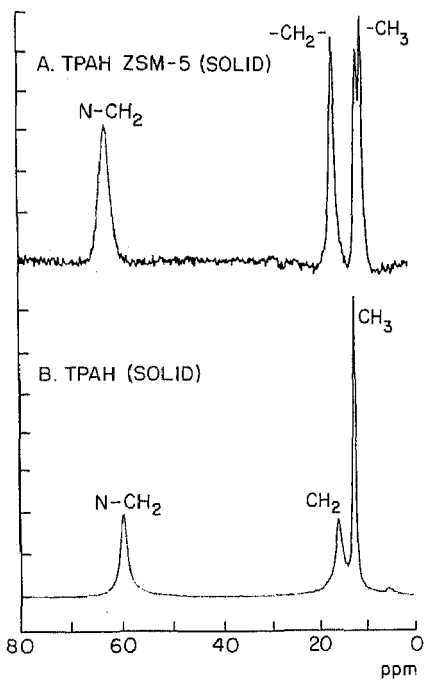


FIG. 1: SOLID-STATE ¹³C NMR SPECTRA OF TPAH ZSM-5 AND TPAH

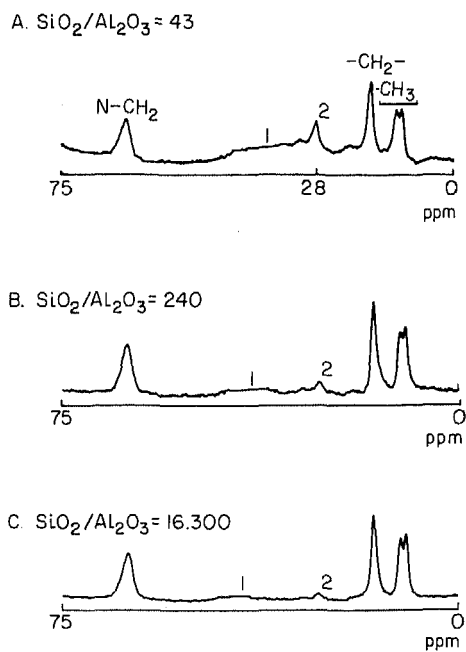


FIG. 2: SOLID-STATE ¹³C NMR SPECTRA OF TPAH ZSM-5 SAMPLES WITH DIFFERING ALUMINIUM CONTENTS (1. DELRIN SIDE-BAND REMOVED; 2. IMPURITY)

Table 1 - Solid-State ^{13}C Chemical Shifts of TPA Ions

Carbon atom	Chemical shifts (ppm)					
	TPAH	TPAC1	TPABr	TPAH ZSM-5	TPAC1 ZSM-5	TPABr ZSM-5
CH_3	12.8	10.8	12.7	10.3	10.0	10.5
		11.8				
		12.3		11.5	11.0	11.5
		12.8				
CH_2	16.0	15.6	16.1	16.6	16.2	16.6
$\text{CH}_2\text{-N}$	60.2	59.8	60.1	63.0	62.4	63.2

Table 2 - ^{13}C NMR Liquid (l) and Solid (s) State Chemical Shifts, of Various Organic Bases Used in ZSM-5 Synthesis

Compound	Chemical Shift (ppm)				
	1*	2	3	4	5
l. $\overset{1}{\text{CH}_3}\overset{2}{\text{CH}_2}\overset{3}{\text{CH}_2}\text{NH}_3^+$	11.8	21.5	42.4		
s. $\overset{1}{\text{CH}_3}\overset{2}{\text{CH}_2}\overset{3}{\text{CH}_2}\text{NH}_3^+/\text{ZSM-5}$	10	24	41		
l. $\overset{1}{\text{CH}_3}\overset{2}{\text{CH}_2}\overset{3}{\text{CH}_2}\overset{4}{\text{CH}_2}\text{NH}_3^+$	14.2	20.2	30.0	40.5	
s. $\overset{1}{\text{CH}_3}\overset{2}{\text{CH}_2}\overset{3}{\text{CH}_2}\overset{4}{\text{CH}_2}\text{NH}_3^+/\text{ZSM-5}$	12.2	20.0	29.8 (28.5)	41.0	49.5
l. $\overset{1}{\text{CH}_3}\overset{2}{\text{CH}_2}\overset{3}{\text{CH}_2}\overset{4}{\text{CH}_2}\text{OH}$	14.8	20.3	30.2	62.6	
s. $\overset{1}{\text{CH}_3}\overset{2}{\text{CH}_2}\overset{3}{\text{CH}_2}\overset{4}{\text{CH}_2}\text{OH}/\text{ZSM-5}$	12.8	19.3	29.7	65.1	

* numbering of carbon atoms (l = liquid; s = solid)

spectrum of TPA⁺ occluded in ZSM-5. However, as elemental analyses revealed a very low halogen level in the TPABr and TPACl ZSM-5 samples, we conclude that the TPA⁺ ions in ZSM-5 possess the same counterion irrespective of the nature of the template used.

