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NOTE

Resolution Enhancement in the ^{29}Si MASS NMR Spectra of High Silica ZSM-5

Among the various techniques used, solid state NMR spectroscopy has emerged as an invaluable tool for characterization of zeolite (1). The NMR technique offers many new insights into the structural aspects of the three-dimensional tetrahedral framework as well as the interactions of sorbed organic molecules in the zeolite channels. Recently, two-dimensional (2-D) NMR techniques, complementary to X-ray methods, have been applied to high silica zeolites to establish three-dimensional lattice connectivities through scalar coupling interactions (J_{Si-Si}) (2). For the successful implementation of 2-D NMR methodology, the signal resolution of the observed ^{29}Si resonance in the 1-D magic angle sample spinning (MASS) spectrum has to be sufficiently high (line width 5 Hz or less) for the crystallographically inequivalent sites to be resolved without severe spectral overlap.

A major souce of line broadening in zeolites with low to moderate Si/Al (ca. < 50) is due to Al. This obscures the detection of various crystallographically distinct T sites in the ^{29}Si MASS spectra. Improvement of Si/Al by dealumination procedure does not always give rise to a highly resolved NMR spectrum because, although the Al broadening effects are removed, broadening due to other causes, such as crystal defects, remains. Synthesis and crystal growth conditions are expected to play an important role in the spatial organization of a defect-free high silica zeolite. The present work was undertaken to investigate these with a view to attain the highest possible resolution in the ^{29}Si MASS NMR spectra of a high silica zeolite (ZSM-5, silicalite-I) by comparing a number of silicalite-I samples synthesized differently.

A number of silicalite samples with MFI (ZSM-5) structure (3) were prepared by hydrothermal synthesis at 443 K for a gel composition of template: $SiO_2 : H_2O = 1 : 70 : 107$. The silica source (fumed silica (> 99.9%) and sodium trisilicate (Fluka, purum)), template (tetra propyl ammonium hydroxide (Aldrich, 99.9%) and tetra propyl ammonium bromide (Aldrich, 99.9%)), and period of crystallization (3–8 days) were varied. During crystallization, the mixture was stirred by shaking the bomb occasionally. The synthesis conditions of silicalite samples (a–d) are given in Table 1. The resulting zeolite crystals were washed thoroughly, dried at 353 K, and calcined in static air at 813 K for 6 h. The zeolite crystals were then treated with 0.1 *M* HCl at 333 K repeatedly three times to remove traces of amorphous mass, dried, and calcined at 813 K for 6 h in static air.

The XRD patterns of silicalite samples a–d (Fig. 1) were taken on a Philips 1730 powder diffractometer using Cu$K\alpha$ as the source of radiation. ^{29}Si MASS NMR spectra were recorded on a Bruker MSL-300 FT-NMR spectrometer at ambient probe temperature (294–297 K). Bloch decay signals were collected with a 45° flip angle, a 2-μ sec pulse and a 2-sec recycle time. Typically 10,000 transients were collected in a 14-kHz spectral window. The sample spinning was kept at around 2.5 kHz. No interfering effects of spinning side bands were seen. For ^{1}H–^{29}Si CP-MASS experiments, the Hartmann–Hahn match condition (4) was established using applied radio frequency fields of 40 kHz and a mixing time of 3 msec.

The powder X-ray diffraction patterns of silicalite I are shown in Fig. 1. The observed XRD patterns can be readily indexed to conform to the monoclinic form of ZSM-5 (5). Although one observes a small qualitative change in the XRD peak intensities in the $2\theta = 22$–$23°$ range, it is hard to obtain any information about the presence and nature of defect sites in the silicalite samples.

The Bloch decay ^{29}Si MASS NMR spectra of silicalite samples a–d synthesized differently (Table 1) are presented in Fig. 2. The progressive increase in NMR signal resolution is clearly indicated from a to d. The resolution of the ^{29}Si signal is greatest for sample d where the line width is typically 5 Hz. With this resolution, clear evidence of the multiplicity of ^{29}Si signals due to the different crystallographically nonequivalent T sites in the monoclinic structure ($P21/n$) is borne out. Considering the peak intensities, 24 distinct Si environments can be counted for sample d.

