An Investigation into the Structure and Position of Organic Bases in ZSM-5-type Zeolites by High-resolution Solid-state ^{13}C N.M.R. Spectroscopy

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Cross-polarization magic-angle-spinning ^{13}C n.m.r. spectroscopy has been used for the first time to investigate the structure and position of organic bases occluded in ZSM-5-type zeolites.

ZSM-5-type zeolites are synthesized from mixtures of silica, alumina, sodium oxide, water, and an organic base. In addition to the relative concentrations of the ingredients, and the temperature and duration of the reaction, it is the nature of the organic base that has a particularly important bearing on the structure and properties of the product. We have studied a number of ZSM-5 and ZSM-11 zeolites, prepared with a wide variety of bases, by both ^{13}C and ^{29}Si solid-state n.m.r. spectroscopy; the results will be published in full elsewhere. Tetrapropylammonium hydroxide (TPAH), however, seems to take a special place among the bases in that it yields ZSM-5 zeolites over a wide range of synthetic conditions. We therefore present our preliminary findings from solid-state cross-polarization magic-angle-spinning (CPMAS) ^{13}C n.m.r. studies on a selected number of ZSM-5 zeolites prepared with TPAH, TPABr (tetrapropylammonium bromide), and TPACl (tetrapropylammonium chloride) as the organic base.†

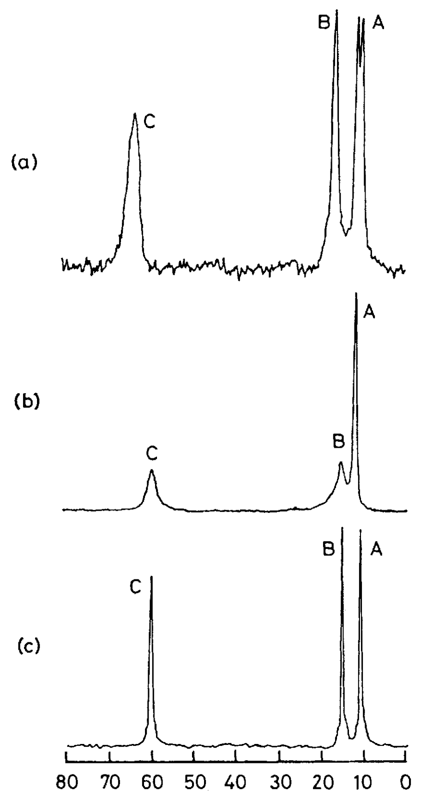

Figure 1. ^{13}C N.m.r. spectra of the tetrapropylammonium ion in various physical states: (a) TPABr [$(^{A}CH_3{}^{B}CH_2{}^{C}CH_2)_4NBr$] occluded in ZSM-5 (CPMAS spectrum); (b) crystalline TPABr (CPMAS spectrum); (c) TPAH (aqueous solution; conventional Fourier transform spectrum).

† An 'Andrew' type rotor made from boron nitride was used[1] on a Bruker CXP-300 spectrometer.

The spectrum of ZSM-5 prepared with TPABr is given in Figure 1(a); for comparison, the spectra of crystalline TPABr and TPAH (aqueous solution) are presented in Figures 1(b) and 1(c), respectively. The spectra show that the TPA^+ ion has remained intact during the zeolite synthesis. This indicates that these ions are present at the intersections of the ZSM-5 channels. The deviating line shapes and intensities in the spectrum of the crystalline TPABr are typically features associated with specific solid-state interactions, both intermolecular and intramolecular, and need not concern us here. It is, however, known from *X*-ray crystallographic studies that TPABr has tetrahedral symmetry[2] and this is borne out by its ^{13}C spectrum.

In view of the inherent symmetry of the TPA^+ ion it is intriguing to see the splitting into a doublet of the methyl signal of TPABr ZSM-5 [Figure 1(a)]. Such splittings in solid-state CPMAS spectra can be due to conformational[3] or crystallographic effects.[4] In our case a simple crystallographic effect can be discounted as the pure TPABr does not exhibit a doublet [Figure 1(b)]. We feel that the origin of this splitting must be sought in the environment of the ion, *i.e.* in the chemical composition or in the pore structure of the zeolite. As it is only the outer, methyl, carbon atom of the TPA ion that experiences this splitting, such an environmental effect must be weak. It is not induced by the counter-ion of the organic base, since similar zeolites such as TPAH ZSM-5 and TPACl ZSM-5 demonstrated the same doublet of the methyl group [see Figure 2(a) for TPAH ZSM-5]. Subsequent elemental analysis of TPABr ZSM-5 proved that there is in