2. Origin of the Doublet in TPAH ZSM-5

In principle [AlO₄]⁻ sites in ZSM-5 may act as the counterions of some of the TPA ions. This could include a sufficiently different environment for the TPA ion and therefore influence the NMR spectrum.

In Figure 2 the ¹³C NMR spectra of TPAH ZSM-5 samples having different silica/alumina ratios are given. They appear to be essentially independent of the alumina content, no difference being detectable in the positions or intensities of the three carbon types, even in Al-free ZSM-5 (silicalite). No effect could be detected either upon varying the number of Na⁺ ions and the H₂O content in the zeolite. Since in ZSM-5 the number of TPA ions largely exceeds the number of aluminium sites, we conclude that anionic [AlO₄]⁻ sites in the zeolite framework probably do not form the charge balancing counterions of the TPA⁺ cations.

ZSM-5 contains two different types of channel: sinusoidal channels with circular ten rings of Si atoms, and straight channels with elliptical ten rings (14). Both channels have a diameter of about 0.55 nm. Since the diameter of the TPA ion is >0.9 nm (13), it can only be located at the intersections of the channels in ZSM-5; all other positions require a severe distortion of the ion. This is in agreement with elemental analysis: generally about 10 % (w) of TPAH is found to be present in ZSM-5, corresponding to 3 to 4 TPA ions per unit cell. Since ZSM-5 contains four intersections per unit cell, we conclude that most intersections are occupied by the organic base. These intersections have a critical dimension of nearly 0.9 nm (15). This means that the propyl groups must partly protrude into the channels of ZSM-5; two into the straight channels and two into the sinusoidal channels. A model study showed that TPAH fits best at the intersections when its symmetry is lowered. It is conceivable that these two channel types introduce slightly different chemical environments for the methyl groups, which would explain the observed splitting (16).

3. Effect of heat treatment on TPAH ZSM-5

In going from TPAH ZSM-5 to the catalytically active form HZSM-5, the Na⁺TPA±ZSM-5 has to be calcined in order to decompose the occluded TPA ions; Na ions are subsequently replaced by NH₄⁺, followed by calcination of the obtained NH₄⁺H±ZSM-5. We followed the first calcination step using solid-state ¹³C NMR, in order to monitor the disappearance of TPAH (see Figure 3). Apparently, the TPA cation is stabilized by the zeolite since even at 350°C TPAH is still present in the zeolite (solid TPAH decomposes at about 240°C) as was also confirmed with Fourier transform infrared (FT-IR) spectroscopy (17). Upon going from 250 to 275°C the ¹³C NMR spectrum changes and one new resonance peak is found at 9.6 ppm. Simultaneously, the 10.5 and 11.5 ppm methyl doublet peaks decrease in intensity. At 325°C the original doublet has almost disappeared. In the temperature range 250-325°C no change of CH₃ vibrations was detected by FT-IR spectroscopy (17). We propose that heating leads to a more symmetrical TPA ion by rotation of the N-CH₂-CH₂ bonds, yielding only a singlet of higher intensity in the NMR spectrum. Such a change would not influence the CH₃ vibrations.

4. ZSM-5 Intermediates Prepared Via Alternative Routes

A cheaper route to synthesize ZSM-5 makes use of butylamine (BA). For BA ZSM-5 we found five peaks (see Figure 4) of which four resonances (as indicated by numerals in the figure) are in good agreement with the protonated form of BA (see Table 2). The fifth peak is tentatively assigned to an impurity of protonated

dibutylamine of which compound three resonances coincide with the BAH^+ resonances. This interpretation is supported by elemental analysis of BA ZSM-5, which showed a C/N ratio >5 .

In contrast with the FT-IR observations of others (18), protonation of the amine was also found using solid-state NMR for ZSM-5 prepared with propylamine (PA), as was confirmed by FT-IR (19). Protonation of amines during zeolite synthesis has already been suggested in the patent literature (20).

