Chapter 20

Synthesis of Pentasil Zeolites With and Without Organic Templates

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Magic-angle-spinning nuclear magnetic resonance spectroscopy (MAS NMR) yields quantitative information about Brönsted acidity and structural defects in zeolites. We have studied samples of pentasil zeolites synthesized with and without organic templates using 1H and 27Al NMR. The influence of mono-, di- and tri-n-alkylamine and tetraalkylammonium compounds (alkyl = methyl, ethyl, propyl and butyl) upon the rate of crystallization, yield and the properties of the products is discussed. By varying the SiO_2/Al_2O_3 ratio and the lengths of the period of crystallization at 175 °C, H_2O/SiO_2=30, Na_2O/SiO_2=0.1 we have arrived optimal reaction conditions for a template-free synthesis of zeolites of ZSM-5 type at SiO_2/Al_2O_3=30-50 and 36-48 h. In all samples the concentration of non-acidic hydroxyl groups (silanol groups) is much higher than could be accounted for by the number of terminal hydroxyls on the external surface of the crystallites. In the H-form of the zeolites the number of acidic OH groups is equal to the number of framework aluminium atoms. We demonstrate that it is possible to synthesize defect-free zeolites of type ZSM-5 without an organic template.

The synthesis of pentasil zeolites is supported by organic cations. Argauer et al. (1) first described syntheses with tetraalkylammonium and tetraalkylphosphonium compounds. The organic cations may not only initiate and sustain a certain crystallization process but also may lead to products of a new structure. This "templating" behaviour is explained by the structure-directing effect of the organic cations in the process of crystallization (2,3).

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In the past numerous syntheses were described using compounds which were assumed to possess this templating property. A few references are given in Table I, beginning with the classic templates, going to more simple molecules and ending with the template-free synthesis. A group-specific arrangement is presented in Table II.

Table I. Organic compounds, which were mostly used in syntheses of zeolites of pentasil-type. Abbreviations are TPA^+ for tetrapropylammonium cation, $TEPA^+$ for triethylmonopropylammonium cation, TBA^+ for tetrabutylammonium cation, TBP^+ for tetrabutylphosphonium cation, TPA for tripropylamine and C_6DN for hexamethyldiamine

Product	Group of compounds	Preferred comp.	References
ZSM-5	tetraalkylammonium cation	TPA^+	(1,4,5)
		$TEPA^+$	(6,7)
	trialkylamine and alkylhalogenide	TPA and propylchloride	(8-11)
ZSM-11	tetraalkylammonium or	TBA^+	(12)
	tetraalkylphosphonium cation	TBA^+, TBP^+	(5)
ZSM-5 like	alkanolamine	$NH_2CH_2CH_2OH$	(13-15)
	diamine	C_6DN	(16)
	mono-n-alkylamine	propylamine	(17-19)
	alcohols and ammonia	C_4H_9OH	(20)
	alcohols	C_4H_9OH	(21)
	template-free		(22,23)

Table II. The different types of organic compounds, which can be used for the syntheses of pentasil zeolites

Type	Examples	References
organic cations	R_4N^+, R_4P^+	(1,4,5,7)
	polymeric cationic compound	(24)
organic molecules	diamine	(16)
	amine	(17-19)
	alcohols	(20,21)
	dioxane	(25)
	2-aminopyridine	(26)
organic anions	alkylbenzolsulfonate	(27)
	polymeric anionic compound	(28,29)

In consideration of the fact that even a template-free synthesis is possible it is not easy to understand that all different groups of compounds should have the same structure-directing effect. For a more plausible explanation we must consider the reaction mixture as a whole and discuss the combined effects of all components. Table III is an attempt to systematize the effects of different components.

Table III. The influence of the relative (referred to SiO_2) amount of different compounds of the reaction mixture upon the properties of the reaction mixture and of the product

Molar ratio	Properties
Al_2O_3/SiO_2	composition of the network
H_2O/SiO_2	viscosity, concentration of hydroxyde ions
OH^-/SiO_2	molecular weight of silicates, conc. of hydroxide ions
Na^+/SiO_2)	
R_4N^+/SiO_2)	cation distribution, templating effect, Al-content

To draw conclusions concerning the templating effect of different molecules, comparable conditions for the crystallization process must be used. In this paper we present a systematic investigation on the effect of mono-, di- and tri-n-alkylamine and tetraalkylammonium compounds (alkyl = C_1 - C_4) upon the rate of crystallization, yield and the properties of the products. Also the field of a template-free synthesis is studied. The products were characterized by magic-angle-spinning nuclear magnetic resonance spectroscopy (MAS NMR) and X-ray diffraction.

Experimental

The template containing samples were synthesized using a procedure based on those given by Union Carbide (30). The batch composition expressed in mole ratios was as follows:

$$1\ R_2O * 4.1\ Na_2O * 50\ SiO_2 * 0.417\ Al_2O_3 * 691\ H_2O$$

with R = C_iN, $(C_i)_2N$, $(C_i)_3N$, $(C_i)_4N^+$ and C_i = C_1-C_4 = methyl-butyl.

Some of the samples were synthesized without Al_2O_3. The syntheses with tetrapropylammonium iodide ($TPA^+ I^-$) as template were carried out with a varying SiO_2/Al_2O_3 ratio in the range 25 - 400. The batch composition of the template-free synthesis was

$$4\ Na_2O * 1\ Al_2O_3 * x\ SiO_2 * 1200\ H_2O$$

where x varies from 10 to 100.

Sodium silicate, sodium aluminate and NaOH were obtained from VEB Chemiekombinat Bitterfeld. The organic templates were guaranteed reagents. At first NaOH was diluted in water and then sodium silicate and sodium aluminate in liquid or diluted form were added under stirring. Afterwards, the organic compound was added under vigorous stirring. The obtained mixture was stirred for further 15 min, and then distributed over several autoclaves in portions of 50 cm^3 per autoclave. The crystallization was conducted in a furnace at 175 °C. The reaction vessels were placed on rotating shafts. After the time of crystallization the autoclave was quickly cooled down. The products were filtered, washed and dried at 100 °C. The procedure of the template-free synthesis was different in only one point: To the diluted aqueous solution of sodium silicate the sodium aluminate was added.

