Inhomogeneity in the interaction between methanol molecules and Brønsted acid sites of H-ZSM-5 directly detected by 2D CPMAS ^{13}C NMR spectroscopy

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1D and 2D exchange ^{13}C NMR investigation of the states of methanol adsorbed on H-ZSM-5 at ambient temperature demonstrates the coexistence of methanol strongly interacting with Brønsted acid sites and methanol physisorbed or hydrogen-bonded, and provides the first spectroscopic evidence of a wide distribution in the strength of its interaction with Brønsted acid sites.

In the micropores of zeolites, the electric field induced by the pore walls has often been assumed to assist the activation of molecules, although no direct evidence has been provided. A recent theoretical calculation[1] predicted that the ionic effect of the zeolite framework alters the state of MeOH adsorbed at a Brønsted acid site: a methoxonium ion is preferred in the narrow channel of chabazite, while a hydrogen-bonded neutral complex is stable in the larger cage of sodalite. H-ZSM-5, an important catalyst for chemical processes such as the MTG (methanol to gasoline) reaction,[2] would exhibit interesting characterisitics with respect to the ionic effect on the acid sites because its pore size is intermediate.[1] There are sites in the two kinds of channel and at their intersections in H-ZSM-5, and the local electric field must be reflected in the states of the molecules adsorbed.[3] There have been extensive experimental studies on the state of MeOH using *in situ* IR analysis,[4–7] temperature programmed desorption,[8,9] and solid-state NMR analysis,[5,10–15] as well as theoretical calculations.[1,16–18] High-resolution solid-state ^{1}H NMR spectroscopy has recently shown that MeOH molecules form 'clusters' on the Brønsted acid sites of H-ZSM-5 at high coverages at ambient temperature.[5,12–14] The hydroxy protons of MeOH and the acidic protons rapidly exchanged in these clusters. IR investigations indicated the formation of hydrogen-bonded species on the acid sites.[6,7] Two research groups recently reached different conclusions based on careful NMR studies of the state of adsorbed MeOH, favouring either a resonant structure including adsorbed methoxonium ion[13] or a hydrogen-bonded neutral complex.[14] One of the major differences between the two studies appears in the observed ^{13}C NMR spectra, with peaks of 53.6 *vs.* 50.5 ppm reported. So, the state of MeOH stoichiometrically adsorbed on the acid sites is still controversial. To the best of our knowledge, all NMR studies on this subject were carried out with MeOH/acidic sites ≥ 1.

In this study, by focusing on low coverages of MeOH, we provide spectroscopic (2D exchange ^{13}C NMR) evidence for the co-existence of the two different species and a wide distribution in strength of interaction between the MeOH molecules and the acid sites. These species adsorbed so firmly that they did not exchange their positions at 298 K even on an NMR timescale of 0.5 s. The present results explain the previous results, which are apparently contradictory.

H-ZSM-5 was prepared from Na-ZSM-5 (Si/Al = 11.9, 7.4 Al atoms per unit cell) which was kindly supplied by Toso Co. Ltd. After ion exchange with ammonium nitrate, the zeolite was heated in a dry He stream at a rate of 0.3 K min^{-1} and was finally calcined at 673 K for 10 h. In the ^{27}Al NMR spectrum of the fully hydrated H-ZSM-5, the intensity of the octahedral Al (extraframework Al) resonance at around 0 ppm was less than one twelfth of that of tetrahedral Al in the framework (*ca.* 50 ppm). The samples for ^{13}C NMR analysis were prepared using a glass high vacuum system (*ca.* 100 cm^{3}). After H-ZSM-5 had been dehydrated at 673 K (heating rate: usually 1 K min^{-1}, *in vacuo*), a calculated amount of ^{13}CH$_3$OH (99 atom% ^{13}C) was introduced at 298 K. The amount of MeOH was varied from 0.5 to 12 molecules per unit cell (MeOH/Al = 0.07–1.6). Then the zeolite was transferred into a small glass cell (*ca.* 0.1 cm^{3}) and the cell was sealed while the sample was cooled with liquid N$_2$. The cell was set in a zirconia rotor, and 1D ^{13}C and ^{27}Al NMR spectra were recorded using a JNM-EX270 spectrometer with a cross-polarisation magic angle spinning (CPMAS) probe. 2D ^{13}C NMR exchange experiments (CP excitation)[19] were carried out with a Chemagnetics CMX-300 Infinity spectrometer. 48 1D spectra with 840 scans for each were recorded. All NMR spectra were recorded at 298 K.

