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A CROSS-POLARIZATION MAGIC-ANGLE-SPINNING ^{29}Si-n.m.r. IDENTIFICATION OF THE SILANOL GROUP RESONANCE IN ZSM 5 ZEOLITES

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A small intensity and rather broad resonance is sometimes observed at ca. - 103 ppm in the high resolution solid state ^{29}Si-n.m.r. spectra of ZSM 5 zeolites. Cross polarization experiments, using the occluded tetrapropylammonium species and adsorbed water or n-hexane as the pool for protons, enable the unambiguous assignment of this resonance to silanol groups. Those are possibly associated to the presence of defects in the zeolite lattice.

High-resolution magic-angle-spinning (HRMAS) solid state ^{29}Si-n.m.r. has recently demonstrated its potentiality in the investigation of zeolites. Silicon-aluminum orderings have been discussed for zeolite type-A [1,2] and assessed for faujasite-type zeolites [3,4] with varying degrees of dealumination. Structural information was inferred from the ^{29}Si-n.m.r. spectra for both zeolite type-A [1,2] and ZSM 5[5]. Recent work also evidenced that the position of the ^{29}Si-n.m.r. resonance was not only dependent on the number of aluminum T-atoms in the first cationic coordination sphere of Si [6] but also on the actual geometry of the T-O-T linkages (T = Al or Si) [7] and on longer range structural features such as the $(T\text{-}O)_n$ ($n = 4\text{-}6$) ring sizes to which the Si atom under consideration pertains [8]. For example, the configuration Si (0 Al) in ZSM 5 zeolites has chemical shifts in the -112 to -116 ppm range (from TMS), compared to ca.-106 ppm for faujasite-type structures. Most recently, the use of cross-polarization (CP) n.m.r. pulse sequences has enabled the obtention of proton-enhanced (PE) HRMAS-^{29}Si spectra which, in turn, provide unambiguous information on the silanol (≡ Si-OH) groups that are present in dealuminated faujasites [9]. The data analysis is based, in this case, on the selective enhancement of the n.m.r. lines corresponding to ^{29}Si nuclei in direct interaction with neighbouring protons. The latter technique is applied in the present paper to the identification of silanol groups in the ZSM 5 framework.

^{29}Si-n.m.r. spectra were obtained on a Bruker CXP-200 spectrometer operating in the Fourier transform mode. The ^{29}Si (39.7 MHz) and ^{1}H (200.0 MHz) r.f.-fields were 49.3 and 9.8 Oe respectively.

The CP-HRMAS spectra were recorded using a single contact sequence [10], the contact and the recycle times being 10.0 ms and 3.0 s respectively. Magic-angle-spinning (Delrin rotor) was at 3.1 kHz. Before Fourier transformation (4K data points), 2000 or 19000 free induction decays were accumulated for the normal or the CP-spectra respectively.

Figure 1 shows the spectra observed for two ZSM 5 materials of widely different Al-content (Si/Al = 34.0 and 235) , either before calcination in nitrogen to remove the occluded organic species (Na,TPA) or after calcination and rehydration in nitrogen at ambient-temperature (Na,H) or adsorption of n-hexane (Na,hex.). Normal spectra (fig. 1.a) are compared to CP-spectra (fig.1.b). The corresponding n.m.r. parameters are listed in table 1.

