Solid-state NMR Evidence for the Strong Binding of Methanol prior to Carbon–Carbon Bond Formation during the Synthesis of Gasoline on Molecular Sieve Catalysts

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Slow magic-angle spinning ^{13}C NMR spectroscopy reveals that strongly bound surface Me–O–Si groups are formed at 250 °C when methanol is adsorbed on SAPO-5; by contrast, in zeolite H-ZSM-5 methanol becomes strongly bound to the framework at room temperature without the formation of methoxy groups.

Solid-state NMR spectroscopy has provided much important information on the structure and properties of molecular sieve catalysts and intracrystalline guest species.[1] We have pioneered the use of sealed Pyrex microreactors which fit exactly in the magic-angle-spinning (MAS) rotors and provide the ideal environment for high-temperature catalytic reactions under essentially static reactor conditions.[2—5]

The nature of the interaction of primary alcohols, in particular methanol, with molecular sieves is of special interest because of the ability of some of them to convert alcohols to hydrocarbons in the gasoline boiling range (30—200 °C).[6,7] The catalysts used in these reactions are always in their hydrogen forms. The specific size constraints of different frameworks then limit the size of product molecules through product selectivity and active-site selectivity.[1—4] The mechanism of the reaction, particularly as concerns the formation of the first C–C bond and the nature of the interactions between the MeOH molecules and the zeolitic framework has been the subject of controversy.[8,9]

Adsorption and IR spectroscopy studies conclude that at low pressures MeOH is bound to the Brønsted acid sites ('bridging' Si–OH–Al groups) in a 1 : 1 stoicheiometry[10] and that MeOH is hydrogen-bonded to the proton of the bridging hydroxy group.[10—12] It has also been established[5] that the proton is transferred from the zeolite to the MeOH molecule. On the other hand, several workers using different techniques proposed[13,14] that methoxy groups are formed at the acid sites and serve as intermediates in further chemical reactions, while a recent computer simulation study concludes[15] that it is the methyl group of MeOH which approaches the framework proton while the MeOH hydroxy group is pointing away from it. We describe the use of ^{13}C MAS NMR for the study of the nature of the interaction of methanol with zeolitic and silicoaluminophosphate molecular sieves.

All the samples were obtained commercially except for the SAPOs which were synthesized in this laboratory.[4] Hydrogen forms of the materials were prepared by ammonium exchange followed by calcination at 550 °C in flowing air. ^{27}Al MAS NMR spectra indicate that the amount of extra-framework aluminium in the samples was always less than 5 mole % of the total Al (*ca.* 1 Al per 600 framework Si atoms). This concentration is negligible in all the arguments which follow. Materials containing enclathrated organic cations were calcined prior to ion exchange in order to remove the organic component. Samples were contained inside specially designed

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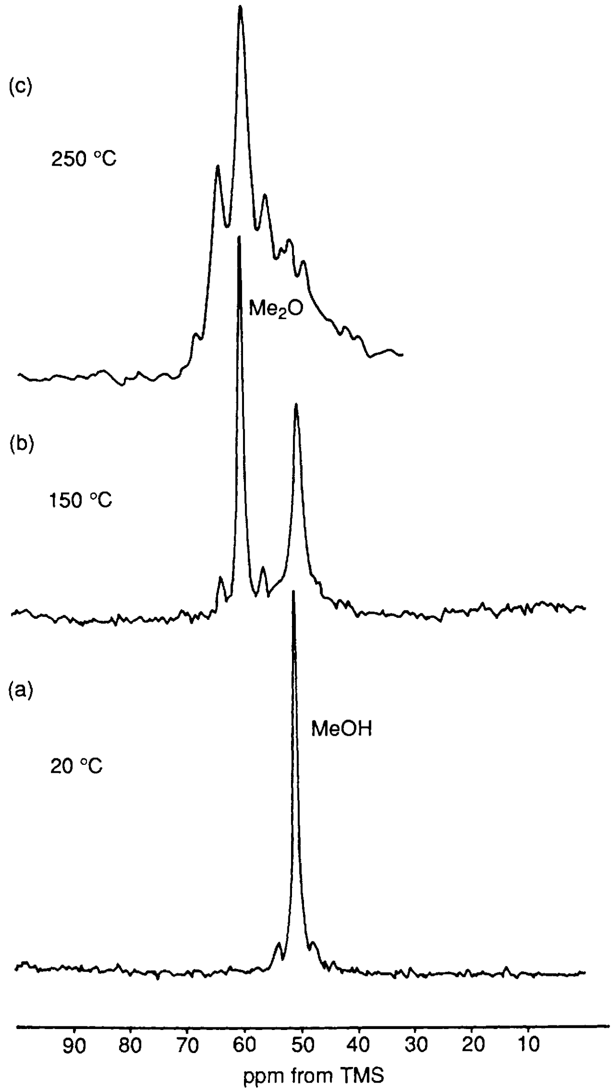