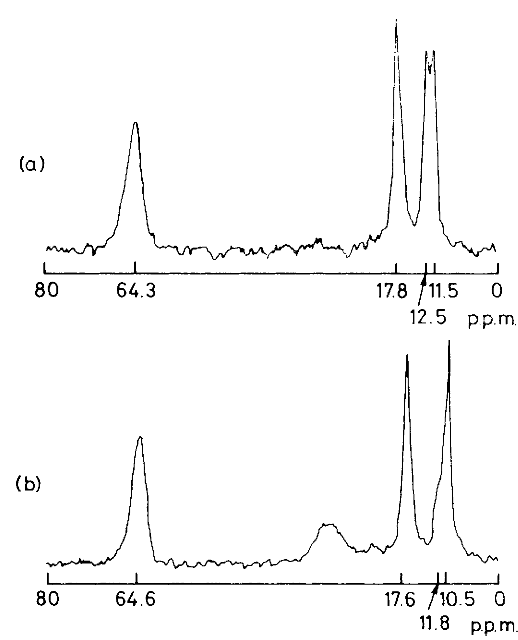

Figure 2. CPMAS ^{13}C n.m.r. spectra of TPAH ZSM-5: (a) following heat treatment at 200 °C; (b) following heat treatment at 350 °C (the 28 p.p.m. signal is probably due to an impurity).

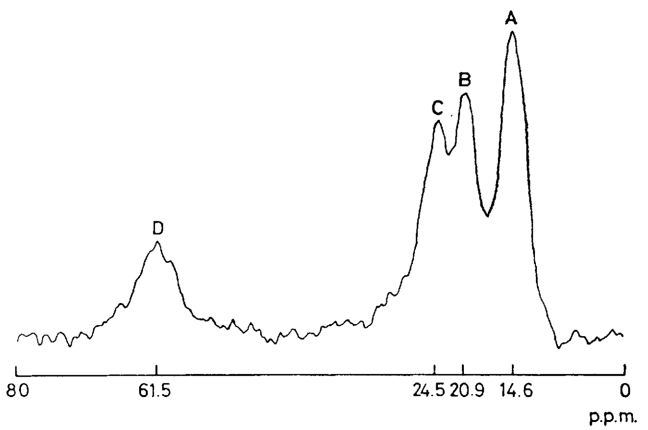

Figure 3. CPMAS ^{13}C n.m.r. spectrum of $(^{A}CH_3{}^{B}CH_2{}^{C}CH_2{}^{D}CH_2)_4$-NOH in ZSM-11.

fact *no* Br^- occluded in the zeolite. The hypothesis that the presence of Al^- sites is an influence in this respect was quickly dismissed as the spectrum of silicalite (Al-free ZSM-5; not shown) was essentially identical with those of Figures 1(a) and 2(a).

Another possibility is that the normally tetrahedral TPA ion loses its symmetry in the pore structure of the zeolite, leading to different chemical shifts. This argument is disproved by the effect of heat-treating the samples at a variety of temperatures: the spectrum of TPAH ZSM-5 recorded after 4 h heat treatment at 350 °C, for example [Figure 2(b); sample as in Figure 2(a)], does not show a doublet. Furthermore the methyl signal shifts slightly to lower frequency (high field), suggesting that we are dealing with TPA ions in different sites. ZSM-5 possesses two types of channels: one straight with elliptical ten-membered rings and the other zigzag-shaped with circular ten-membered rings. It is possible that these channels constitute slightly different chemical environments for the methyl groups leading to the observed splitting. Methyl group splitting has, however, been observed only in the case of the TPA ion. It is of interest to note that other bases do not remain chemically intact during the zeolite synthesis. ZSM-11 has only one type of channel, *viz* straight channels, and we have only observed methyl group singlets for organic bases occluded in ZSM-11 as shown for tetrabutylammonium hydroxide ZSM-11 (see Figure 3).

In conclusion, we have seen that the tetrapropylammonium ion is occluded, chemically intact, into ZSM-5-type zeolites during their synthesis. In addition splitting of the ^{13}C signal of the methyl carbon atom points to the presence of at least two dissimilar sites within the zeolite. This clearly demonstrates that the CPMAS ^{13}C n.m.r. spectrum is sensitive to weak interactions between organic molecules and the frameworks of zeolites, and is therefore a powerful tool in the investigation of the structure of such bases occluded in zeolites.

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