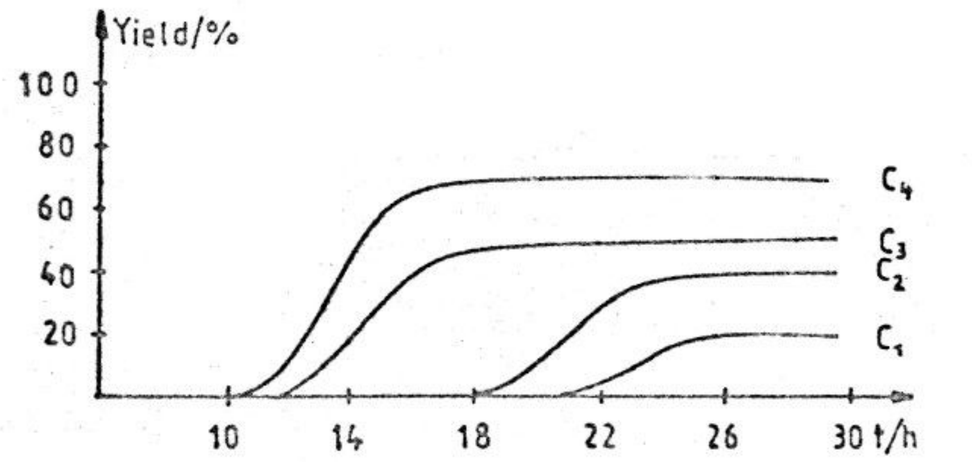
The synthesized samples were analyzed by X-ray powder diffraction for qualitative and quantitative phase identification. The unit used was a Philips Model with a vertical goniometer and a scintillation counter, utilizing Ni-filtered CuK_α radiation. For quantitative phase identification an external standard sample of α-Al_2O_3 was used. The percentage crystallization was calculated using the averaged peak intensities at 2Θ=35.2° and 2Θ=47.3° of the reference sample, and the peak intensity at 2Θ=23.2° for the sample under study (31).

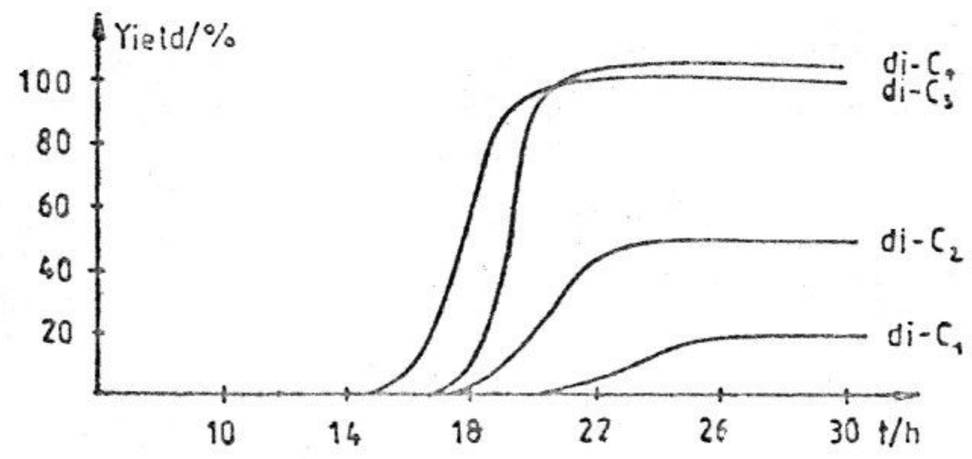
X-ray and aluminium MAS NMR measurements were carried out on samples rehydrated in a desiccator over an aqueous NH_4Cl solution. A portion of the zeolites synthesized with organic templates was heated for 5 h at 600 °C to remove organic compounds. The Na^+/H^+ ion exchange was carried out at room temperature with an aqueous solution of 0.5 N HCl. The preparation of ^1H MAS NMR samples was performed under shallow bed activation conditions in a glass tube of 5.5 mm inner diameter and 10 mm height of the zeolite layer. The temperature was increased at a rate of 10 K/hr. After maintaining the samples at the final activation temperature of 400 °C under a pressure below 10^{-2} Pa for 24 hrs., they were cooled and sealed.

NMR measurements were performed on a home-made spectrometer HFS 270 and on a BRUKER spectrometer MSL 300. As a reference for intensity measurements of the aluminium NMR a well-characterized sample of ZSM-5 with a framework Si/Al-ratio of 15 was used. The total concentration of OH groups in the activated samples was determined by comparison of the maximum amplitude of the free induction of the samples with those of a capillary containing an aqueous solution in a probe with a short ring-down time. To separate the relative intensities of different lines in an ^1H MAS NMR spectrum quantitatively, the signals of the spinning side bands were added to the main signal. The home-made MAS equipment for the rotation of the fused glass ampoules was carefully cleaned to avoid spurious proton signals.

Results and Discussion

Synthesis. Figure 1 shows the crystallization of template-containing zeolites as a function of time. The aluminium-free syntheses using TEA^+, TPA^+ and TBA^+ as template give products with pentasil structure (silicalite I or II) without other phases. TMA^+ and all other amines mentioned above yield in the aluminium-free syntheses as the first crystalline phase only magadiite, an aluminium-free sheet silicate. The aluminium containing syntheses give different phases with pentasil structure, sheet structure and an amorphous phase. Table IV presents the maximum percentage crystallization of the pentasil phase. The value of about 100% for TEA^+, TPA^+, TBA^+, di-and tri-n-propylamine and di- and tri-n-butylamine proves that these syntheses yield only the pentasil phase. X-ray diffraction analysis shows that TPA^+ and TBA^+ lead to the ZSM-5 and ZSM-11 structure type, respectively. Figure 2 shows a comparison of the X-ray diffraction patterns. The most intense diffraction lines occur at 2Θ=20°-27°. Going from the tetraalkylammonium to the alkylamine compounds a splitting of the 23.2° line can be observed. The form of the splitted line seems to be typical for the template. Similar patterns have been measured for the following zeolites of pentasil type (32): NU-5 (EP 54 386), ZSM-8 (NL 7 014 807) and ZETA-1 (DE 2 548 695). It is not clear whether the