Figure 1. ^{13}C MAS NMR spectra of methanol adsorbed on SAPO-5. (a) room temperature spectrum; (b) spectrum of a sample heated to 150 °C for 10 min; (c) sample heated to 250 °C for 10 min.

Pyrex capsules which could be spun inside the MAS NMR probehead at rates of up to 3 kHz.[16] The design of the capsule allowed the samples to be dehydrated at 400 °C under a pressure of 10^{-5} Torr before adsorption of the desired organic species. Capsules could then be sealed while keeping the sample at liquid nitrogen temperature in order to prevent the onset of chemical reactions. High-resolution ^{13}C MAS NMR spectra were acquired at 100.613 MHz using high-power proton decoupling only. Chemical shifts are referred to external tetramethylsilane (TMS).

Figure 1(a) shows the spectrum of MeOH adsorbed on SAPO-5 at room temperature and not subsequently heated. A single sharp resonance is observed at 50 ppm corresponding to relatively highly mobile adsorbed MeOH.[2—5] After heating the sample to 150 °C for 10 min 37% of the MeOH has been converted to dimethyl ether which, judging from its narrow spectral line [Figure 1(b)], is also highly mobile. Further heating to 250 °C for an additional 10 min results in the spectrum shown in Figure 1(c). Although a number of broad spectral features are in evidence, they all correspond to two chemical species, one at 50 ppm due to methanol and a broader signal at 60 ppm with associated spinning sidebands.

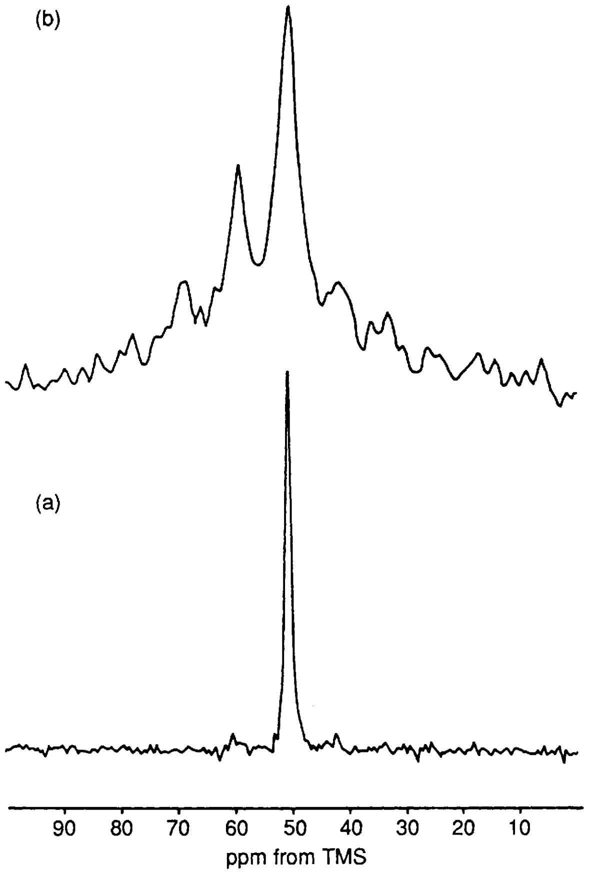

Figure 2. Room temperature ^{13}C MAS NMR spectra of methanol adsorbed on zeolite H-ZSM-5. (a) 6 molecules of MeOH per Brønsted acid site; (b) 1 molecule of MeOH per Brønsted acid site.