ZSM-5 can also be prepared with ethanol (EtOH) and butanol-1 (BOH) as templates. The ^{13}C NMR spectrum of EtOH ZSM-5 suggests that very little carbon-containing material remained occluded in the zeolite after drying at 120°C . This was confirmed by elemental analysis. Actually, no resonances of ethanol were found; the only resonance observed at 30.7 ppm is ascribed to aliphatic carbon atoms resulting from oligomerization of ethylene formed by decomposition of ethanol. We conclude that ethanol diffuses out of the zeolite lattice and partly decomposes. Similar results were obtained for BOH ZSM-5: only weak resonances due to BOH carbon atoms were found (Table 2). The weak resonances and the relatively high percentage of carbon present again suggest that BOH also decomposes during the synthesis and diffuses out of the zeolite during drying at 120°C .

In addition, we measured the solid-state ^{13}C NMR spectra of tripropylamine (TPA) ZSM-5, tributylmethylammonium hydroxide (BMAH) ZSM-5, tetrabutylammonium hydroxide (TBAH) ZSM-11 and tetrabutylphosphonium hydroxide (TBPH) ZSM-11 (see Table 3). For all these samples the ^{13}C resonances are considerably broader than those for TPAH ZSM-5. This might be caused by the presence of contaminating silicate material, or a different interaction with the zeolite framework. As a result of these increased linewidths, no clear splitting of the alkyl-chain methyl group resonance can be seen, although a shoulder of weak intensity (14.3 ppm) is observed for the methyl signal in BMAH ZSM-5 (13.1 ppm).

CONCLUSIONS

1. TPAH remains intact during the synthesis of ZSM-5, even at remarkably high temperature - this is in contrast to the behaviour of other templates such as BA, EtOH and BOH, which decompose partly or diffuse out of the framework during the synthesis. This probably explains why ZSM-5 of poorer crystallographic quality is obtained via the alternative routes using these templates.
2. A remarkable splitting of the methyl carbon ^{13}C NMR signal of TPAH in ZSM-5 has been found. This is independent of counterion, aluminium, sodium or water content of the zeolite and must therefore be related to the unique ZSM-5 framework structure.

Part 2. ^{29}Si solid-state NMR of ZSM-5

We have studied the ^{29}Si solid-state NMR spectra of $\text{Na}^+\text{TPA}^+\text{ZSM-5}$; $\text{Na}^+\text{H}^+\text{ZSM-5}$; $\text{NH}_4^+\text{H}^+\text{ZSM-5}$ and $\text{H}^+\text{ZSM-5}$ prepared via various synthesis routes; some preliminary results are reported here. It was found that the ^{29}Si NMR spectra of ZSM-5 can be classified into two types:

Type I (See Figure 5A,B)

Most of the samples exhibit a ^{29}Si NMR spectrum with one broad Si(O Al) resonance at -112 ppm and sometimes a shoulder at -115 ppm. An additional resonance is found at -102 ppm. This resonance is independent of the aluminum content and is therefore assigned to Si(1 OH), as was confirmed by cross-polarization (see

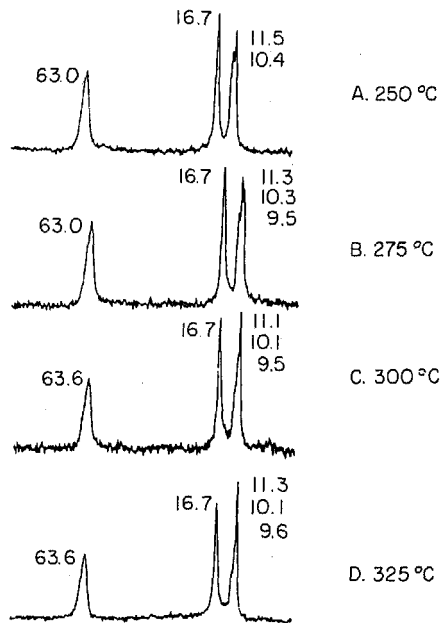


FIG. 3: SOLID-STATE ^{13}C NMR SPECTRA OF HEAT-TREATED TPAH ZSM-5

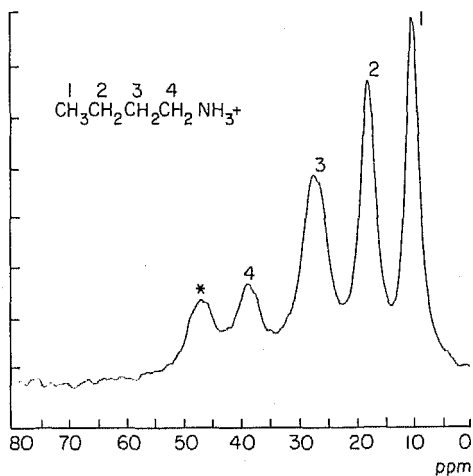


FIG. 4: SOLID-STATE ^{13}C NMR SPECTRUM OF BAH^+ ZSM-5 (*SEE TEXT)