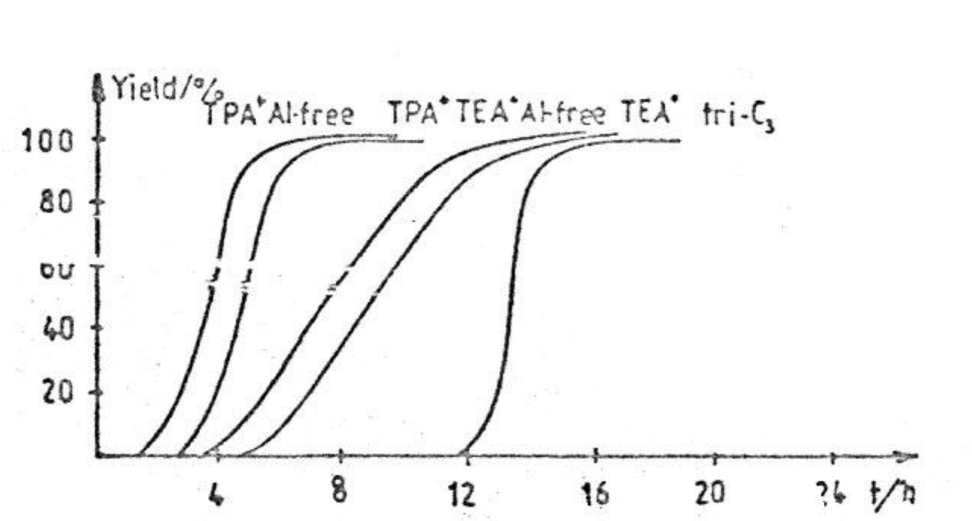


Figure 1. Yield of pentasil zeolites (percentage crystallization) as a function of time. Abbreviations are C_4 for mono-n-butylamine, C_3 for mono-n-propylamine, C_2 for mono-n-ethylamine, C_1 for mono-n-methylamine, di-C_4 for di-n-propylamine, di-C_3 for di-n-propylamine, di-C_2 for di-n-ethylamine, di-n-C_1 for di-n-methylamine, TPA^+ Al-free for the aluminium-free synthesis with the tetrapropylammonium cation, TPA^+ for tetrapropylammonium cation, TEA^+ Al-free for the aluminium-free synthesis with the tetraethylammonium cation, TEA^+ for tetraethylammonium cation and tri-C_3 for tri-n-propylamine.

Table IV. The yields of syntheses measured in mass% of crystalline pentasil in dependence on the template. The experimental error is about ±10%

Template	methyl	ethyl	propyl	butyl
mono-n-alkylamine	21	40	50	70
di-n-alkylamine	20	55	100	100
tri-n-alkylamine	11	77	106	101
tetraalkylammonium cation	23	90	100	103

patterns are due to a special phase or due to an intergrowth ZSM-5/ZSM-11, cf. (33,34).

Magadiite apart from pentasil phases can be found in zeolites synthesized with mono-n-methyl-, -ethyl-, -propyl- or -butylamine, with di-n-methyl-, -ethyl- or -propylamine, with tri-n-methyl- or -ethylamine and with tetramethylammonium iodide. Table IV shows that the zeolite content increases with the number of carbon atoms per group and with the number of alkyl groups.

Values describing the kinetics of crystallization with organic compounds are presented in Table V. Figure 3 shows how the values t_o = induction period, t_g = period of growth and k = percentage crystallization per hour can be determined from the curves presented in Figure 1. Aluminium decelerates the synthesis as can be shown by comparison of the aluminium-containing and the aluminium-free syntheses using TPA^+ and TEA^+ as template. Compounds containing the propyl group give the best structure directing effect and among them the shortest induction period has beeen found for TPA^+ and the maximum crystallization rate for tri-n-propylamine.

Table V. The induction period t_o, the period of growth t_g, the crystallization rate k (percentage crystallization per hour) and the maximum percentage crystallization (mpc) in dependence on the different templates used in pentasil syntheses

Template	t_o (h)	t_g (h)	k (% h^{-1})	mpc (%)
mono-n-methylamine	20.8	3.5	6	21
mono-n-ethylamine	18.8	4.2	10	40
mono-n-propylamine	12.7	3.6	14	50
mono-n-butylamine	11.8	3.2	22	70
di-n-methylamine	21.0	4.1	5	20
di-n-ethylamine	18.8	2.9	19	55
di-n-propylamine	16.0	2.2	46	100
di-n-butylamine	18.5	2.0	50	100
tri-n-propylamine	13.2	0.9	118	106
TEA^+	6.0	4.0	24	98
TPA^+	4.3	1.0	100	100
TEA^+ (Al-free)	5.2	4.2	25	104
TPA^+ (Al-free)	3.0	0.5	216	108