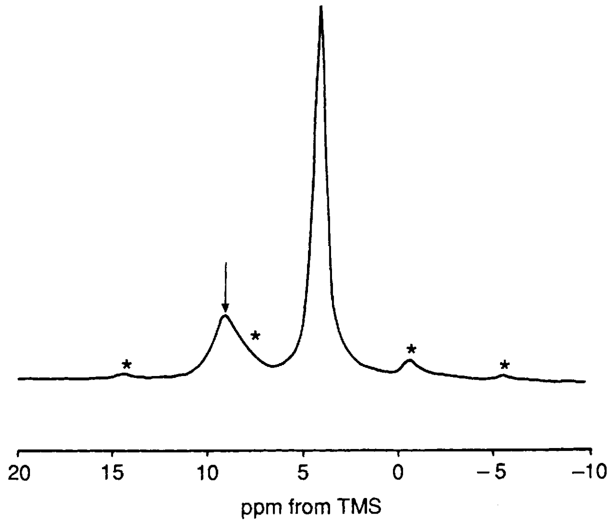

Figure 3. ^{1}H MAS NMR spectrum of MeOH adsorbed on zeolite H-ZSM-5. Asterisks denote spinning sidebands, arrow points to the position of the resonance from the methanol hydroxy group.

The greatly increased linewidth of the latter signal together with the presence of sidebands in this typical solid-state spectrum indicate the presence of considerable chemical shift anisotropy resulting from much reduced molecular mobility. The MAS spinning frequency used for these experiments was less than 1 kHz. It is clear that the application of normal, much higher, spinning frequencies would average this anisotropy thus concealing important chemical information.

The likely origin of the broad new signal could be either: (i) Me_2O which has become more strongly bound to the framework; and (ii) strongly bound surface Me–O–Si methoxy groups which would have a very similar chemical shift to that of Me_2O. Being anchored at the surface of an aluminium-rich molecular sieve, these methoxy groups undergo both chemical shift and dipole–quadrupole broadening effects brought about by the vicinity of ^{27}Al nuclei. Since it is difficult to visualise the reasons or the mechanisms for (i) to occur since the structure of SAPO-5 does not contain secondary cages or pockets which might trap the Me_2O, alternative (ii) is much more likely. After subsequent heating of the sample to 300 °C and above, MeOH is converted to a mixture of mobile alkenes and aliphatic compounds[2—3] which can be observed with slow MAS and which give narrow spectral lines without spinning sidebands. This demonstrates the progression from weakly bound MeOH which dehydrates to weakly bound Me_2O then to a strongly bound reaction intermediate and finally to a weakly bound hydrocarbon product. Similar results were obtained for the molecular sieve SAPO-34 (not shown) except that the strongly bound species at 60 ppm was already observed at a lower temperature of 150 °C.

Figure 2 shows the spectra of MeOH adsorbed on zeolite H-ZSM-5. The samples were not heated prior to the NMR measurement. When the concentration of MeOH is 6 molecules per Brønsted acid site [Figure 2(a)] a single narrow peak at 50 ppm is found. The assignment of this resonance is elucidated by reference to the ^1H MAS NMR spectrum (Figure 3) which shows the hydroxy resonance at 9.4 ppm. This is characteristic of very strongly hydrogen-bonded methanol or methoxonium ion. The latter can only partly contribute to the resonance as there are 6 methanol molecules per Brønsted acid site and therefore not enough acidic sites to protonate every methanol molecule. We believe that the spectrum indicates that methanol is forming mobile, charged hydrogen-bonded clusters around a central protonated methanol molecule at the Brønsted acid site.[5] It is clear, however, that despite this strong hydrogen bonding the narrow ^{13}C resonance [Figure 2(a)] indicates a substantial degree of mobility of the molecules within this cluster. However, when only *ca.* 1 molecule of MeOH is adsorbed per site, it is more firmly anchored as shown by the substantial NMR line broadening in the ^{13}C spectrum and the appearance of several orders of spinning sidebands (spinning rate 1 kHz). The chemical shift of the signal clearly shows that it corresponds, in this case, to intact MeOH hydrogen-bonded at the Brønsted acid site rather than to surface methoxy groups which do not form at room temperature. This demonstrates a different reason for the decreased mobility of surface species than was observed on SAPO-5. In ZSM-5 a methanol species is very strongly co-ordinated at the Brønsted acid site, prior to the initial dehydration step. In SAPO-5 a strongly bound species is formed after the initial dehydration step and prior to the formation of a C–C bond. These two strongly bound species which, although isolated in different systems, are clearly important in the catalytic steps which immediately follow their formation.

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