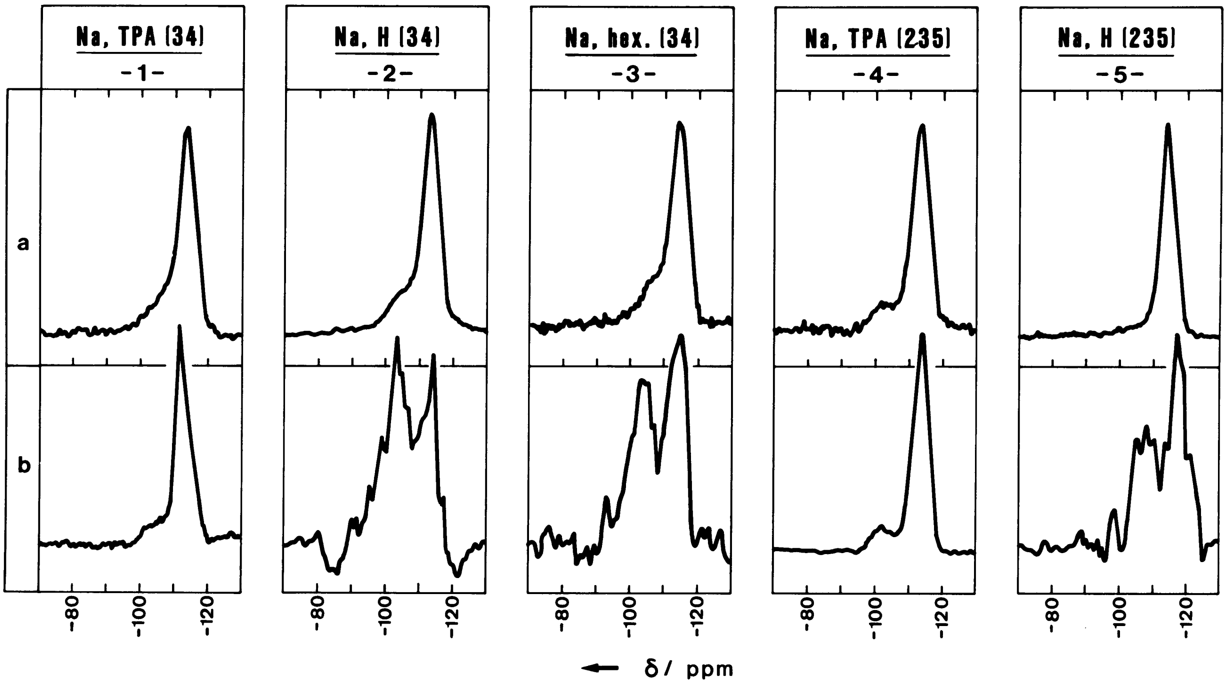

Figure 1. High resolution solid state ^{29}Si-n.m.r. spectra of various ZSM 5 zeolites. Upper spectra without (a), lower spectra with cross-polarization (b).

All spectra show essentially three resonances at ca.-103, -113, and -116 ppm respectively. No special effort was devoted to increasing the resolution in the -112 to -117 ppm range [5,11] as the attention was focussed on the behavior of the -103 ppm resonance.

A comparison of spectra 1 and 4 clearly indicates that this resonance is not due to a Si(1 Al) ordering as it is better resolved for decreasing Al content in the samples under investigation.

In addition, its contribution to spectrum 4 (ca. 15%) is too high to be explained by the presence of Al (less than 0.5%) and it is observed to depend on the thermal treatment of the zeolite. Si-OH groups in faujasite have a resonance at -101 ppm[9] and it is thus logical to assume that the -103 ppm resonance in zeolite ZSM 5 should be attributed to silanol groups.

Table 1. ^{29}Si-n.m.r. chemical shifts,relative (in brackets) and total line intensities in ZSM 5 zeolites

n° [a]	Sample [b,e]	Si/Al [c]	Si/Na [c]	δ^d(ppm) ÷ [I %]			I ($a.u.g^{-1}$)
1a	(Na,TPA) - ZSM 5	34	220	-102.1 [10]	-112.2 [75]	-116.6 [15]	173
1b	(Na,TPA) - ZSM 5			-102.4 [10]	-112.0 [80]	-117.0 [10]	193
2a	(Na,H) - ZSM 5	34	220	-102.4 [20]	-112.2 [70]	-116.4 [10]	228
2b	(Na,H) - ZSM 5			-101.7 [55]	-112.4 [45]	-	9
3a	(Na,hex.) - ZSM 5	34	220	-102.7 [15]	-112.7 [70]	-117.2 [15]	180
3b	(Na,hex.) - ZSM 5			-102.3 [45]	-113.1 [55]	-	16
4a	(Na,TPA) - ZMS 5	235	2000	-102.1 [15]	-112.4 [70]	-116.1 [15]	156
4b	(Na,TPA) - ZSM 5			-101.9 [15]	-112.2 [70]	-116.1 [15]	408
5a	(Na,H) - ZSM 5	235	2000	-102.6 [5]	-112.6 [70]	-115.8 [25]	337
5b	(Na,H) - ZSM 5			-103 [40]	-112.4 [60]	-	2