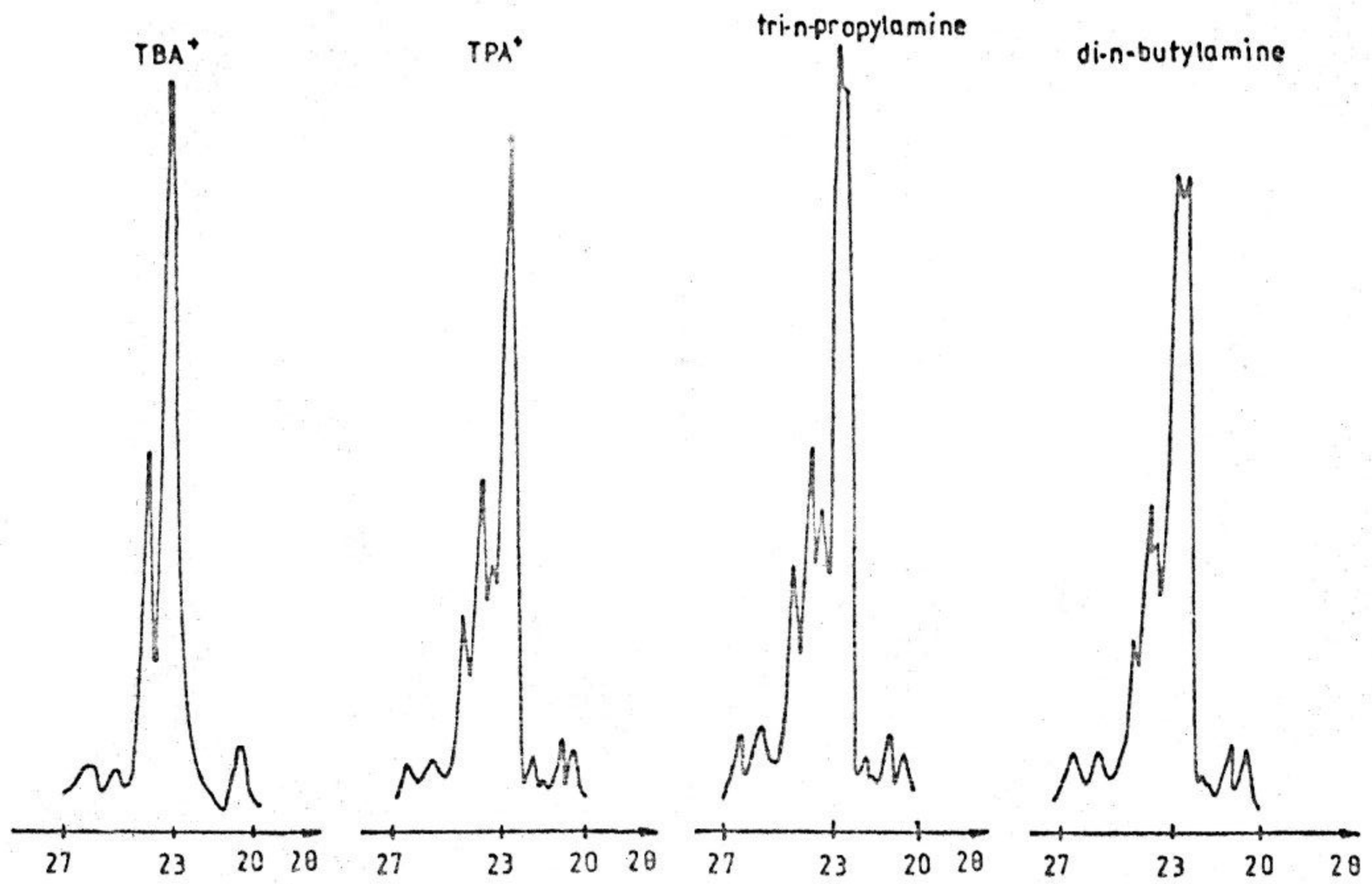


Figure 2. X-ray diffraction patterns.

Figure 4 presents the isothermal phase transformation diagram of the template-free syntheses in which the SiO_2/Al_2O_3 ratio and the time t of crytallization are varied. The SiO_2/Na_2O^3 and H_2O/SiO_2 ratios are 10 and 30, respectively. The pentasil phase could only be synthesized for n = SiO_2/Al_2O_3 = 30 - 50 and t = 36 - 72 h. Outside of this area amorphous material, mordenite, sheet structures similar to kenyaite, quartz and crystobalite can be found. For values of n less than 25 the crytalline product is mordenite. For 30 < n < 50 a yield of 95% (related to the SiO_2 content) ZSM-5 type, which was proved by X-ray diffraction pattern, could be found. Depending on n and the crystallization time, t, a more or less large amount of amorphous material is produced. This is shown in Figure 5. A long crystallization time causes recrystallization and is harmful to the yield of ZSM-5 products.

The influence of the compounds in the crystallization mixture upon the morphology of crystallites is illustrated by the scanning electron micrographs presented in Figures 6-8. Figure 6 shows that in the aluminium-free syntheses TPA^+ gives spherical crystallites with a diameter of 2-3 µm and TEA^+ gives rhombic crystallites with sizes of about 1x2x5 µm. Figure 7 demonstrates the influence of the SiO_2/Al_2O_3 ratio on the morphology. With increasing ratio the size and the smoothness of the crystallites increase. The template-free synthesized zeolites with a SiO_2/Al_2O_3 ratio of 30 show flaking surfaces (see Figure 8).

In conclusion the syntheses performed in this work show:
- The real structure directing effect is caused by the TEA^+, TPA^+, and TBA^+ cations. These cations cause the structure directing effect also in the aluminium-free syntheses.
- Amines support the synthesis of aluminium containing pentasils in dependence on their number of carbon atoms.
- A template-free synthesis can be performed in a limited range of the SiO_2/Al_2O_3 ratio. Based on these results a zeolite of pentasil-type is industrially produced by Chemiekombinat Bitterfeld, GDR.

NMR-characterization. Corbin et al. (35) were able to show by a systematic study that ^{27}Al MAS NMR gives the true Si/Al ratio with a mean error of 10 %, if two conditions are met: a) The amount of paramagnetic species is less than 0.05 % and b) the sample does not contain "NMR-invisible" aluminium. Chemical analyses of the samples under study showed that condition one is fulfilled. If samples contain "NMR-invisible" aluminium a difference between the concentration determined by chemical analysis and the framework aluminium concentration determined by NMR should be observed. From the absence of such a difference we conclude that "NMR-invisible" aluminium species do not exist in our samples. Also a line at the position of about 0 ppm due to octahedrally coordinated non-framework aluminium and a broad line at about 30 ppm due to tetrahedrally coordinated non-framework aluminium (36) could not be observed. The values for the concentration of framework aluminium atoms derived from the intensities of the line at about 60 ppm (see below) are in good agreement with those corresponding to the amount of alumina used in the synthesis mixtures. In conclusion, through the ^{27}Al MAS NMR measurements it was possible to show that all aluminium atoms are incorporated in tetrahedrally oxygen coordinated framework positions.

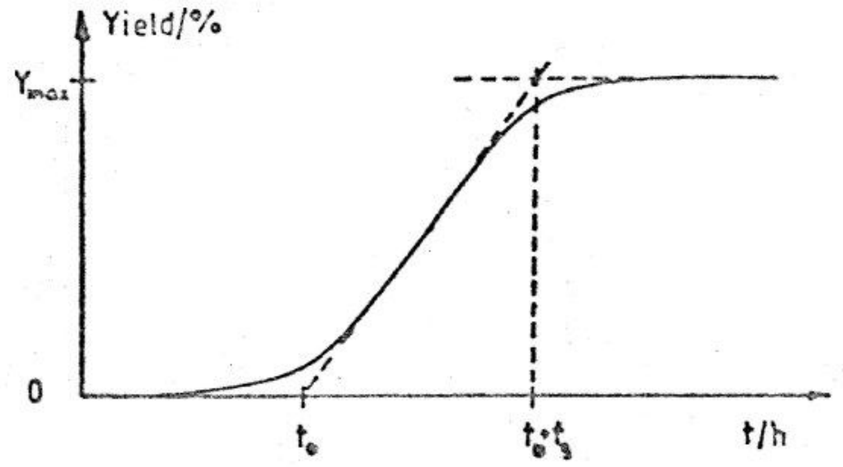


Figure 3. Crystallization as a function of time. t_o denotes the induction period, t_g the period of growth and the rate of crystallization, k, can be calculated using the maximum percentage crystallization, Y_{max}, by $k = Y_{max}/t_g$.