The ^{1}H–^{29}Si CP-MASS spectra for the silicalite samples are presented in Fig. 3. Two signals, one at -106 ppm and the second at -112 ppm, are identified as Q_3 and Q_4 [Si–O–Si] defect sites, respectively. The Q_2 [Si(OH)$_2$] defect site at -96 ppm is, however, less prominent (Fig. 3a). Since organic templates have been already removed by calcination, the CP enhancement is only by the hydroxyl protons. At a constant mixing time of 3 msec, the signal intensity for Q_4 and Q_3 defect sites is found to

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TABLE 1

Conditions of Hydrothermal Synthesis of High Silica ZSM-5 (Gel Composition, Template : SiO_2 : H_2O = 1.0 : 7.0 : 107; Temperature = 443 K)

Zeolite sample	Silica source	Template	pH of synthesis mixture	Period of crystallization (days)
a	Fumed silica	TPAOH	11.5	3.1
b	Na-trisilicate	TPAOH	11.8	3.2
c	Na-trisilicate	TPABr	11.0	3.1
d	Na-trisilicate	TPABr	11.0	8.0

decrease from sample a to d, giving rise to an inverse relationship between the number of defect sites detected by CP-MASS NMR and the ^{29}Si signal resolution obtainable in the 1-D MASS spectra. In fact, the number of defect sites detected by CP-MASS NMR is the smallest for sample d and has therefore offered the greatest signal resolution in its Bloch decay spectrum (Fig. 3d). These terminal silinol groups are not an integral part of an ordered three-dimensional tetrahedral framework. The lack of local structural ordering at these defect Si sites leads to a distribution of isotropic chemical shifts (6) for the various Si–O–Si bond environments, thus masking the fine signal resolution observable for the defect-free crystalline parts of the zeolite. This appears to be the main cause of signal broadening in ^{29}Si MASS NMR spectra of highly siliceous ZSM-5. It may also be noted for sample c that the various framework T sites are not resolved in the ^1H–^{29}Si CP-MASS spectrum (compare Figs. 2c and

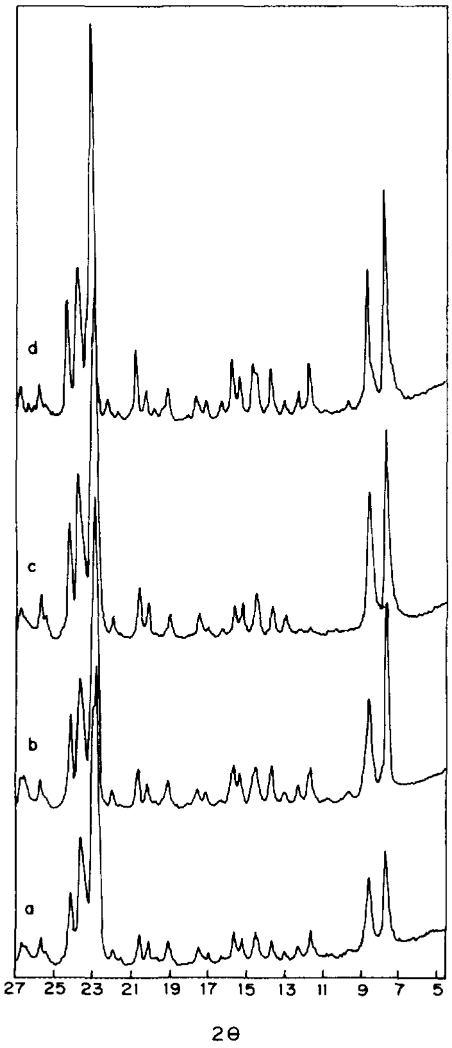

FIG. 1. XRD patterns for high silica ZSM-5 (silicalite I) samples a–d.