Fig. 1 shows the CPMAS ^{13}C NMR spectra for samples having 0.5–12 molecules per unit cell (molecule uc^{-1}) of MeOH adsorbed on H-ZSM-5. The spectra in Fig. 1(*a*) were recorded by single pulse excitation with proton decoupling and the ordinate for each spectrum was normalized by the sample weight. Therefore, the peak intensities are proportional to the number of nuclear spins. The spectra in Fig. 1(*b*) were recorded by CP to improve the signal-to-noise ratio. Similar spectra were obtained using the two methods. This indicates that the CP efficiencies for the signals were similar in these measurements and the relative intensities in each spectrum in Fig. 1(*b*) can be regarded as nearly quantitative. In the case of 12 molecule uc^{-1} (MeOH/Al = 1.6), a broad peak was observed at 51.5 ppm. When the amount of MeOH was decreased to 8 molecule uc^{-1} (MeOH/Al = 1.1), the peak shifted downfield to 52.7 ppm, suggesting an increased interaction of MeOH with the acid sites. A further decrease in the amount of MeOH to 4 molecule uc^{-1} (MeOH/Al = 0.54) caused a splitting of the signal into a narrow peak at 51.5 ppm and a broad shoulder at *ca.* 54 ppm. These two signals were observed more clearly at 2 molecule uc^{-1}. As the

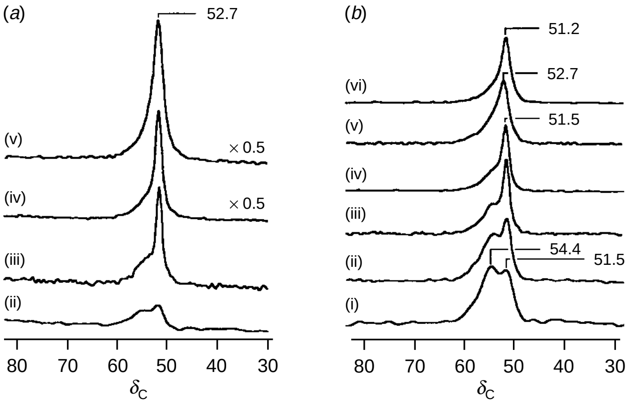

Fig. 1 CPMAS ^{13}C NMR spectra of ^{13}CH$_3$OH adsorbed on H-ZSM-5 at various coverages of MeOH at 298 K; (*a*) single pulse excitation with proton decoupling and (*b*) cross polarization. (i) 0.5 (0.07), (ii) 1 (0.13), (iii) 2 (0.27), (iv) 4 (0.54), (v) 8 (1.1) and (vi) 12 molecule uc^{-1} (MeOH/Al = 1.6). MAS rate = 6 kHz.

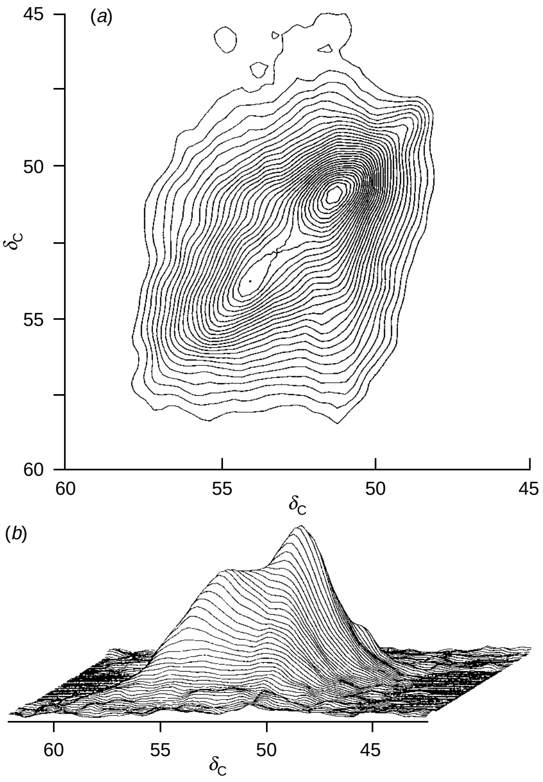

Fig. 2 2D exchange ^{13}C NMR spectrum of $^{13}CH_3OH$ adsorbed on H-ZSM-5 at 298 K; (*a*) contour plot and (*b*) stack plot. Adsorption = 1 molecule uc^{-1}. Mixing time = 0.5 s. MAS rate = 3.5 kHz.

amount of MeOH decreased to 1 molecule uc^{-1} (MeOH/Al = 0.13) and 0.5 molecule uc^{-1} (MeOH/Al = 0.07), the peak at 51.5 ppm decreased and the broad signal at *ca.* 54 ppm became dominant.