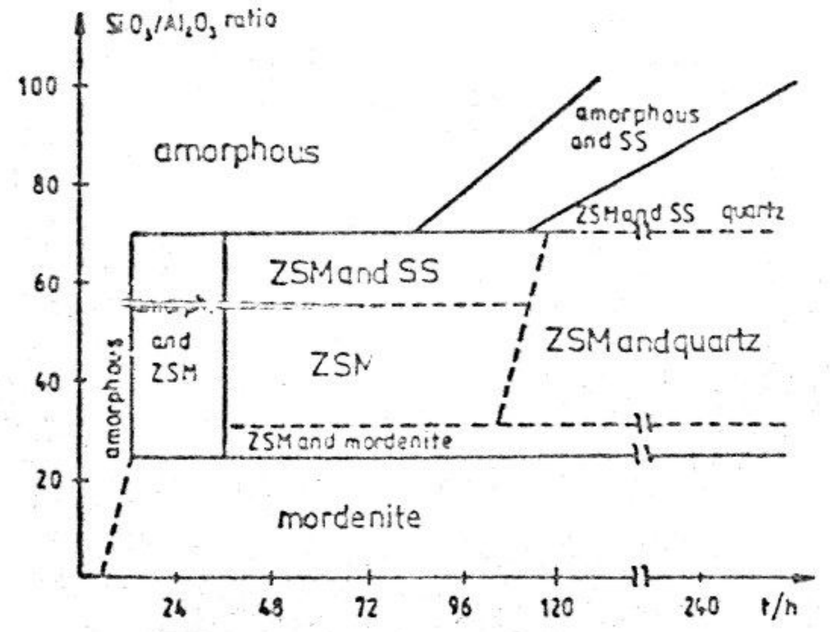


Figure 4. Isothermal phase transformation diagram of the template free syntheses. SS denotes sheet structures.

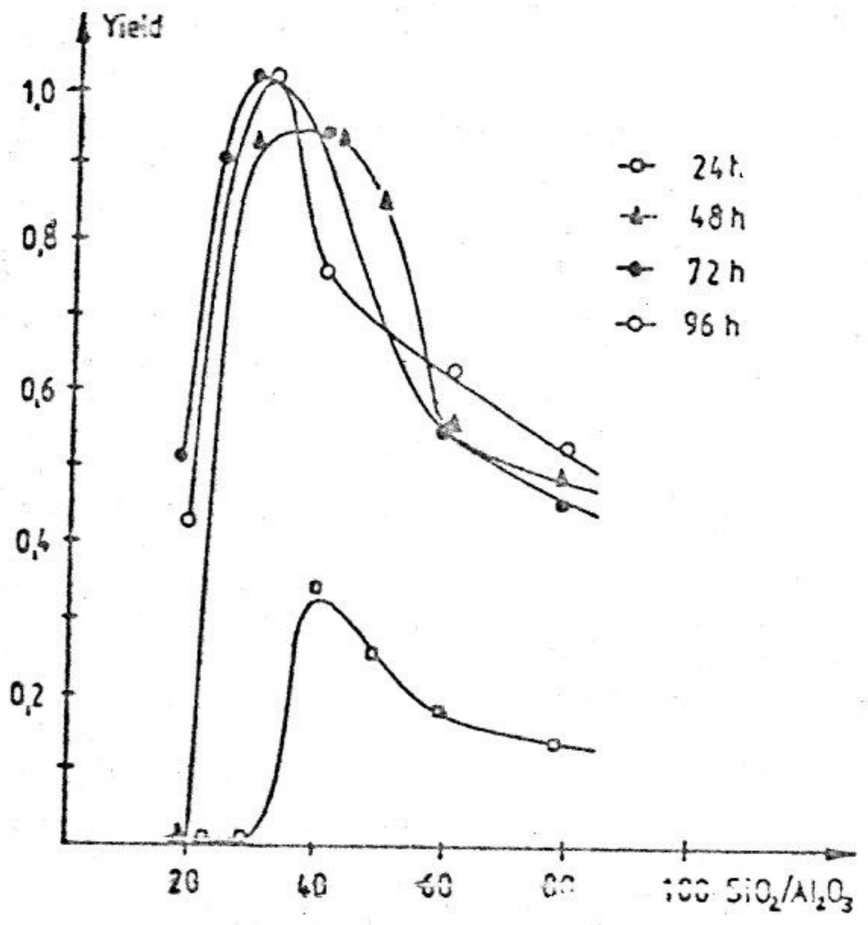


Figure 5. Yield of pentasil zeolites as a function on the SiO_2/Al_2O_3 ratio for different crystallization times.

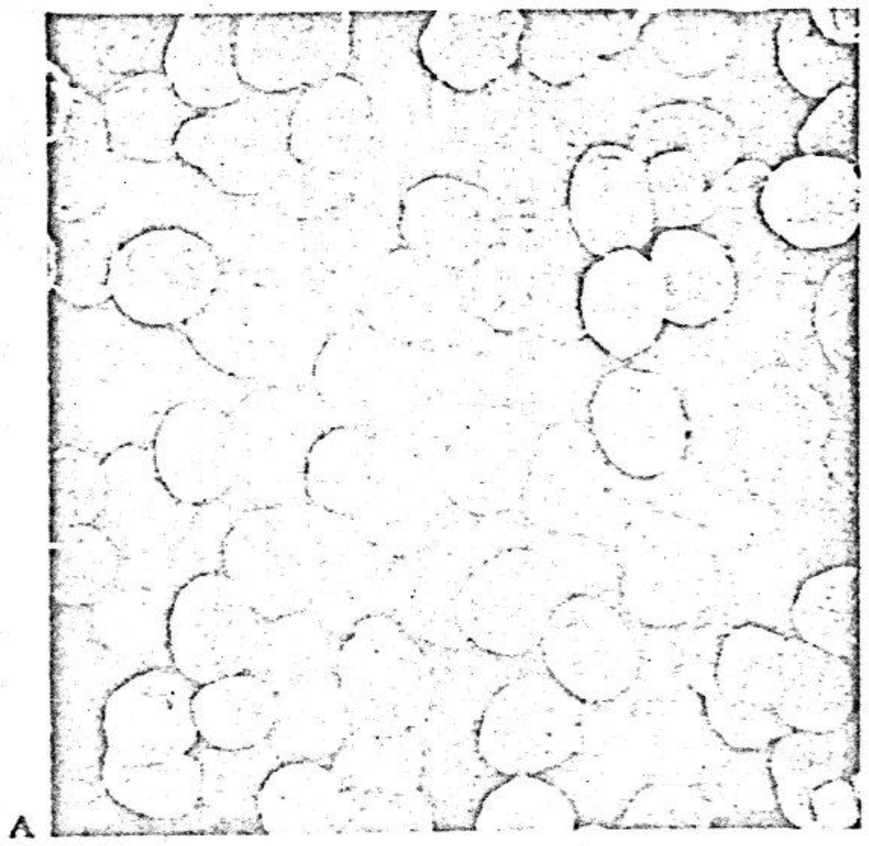


Figure 6. Scanning electron micrographs of the products of the aluminium-free syntheses with TPA^+ (A) and TEA^+ (B) as template. (3000 x)