Table 3 - ^{13}C NMR Liquid (l) and Solid (s) State Chemical Shifts, of Various Organic Bases Used in ZSM-5 and ZSM-11 Synthesis

Compound	Chemical Shift (ppm)					
	1*	2	3	4	5	
$^1\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$ [$\text{CH}_2\text{CH}_2\text{CH}_2$] $_3\text{N}$	ZSM-5	11.2	19.0	56.2		
$^1\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ [$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$] $_3\text{CH}_2\text{OH}$	ZSM-5	13.1	20.0	24.1	49.6	65.9
$^1\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NOH}$ [$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$] $_4\text{NOH}$	ZSM-11	14.6	20.9	24.5	61.5	
$^1\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{POH}$ [$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$] $_4\text{POH}$	ZSM-11	13.8	23.3**			

* numbering of carbon atoms (l = liquid; s = solid)
** overlapping resonances of carbon atoms 2, 3 and 4

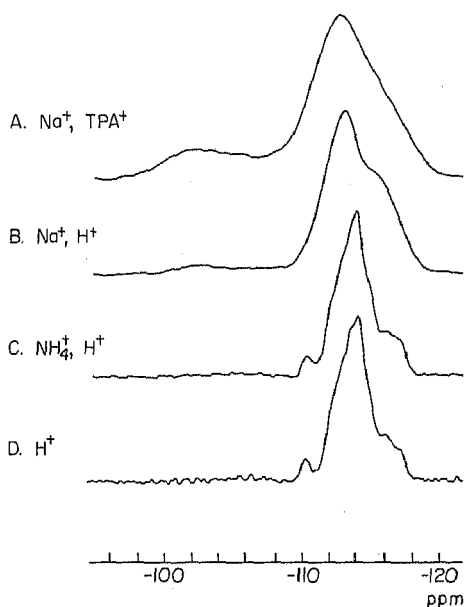


FIG. 5: SOLID-STATE ^{29}Si NMR OF ZSM-5

- A. Na^+ , TPA^+ ZSM-5 AFTER DRYING AT 120°C .
- B. Na^+ , H^+ ZSM-5 AFTER CALCINATION AT 500°C OF A.
- C. NH_4^+ , H^+ ZSM-5 AFTER Na^+ EXCHANGE OF B.
- D. H^+ ZSM-5 AFTER CALCINATION AT 500°C OF C.

below). The type I spectrum is obtained for all $\text{Na}^+\text{TPA}^+\text{ZSM-5}$ and $\text{Na}^+\text{H}^+\text{ZSM-5}$ intermediates and most $\text{H}^+\text{ZSM-5}$ samples studied.

Type II (See Figure 5C,D)

ZSM-5 prepared via TPAH, and having a low alumina content (0.3%) exhibits a ^{29}Si NMR spectrum with several resonances in the region of $\text{Si}(0 \text{ Al})$. Both the positions and the relative intensities of the type II spectra closely resemble the spectrum of ref. 7. As is argued there, these resonances are probably related to the different tetrahedral Si positions in ZSM-5. Figure 5 indicates that a type I spectrum of $\text{Na}^+\text{TPA}^+\text{ZSM-5}$ is transformed into a type II spectrum by converting the Na^+ , TPA^+ form into the NH_4^+ or H^+ form. We further found that a H ZSM-5 showing initially a type I spectrum exhibits, after heat treatment at 800°C for 4 h, a type II spectrum (21).

Cross-polarization (CP) is an effective method of identifying silanol groups (5). Application of CP to the above mentioned spectra reveals that in going from Figure 5A to 5D, the number of silanol groups is reduced drastically, yielding finally a type II spectrum (21). This means that the transformation of a type I into a type II spectrum is accompanied by removal of silanol groups. Silanol groups are present at the outer surface of the zeolite crystal and inside the zeolite, in crystallographic defects of the silicate lattice. High temperature treatment removes the silanol groups and thereby the defects (21). Similar effects occur upon the replacement of Na^+ by NH_4^+ ions. Na^+ ions prevent the condensation of silanol groups to form silicate rings. After the removal of Na^+ ions by ion exchange with NH_4^+ silicate ring closure is facilitated by expulsion of NH_3 (Figure 5C). The chemical shifts in ^{29}Si NMR are probably related to the Si-O-Si bond angle (22). On the basis of these considerations a relationship might be drawn between the observed $\text{Si}(0 \text{ Al})$ resonances and the positions of Si in the 4, 5, 6 and 10 rings present in the ZSM-5 framework.