The origins of these signals were investigated by the following experiments. First, the ^{13}C NMR spectrum of adsorbed MeOH was measured for H-ZSM-5 with a higher Si/Al ratio (26) at 1 molecule uc^{-1}. The intensity of the broad peak at 54 ppm decreased as compared with H-ZSM-5 with Si/Al = 11.9, while its linewidth was almost unchanged. Next, the degree of dealumination of H-ZSM-5 was increased by accelerating the rate of temperature rise in the pretreatment *in vacuo* from 1 to 3, and then to 10 K min^{-1}. Accordingly, the peak intensity at *ca.* 0 ppm (extraframework Al) relative to that at *ca.* 50 ppm (Al in framework) in the ^{27}Al NMR spectrum (measured after full rehydration) increased from 0.13 to 0.15, and then to 0.17. ^{13}C NMR measurements for these zeolite samples at 1 MeOH molecule uc^{-1} showed that the broad signal at 54 ppm decreased with an increase in the dealumination. On the basis of these two experiments, it may be concluded that the broad signal is not connected with extraframework aluminium sites, but it corresponds to a species strongly interacting with the Brønsted acid sites. In the case of silicalite, the ^{13}C NMR spectrum at 1 MeOH molecule uc^{-1} gave a single sharp peak at 51.0 ppm. This shows that the narrow peak at *ca.* 51 ppm is due to MeOH weakly interacting with the zeolite.

Two research groups recently performed careful studies using temperature-variable ^{1}H, ^{13}C and ^{2}D NMR spectroscopy, and reached different conclusions. Thursfield and Anderson observed a signal at 53.6 ppm and proposed a resonance structure between an adsorbed methoxonium ion and a hydrogen-bonded MeOH molecule.[13] On the other hand, Hunger and Horvath found a peak at 50.5 ppm and assigned it to a hydrogen-bonded neutral complex in which the hydroxy proton of MeOH and the acidic proton of H-ZSM-5 rapidly exchange their positions.[14] These two different results become consistent if the variation of the major species with coverage shown in Fig. 1 is taken into account: the major species at MeOH/Al = 1 gives a peak at 51 ppm, while at low coverage the species strongly interacting with the Brønsted acid sites and hydrogen-bonded MeOH coexist. The two species do not exchange with each other on the NMR timescale.

The broadness of the ^{13}C NMR peak of the strongly bonded species (54 ppm) is notable. In order to elucidate the mechanism of broadening and the exchangeability of the species, a 2D exchange ^{13}C NMR spectrum was measured at 1 molecule uc^{-1} with a mixing time of 0.5 s. As shown in Fig. 2, no cross-peak was observed, so the species observed do not exchange at 298 K at low coverage even on the long timescale of 0.5 s. Fig. 2 provides additional important information. The broad peak for the strongly adsorbed species appears as a long narrow ridge along the diagonal, demonstrating the presence of inhomogeneous broadening. That is, the width of the peak is not due to a short T_2 induced, for example, by strong dipole interactions with other nuclei such as ^{27}Al and neighbouring ^{13}C. The linewidth, which is insensitive to change in the MAS rate, shows that it is not due to residual anisotropy of the chemical shifts or a misadjusted magic angle. Therefore, it was concluded that the broad peak came from several species which have different chemical shifts, reflecting the different strengths of interaction between MeOH and the Brønsted acid sites. This is the first NMR detection of inhomogeneous adsorption states presumably due to the different environments of adsorption in the zeolites. Since the linewidth of the peak is almost unchanged when the Si/Al ratio is varied, this inhomogeneity of adsorbed MeOH is thought to be intrinsic to the H-ZSM-5 structure.

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Notes and References

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