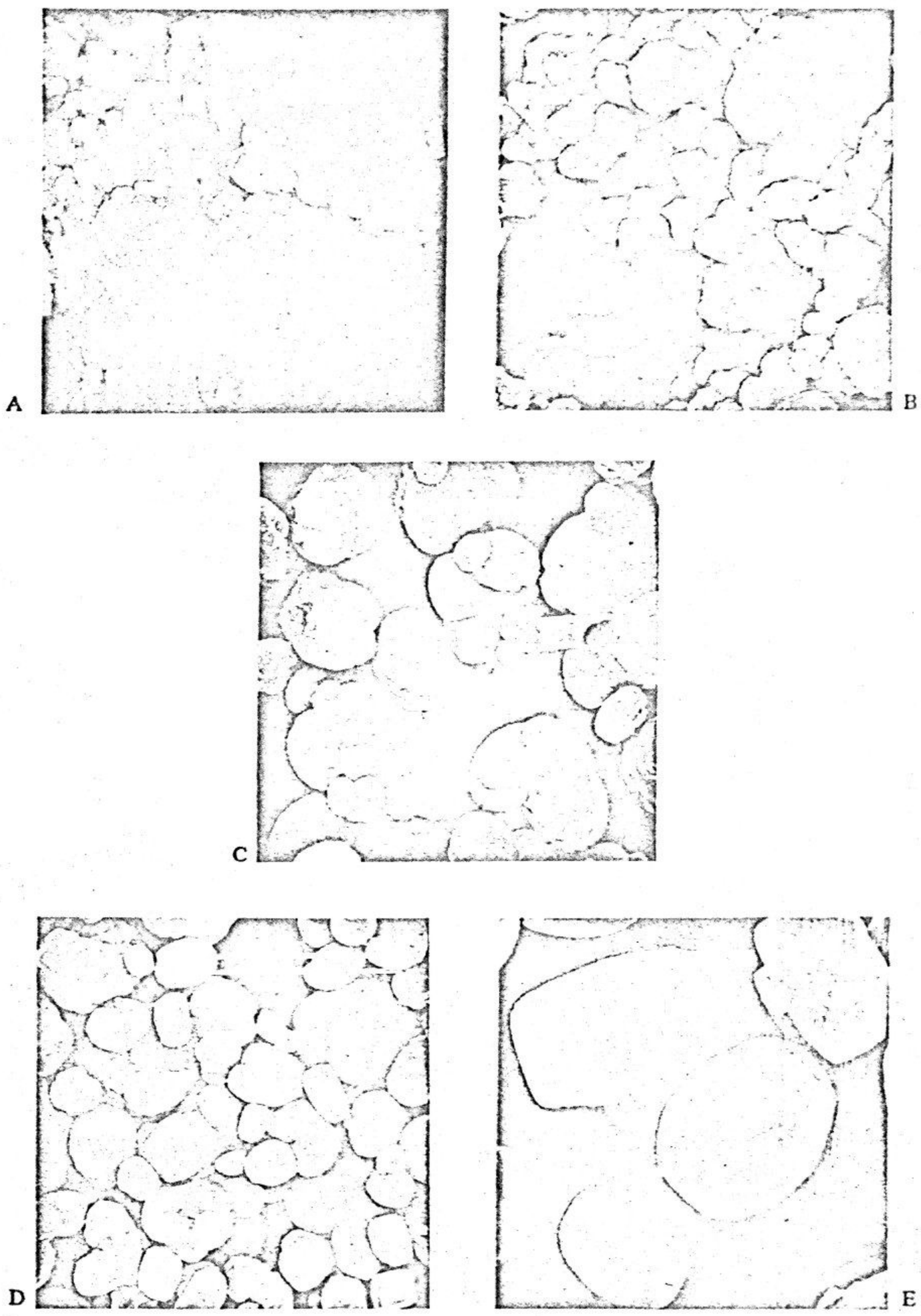


Figure 7. Morphology of pentasil zeolites synthesized with TPA^+ as template in dependence on the SiO_2/Al_2O_3 ratio of 25 (A), 50 (B), 100 (C), 200 (D) and 400 (E). (5000x)

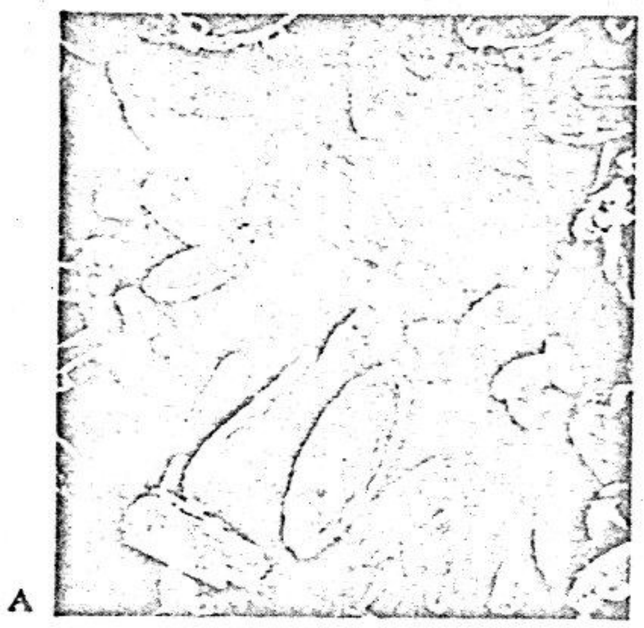


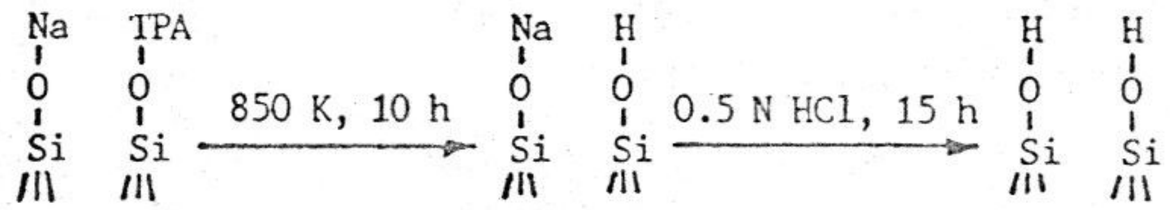
Figure 8. Scanning electron micrographs of the products of the template-free syntheses performed at 175 °C (A) and 200 °C (B). (8000x)

The line width of the corresponding ^{27}Al MAS NMR signal is determined by second-order quadrupole interaction. That means, it is determined by the deviation from the ideal tetrahedral symmetry of the AlO_4 units. The highest degree of symmetry resulting in a line width of 7±1 ppm (at 6.3 T) is observed for the pentasil phase. The quartz phase, mordenite and the amorphous phase gave line widths of 9 ppm, 14 ppm and 18 ppm, respectively. The shift of the centre of gravity of the lines with respect to the resonance position of the aluminium-hexaaquo complex is 47-56 ppm. Taking into account the quadrupole correction for the shift, which has a maximum value equal to the line width (37) a chemical shift of ca. 60 ppm results for all lines.