CONCLUSION

The existence of two types of ^{29}Si solid-state NMR spectra for HZSM-5 is related to the amount of crystallographic defects, where silanol groups are present.

ACKNOWLEDGMENT

We gratefully acknowledge elucidating discussions with Ir. A.G.T.G. Kortbeek.

Since this work was done, Nagy, et al. (23) have published the ^{13}C solid-state NMR spectra of $\text{TPA}^+\text{ZSM-5}$, $\text{TBA}^+\text{ZSM-11}$ and $\text{TBP}^+\text{ZSM-11}$. The ^{13}C NMR spectrum of $\text{TPA}^+\text{ZSM-5}$ is in agreement with our spectrum published in ref. 4, but both the spectra of TBA^+ and $\text{TBP}^+\text{ZSM-11}$ apparently differ from ours. The spectra of Nagy, et al. show a clear splitting of the methyl resonance for $\text{TBA}^+\text{ZSM-11}$, whereas for $\text{TBP}^+\text{ZSM-11}$ a less well-defined splitting is observed. A methyl-peak lineshape comparable to the latter was obtained by us for BMAH ZSM-5 and TBAF ZSM-11. The one TBAH ZSM-11 sample for which we observed a clear splitting of the methyl resonance in the spectrum contained some 50% ZSM-5 as an impurity, as determined by X-ray diffraction.

REFERENCES

1. D. W. Breck, "Zeolite Molecular Sieves," (Wiley, 1974).
2. E. M. Flanigen, Pure & Appl. Chem., 52 (1980) 2191.

3. E. G. Derouane, S. Detremmerie, Z. Gabelica and N. Blom, *Appl. Catal.*, 1 (1981) 201.
4. G. Boxhoorn, R. A. van Santen, W. A. van Erp, G. R. Hays, R. Huis and D. Clague, *J. Chem. Soc. Chem. Comm.* (1982) 264.
5. E. Lippmaa, M. Mägi, A. Samoson, G. Engelhardt, and A. R. Grimmer, *J. Amer. Chem. Soc.*, 102 (1980) 4889.
6. J. B. Nagy, J. P. Gilson and E. G. Derouane, *J. Chem. Soc. Chem. Comm.* (1981) 1129.
7. C. A. Fyfe, G. C. Gobbi, J. Klinowski, J. M. Thomas and S. Ramdas, *Nature*, 296 (1982) 530.
8. J. B. Nagy, Z. Gabelica and E. G. Derouane, *Chem. Lett.* (1982) 1105.
9. a. US 4,011,278 (1977); b. Dutch 7610763 (1976) (ICI), c. Dutch 7411825 (1974) (Mobil), d. US 4,108,881 (1978).
10. G. R. Hays, A. D. H. Clague and R. Huis, *Bull. Magn. Reson.* 2 (1980) 120.
11. J. Tegenfeldt and U. Haeberlen, *J. Magn. Res.* 36 (1979) 453.
12. E. A. Stejskal and J. Schaefer, *J. Magn. Res.* 18 (1975) 560.
13. A. Zalkin, *Acta Crystallogr.* 10 (1957) 557.
14. G. T. Kokotailo, S. L. Lawton, D. H. Olson and W. M. Meier, *Nature*, 272 (1978) 437.
15. E. G. Derouane and Z. Gabelica, *J. Catal.* 65 (1980) 486.
16. G. D. Price, J. J. Pluth, J. V. Smith, J. M. Bennett and R. L. Patton, *J. Amer. Chem. Soc.* 104 (1982) 5971.
17. I. L. C. Freriks and G. Boxhoorn, unpublished results.
18. H. Bremer, W. Reschetilowski, K. Wendlandt, J. Papp and J. Papp, Jr., *Z. Chem.* 22,7 (1982) 275.
19. P. H. G. van Kasteren and G. Boxhoorn, unpublished results.
20. US 4,139,600 (Mobil) (1979).
21. G. Boxhoorn, A. G. T. G. Kortbeek, N. C. M. Alma and G. R. Hays, *Zeolites* 4 (1984) 15.
22. R. H. Jarman, *J. Chem. Soc., Chem. Commun.* (1983) 512.
23. J. B. Nagy, Z. Gabelica and E. G. Derouane, *Zeolites* 3 (1983) 43.