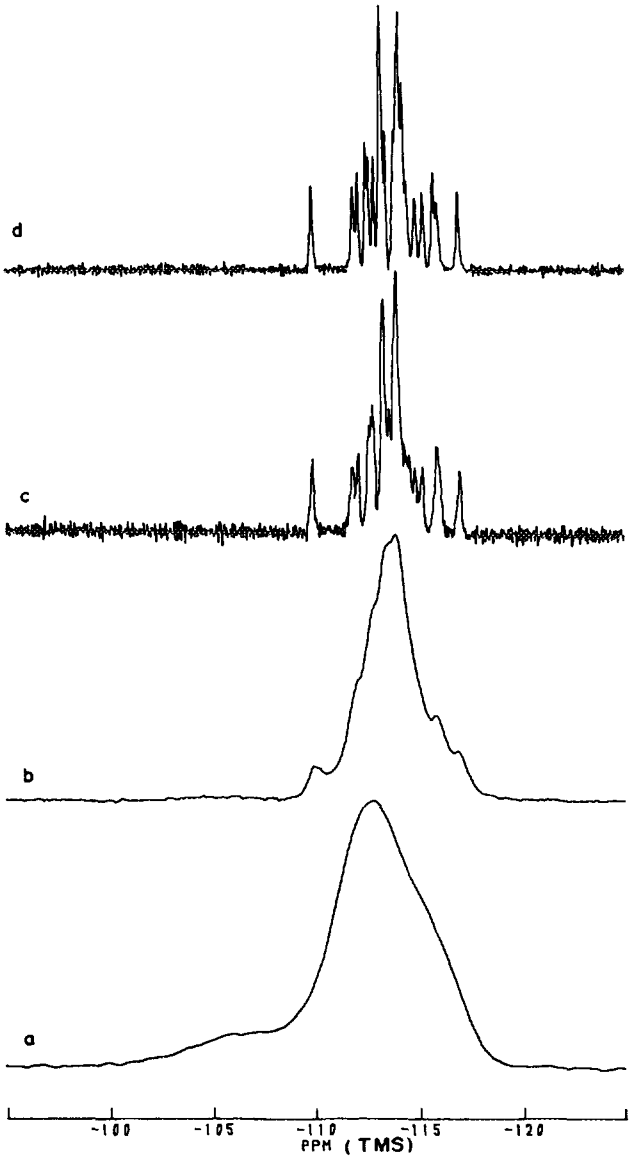

FIG. 2. ^{29}Si MASS NMR spectra of high silica ZSM-5 (silicalite I) samples a–d. (The free induction decays were apodized with a sine bell window function before Fourier transformation.)

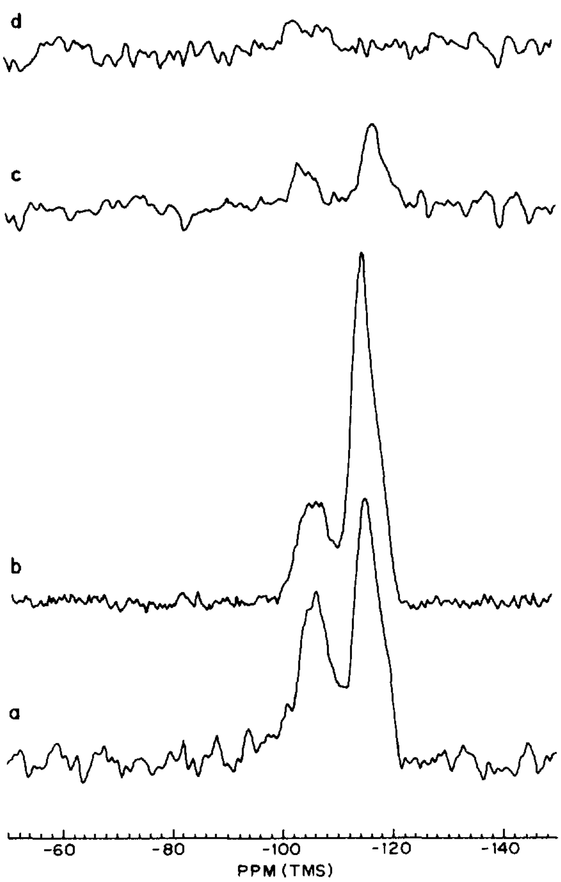

FIG. 3. ^1H–^{29}Si CP-MASS NMR spectra of high silica ZSM-5 (silicalite I) samples a–d. (The free induction decays were apodized with a exponential function (LB = 5Hz) before Fourier transformation.)

3c). Since cross-polarization occurs by hydroxyl protons, only those ^{29}Si spins in the immediate vicinity of the defect sites are cross-polarized. The resolvable T sites in the regularly ordered crystalline phase of the zeolite are not cross-polarized due to long ^1H–^{29}Si internuclear distances. Hence they do not lead to the same resolution as observed in Bloch decay spectra.

It is noted that the defect sites may be taken care of during the process of synthesis of the zeolite. The Si/OH ratio in the gel before crystallization is a crucial parameter to be controlled. In the cases where the template is TPAOH, the OH concentration is contributed by the template itself and hence an increase in the defect sites may be observed here over the case where TPABr is used as a template. This feature is clearly borne out in the NMR results for b and c. Additionally, the crystallization period seems to play an important role. The best NMR results are therefore obtained only for crystals of ZSM-5 which were carefully grown by optimizing synthetic and crystal growing conditions.

From the above observations, the following conclusions can be drawn. It is necessary to have defect free crystals of the zeolite for obtaining the highly resolved ^{29}Si MASS NMR spectra required for 2-D NMR studies. The defect sites, viz. the silinol groupings such as Si(OH) and $Si(OH)_2$ formed due to termination in lattice connectivities associated with Si–O–Si, can be conveniently detected by ^1H–^{29}Si CP-MASS studies. The defect sites in the zeolite can be eliminated or reduced using TPABr instead of TPAOH as a template and also optimizing the period of crystallization.

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