Therefore, through a measurement of the chemical shift of the ^{27}Al MAS-NMR line it is not possible to distinguish between different phases in the product. The amorphous and the crystalline phases give a difference only in the line width.

^{1}H MAS NMR spectra are presented in Figure 9. Two different signals can be seen in the spectra of the hydrogen forms. Line (a) at 2 ppm is due to non-acidic hydroxyl groups (silanol groups) at the outer surface of zeolite crystallites, at framework defects and in the amorphous part of the sample. Line (b) at 4.3 ppm is caused by bridging (acidic) OH groups (38). Further lines due to different types of acidic OH groups or AlOH groups on non-framework aluminium species (38), could not be observed in these spectra. Values for the concentration of framework aluminium atoms and of the hydroxyl protons giving rise to lines (a) and (b) are presented in Tab. 6. The number of terminal OH groups per gram of dried zeolite, n_T, is calculated by $n_T = 0.12 \times 10^{20} d^{-1}$, where d denotes the diameter of the crystallites (μm).

The intensities of line (a) in Table VI show that for all specimens the values for the concentration of SiOH groups are much greater than the values obtained from a calculation of the number of terminal OH groups. The extremely high concentration of silanol groups observed for TPA^+/ZSM-5 zeolites is in accordance with our previous findings (38,39). The number of these SiOH groups is larger, by a factor of up to 1000, than the number which is necessary to terminate the external crystal surface. From the absence of amorphous material (within the accuracy of the X-ray measurements) it follows that up to 8% of the framework Si are present as SiOH groups. This means, that the ZSM-5 synthesis with TPA^+ as template leads to a highly disturbed lattice with a high concentration of non-intact Si-O-Si bonds. The enhanced concentrations of SiOH groups in the hydrogen form of the zeolites indicate that, after sample calcination, about half the defect sites are present as Si-O-Na, the other half being present as internal silanol groups. The treatment with 0.5 N HCl leads to the exchange of Na^+ cations on the defect sites with H^+, thus forming a maximum number of silanol groups. This behaviour can be explained (36) by the following reaction scheme of a defect site:



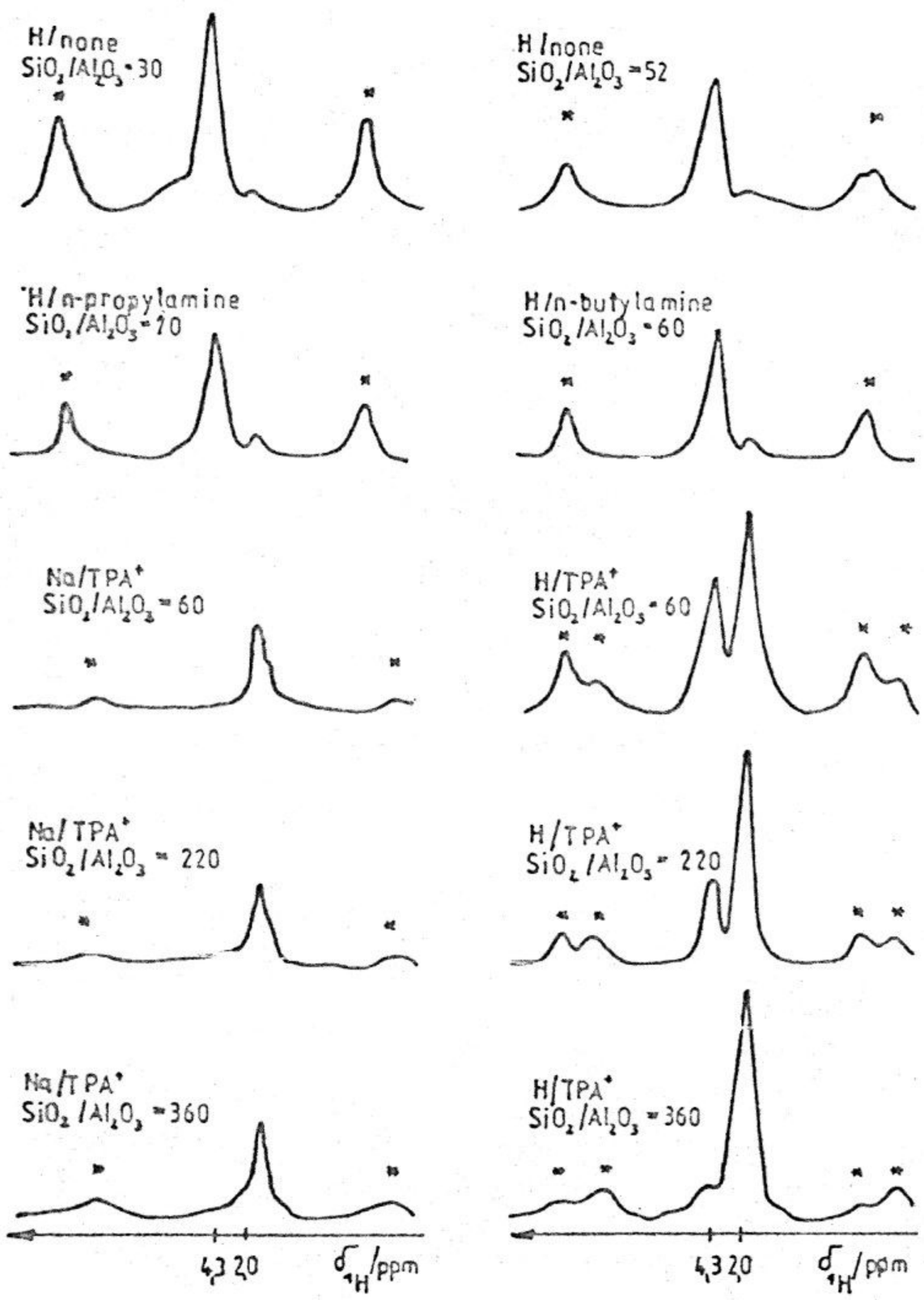


Figure 9. ^{1}H MAS NMR spectra. * denotes spinning sidebands.