(a) a- normal MAS spectrum ; b- CP-MAS spectrum.

(b) (Na,TPA)-ZSM 5 precursors synthesized according to procedure B of ref.15 ; (Na,H)-ZSM5 zeolites obtained from precursors calcined in dry N_2 at 550°C for 14h ; (Na,hex.)-ZSM 5 samples prepared from the activated samples with N_2/n-hexane flow (P/P_0 = 0.18) at 20°C for 1h.

(c) Atomic ratios as determined by proton induced γ-ray emission[13].

(d) Chemical shift values referred to Me_4Si.

(e) $[H_2O]$/u.c. : 13 ± 0.5 (1a,b) ; 30 (2a,b) ; 5 ± 0.2 (4a,b) and ∿10 (5a,b) [14].

Little or no polarization transfer occurs in the non-calcined zeolite that has the lowest Si/Al ratio (Na,TPA;34) indicating that the available protons in the zeolite (from TPA and structural water) have no noticeable interaction with silicon. In contrast, the zeolite with low Al content (Na,TPA;235) showing a distinct resonance at -103 ppm, presents an enhancement of ca. 2.8, the relative peak intensities staying identical. Magnetization transfer hence takes place between ^{1}H and ^{29}Si probably because of the presence of the silanol groups and the additional presence of the proton pool from the TPA species. An explanation for the different behaviors of both systems should be searched for in two directions. Firstly, the high Si/Al ratio system contains clearly more terminal Si-O-R groups (R = H or Na, Na being eventually hydrated). Secondly, there should also be a difference in the binding mode of the TPA species to the zeolite framework. TPA certainly acts partly as a charge compensating and rather immobile cation in the first case (Si/Al = 34) and as a more labile organic neutral entity in the second one (Si/Al = 235).

Calcination of the precursors and their exposure to air at ambient temperature to yield the (Na-H)-forms, increases the resonance at ca. -103 ppm at the higher Al content but erases it at the lowest Al level. These observations can be understood by considering that framework defects in high silica content materials will be annealed at high temperature by successive T-jumps [12] whilst they can be formed in related conditions by Al-migration when the Al content is high enough. It is obvious from spectra 2a,b and 5a,b that cross-polarization drastically reduces the total spectral intensity and increases the relative intensity of the silanol group resonance at -103 ppm, thereby also confirming its assignment. Indeed, water molecules will be adsorbed preferentially on those specific adsorption centers. The adsorption of n-hexane is found to have a nearly similar effect. In this case however, the silanol resonance stays smaller than that of the other ^{29}Si nuclei. It is obvious from these data that water and n-hexane do contribute to the magnetization transfer from ^{1}H to ^{29}Si. The decrease in total spectra intensity probably finds its origin in the high mobility of protons in such structures. Further studies are necessary to assess exactly the influence of mobility and relaxation times on the line intensites.

Nevertheless, the present work has enabled the unambiguous assignment to silanol groups of the -103 ppm resonance that is sometimes observed in ZSM 5 type zeolites. It also demonstrates that lattice defects can be evidenced by ^{29}Si-n.m.r. more distinctly in the cross-polarization mode. A particularly striking example for this purpose is that of spectra 5a and 5b. Finally, there is some indication that one might obtain some information on the dynamics of the interaction between occluded/adsorbed molecules and the zeolite framework by monitoring relative and total spectra intensity changes.

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