Table VI. Concentrations of hydroxyl species and framework aluminium atoms in the hydrogen (H) or sodium (Na) form of pentasil zeolites synthesized with different organic templates and without organic templates

Form/Template	Crystallite diameter (μm)	SiO_2/Al_2O_3 ratio	Concentration (10^{20} species per gram) Protons, line (a)	Protons, line (b)	Framework Al atoms
H/none	3.2	30	0.6	4.9	5.8
H/none	3.0	52	0.5	3.2	3.6
H/mono-n-propylamine	1.2	70	0.4	3.2	2.7
H/mono-n-butylamine	1.1	60	0.5	3.5	3.2
Na/TPA$^+$	1.7	60	1.5	0.0	3.2
H/TPA$^+$	1.7	60	3.7	3.5	3.2
Na/TPA$^+$	1.5	220	1.3	0.0	0.9
H/TPA$^+$	1.5	220	3.6	1.2	0.9
Na/TPA$^+$	2.1	360	1.6	0.0	0.6
H/TPA$^+$	2.1	360	3.8	0.5	0.6

Since a hydrothermal treatment at 1100 K for 5 days leads to a healing of the zeolitic framework, most of the internal SiOH groups must be vicinal: Neighbouring framework defects (vicinal SiOH groups) are transferred via dehydration into intact Si-O-Si bonds (36).

By contrast, ZSM-5 specimens from organic-free batches and those synthesized by n-butyl- and n-propylamine possess relatively intact lattices with only a small concentration of internal silanol groups (see Figure 9 and Table VI).

Concerning the concentration of Brönsted sites (acidic bridging OH groups) we found that for the hydrogen form of the zeolites the number of bridging hydroxyl groups is in good agreement with the number of framework aluminium atoms.

Literature Cited

1. Argauer, R. J.; Landolt, G. R. U.S. Patent 3 702 886, 1972.
2. Flanigen, E. M. Adv. Chem. Series 1973, 121, 119.
3. Rollmann, L. D. Adv. Chem. Series 1978, 173, 176.
4. Dwyer,Y. N.; Jenkins, E. E. U.S. Patent 3 941 871, 1976.
5. Chen, Y. N.; Miale, N. J.; Readan, J. W. U.S. Patent 4 112 056, 1978.
6. Kalkarmi, S. B.; Shitalkar, V. B.; Katasthane, A. N.; Borade, R. B.; Datunasamg, P. Zeolites 1982, 2, 133.
7. Borade, R. B.; Chandrankar, A. J.; Kulkarni, S. B.; Ratasany, P. Indian. J. Technol. 1983, 21, 358.
8. Schwartz, A. B. Patent BP 1 365 318, 1974.
9. Rollmann, L. D. Patent DE 2 817 577, 1978.
10. Dwyer F. G.; Klocke, D. J. Patent DE 2 822 725, 1978.
11. Gabelica, Z.; Derouane, E. G. ACS Symp. Ser. 1985, 248, 219
12. Chu, P.; Woodbury, N. J. U.S. Patent 3 709 979, 1973.
13. Ball, W. J.; Palmer, V. W.; Stewart, P. G. Patent EP 2900, 1979.

14. Ball, W. J.; Palmer, V. W.; Stewart, P. G. Patent EP 2899, 1979.
15. Ball, W. J.; Palmer, V. W.; Stewart, P. G. U.S. Patent 4 346 021, 1982.
16. Rollmann, L. D. U.S. Patent 4 108 881, 1978.
17. Rubin, M. V.; Rosinski, E. J.; Plank, Ch. J. Patent DE 2 442 240, 1975.
18. Rubin, M. V.; Rosinski, E. J.; Plank, Ch. J. U.S. Patent 4 151 189, 1979.
19. Bremer, H.; Reschetilowski, W.; Son, D. Q.; Wendland, K.-P.; Nau, P.-N.; Vogt, F. Z. Chem. 1981, 21. 77.
20. Post, M. F. M.; Nanne, J. M. Patent DE 2 913 552, 1979.
21. Post, M. F. M.; Nanne, J. M. Can. Pat. 1 135 679, 1982.
22. Roscher, W.; Bergk, K.-H.; Pilchowski, V.; Schwieger, W.; Wolf, F.; Fürtig, H.; Hädicke, U.; Höse, W.; Krüger, W.; Chojnacki, K.-H. Patent DD-WP 207 186, 1984.
23. Roscher, W.; Bergk, K.-H.; Pilchowski, V.; Schwieger, W.; Wolf, F.; Fürtig, H.; Hädicke, U.; Höse, W.; Krüger, W.; Chojnacki, K.-H. Patent DD-WP 207 185, 1984.
24. Kerr, G. T.; Rollmann, L. D. Patent DE 2 705 436, 1978.
25. Klotz, M. R. U.S. Patent 4 377 502, 1983.
26. Whittam, T. V. Patent EP 59359, 1982.
27. Hugiwara, H.; Kiyozumi, Y.; Kurila, M.; Sato, T.; Shimudu, H.; Szuki, K.; Shin Ch. Chem. Letters 1981, 11, 1653.
28. Roscher,W.; Bergk, K.-H.; Pilchowski, V.; Schwieger, W.; Wolf, F.; Fürtig, H.; Hädicke, U.; Höse, W.; Krüger, W.; Chojnacki, K.-H. Patent DD-WP 207 184, 1984.
29. Lowe, B. M.; Aroya, M. Patent EP 77624, 1983.
30. Grose, R. W.; Flanigen, E. M. U.S. Patent 4 061 724, 1977.
31. Bergk, K.-H.; Schwieger, W. Abstr. Internat. Conf. on Zeolites, Portoroze, 1984.
32. Jacobs, P.; Martens, A. I. A. In Synthesis of Highsilica Aluminosilicate Zeolites; Dellmann B. and Yales, I. T. Eds.; Studies in Surface Science and Catalysis, Vol. 35, Elsevier (1987).
33. Kokotailo, G. T.; Meier, W. M. Chem. Soc. Spec. Publ. 1980, 33, 13
34. Koningsveld, H. van; Jansen, J. C.; Bekkum, H. van Zeolites 1987, 7, 564.
35. Corbin, D. R.; Burgess, B. F.; Vega A. J.; Farlee, R. D. Analytical Chemistry 1987, 59, 2722.
36. Hunger, M.; Kärger, J.; Pfeifer, H.; Caro, J.; Zibrowius, B.; Bülow, M.; Mostowicz, R. J. Chem. Soc., Faraday Trans.I, 1987, 83, 3459.
37. Freude, D.; Haase, J.; Klinowski, J.; Carpenter, T. A.; Ronikier, G. Chem. Phys. Letters 1985 119, 365.
38. Freude, D.; Hunger M.; Pfeifer, H. Proceedings of the Fourth International Symposium on Magnetic Resonance in Colloid and Interface Science, Münster, July 1986; Z. Physik. Chem. NF 1987, 152, 171.
39. Hunger, M.; Freude, D.; Fröhlich, T.; Pfeifer, H.; Schwieger, W. Zeolites 1987, 7, 108.

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