Perfluorotributylamine as a probe molecule for distinguishing internal and external acidic sites in zeolites by high-resolution ^{1}H MAS NMR spectroscopy

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^{1}H MAS NMR spectra of perfluorotributylamine adsorbed on HZSM-5 zeolites loaded with or without molybdenum show that it is a promising probe molecule for distinguishing the internal and external acidic sites in zeolites as well as for determining the position of silanols and some non-framework Al species.

Molybdenum-loaded HZSM-5 zeolites are promising catalysts for the conversion of methane to benzene under non-oxidative conditions.[1–7] The acidic sites in HZSM-5 zeolites are thought to play an important role in the aromatization of the primary product, ethylene, to benzene.[2,3] Until now, it has not been easy to distinguish the internal and external acidic sites in zeolites and to obtain quantitatively the concentration of acidic sites on the external surface of zeolites, though some methods such as IR spectroscopy[8,9] have been developed for the characterization of the external acidic sites of zeolites using base molecules with different sizes. High-resolution ^{1}H MAS NMR is a direct and senstitive tool able to characterize the local environment of protons in zeolites, and different acidic sites can be distinguished by chemical shifts induced by selective adsorption of certain probe molecules.[10] Here we use ^{1}H MAS NMR spectroscopy for quantitative determination of external acidity, as well as the position of non-acidic hydroxy groups (silanols) and some non-framework Al species of the zeolites, using perfluorotributylamine [$(n\text{-}C_4F_9)_3N$] as a probe molecule. Perfluorotributylamine is a weakly basic molecule with a diameter of 0.94 nm,[11] and is much larger than the pore size of microporous zeolites such as ZSM-5 (0.55 nm) and Y (0.74 nm).

NaZSM-5 zeolite samples with controlled particle sizes were prepared by varying the duration and temperature of crystallization as well as the amount of alkali metal salt such as NaCl.[12] Fully exchanged HZSM-5 with a Si/Al ratio of 28 (determined by ^{29}Si MAS NMR, and consistent with the value of 25 obtained by inductively coupled plasma analysis) was obtained by ion exchange of NaZSM-5 with a 0.4 M aqueous solution of NH_4NO_3. A Mo-HZSM-5 sample was prepared by impregnating the above-mentioned HZSM-5 zeolites (average particle sizes 70 nm by transmission electron microscopy) with an aqueous solution of $(NH_4)_6Mo_7O_{24}$, and calcined in air at 773 K.

In order to simulate catalytic reaction conditions in an environment suitable for NMR spectroscopy, we designed and fabricated a special device for on-line treatment of zeolite samples (Fig. 1).[13] With this system, the solid samples can be heated up to *ca.* 1000 K in a vacuum for dehydration, and can be exposed to several different gases together or separately. After treatment, the sample can be filled *in situ* into a NMR rotor by a tamper, sealed with a cap from the plug rack and transferred to the spectrometer without exposure to air. In the present experiment, the zeolites were dehydrated typically at 673 K and a pressure below 10^{-2} Pa for 10–20 h. Selective adsorption of perfluorotributylamine (from Acros Organics) was performed by exposing the dehydrated sample to saturated vapor at room temperature for 30 min. After equilibration, the samples were degassed at 298 K to remove the physical adsorbates on the surface.

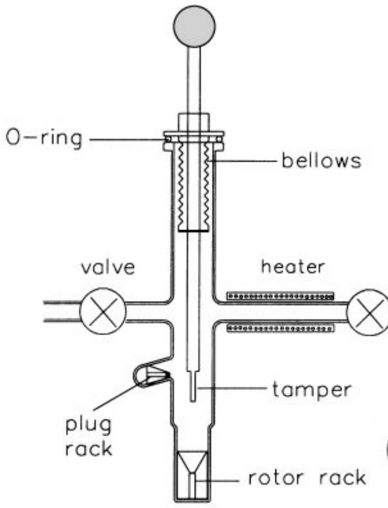

Fig. 1 Schematic diagram of the evacuating, loading and sealing apparatus of the solid samples for the solid-state MAS NMR study.

^{1}H MAS NMR spectra were recorded at 400.1 MHz on a Bruker DRX-400 spectrometer with a BBO MAS probe using 4 mm ZrO_2 rotors. The pulse width was 1 µs for a $\pi/10$ pulse, and 200 scans were accumulated with a 4 s recycle delay. Samples were spun at 8 kHz, and chemical shifts were referenced to a saturated aqueous solution of sodium 4,4-dimethyl-4-silapentanesulfonate. The Bruker software WINNMR was employed for deconvolution using fitting of Gaussian–Lorentzian lineshapes.

The upper curves in Fig. 2 show the ^{1}H MAS NMR spectra of HZSM-5 zeolite and a sample loaded with 6 wt% molybdenum before adsorption of perfluorotributylamine. At least five peaks can be clearly observed in the ^{1}H MAS NMR spectra (see the corresponding quantitatively deconvoluted spectra in Fig. 2). Besides the usually observed bridging hydroxy peak at about δ 3.9, the non-framework AlOH peak at δ 2.4 and the non-acidic silanol peak at about δ 1.7 can be identified. Moreover, a broad resonance at about δ 5.8 is also visible, which is ascribed to a second Brønsted site having an additional electrostatic interaction with the zeolite framework.[10] The narrow signal at about δ 4.9 can be assigned to an extremely small amount of water residing in the zeolite cages.[14] It is apparent from these spectra that the total ^{1}H signal intensity decreases upon loading molybdenum, and the resonances at δ 1.7 and 2.4 are preferentially reduced compared to those at δ 3.9 and 5.8. These results reveal that in the 6 wt% Mo–HZSM-5 sample prepared by impregnation, the molybdate ions preferentially react with the silanols and the non-framework AlOH groups on the surface of the zeolites. After adsorption of perfluorotributylamine, the intensity of the peak at δ 3.9 decreases, while that of the peak at about δ 5.8 ppm increases [see upper and lower curves in Fig. 2(*a*)]. This fact suggests that a portion of the bridging hydroxy groups located on the external surface of the zeolite interact with the perfluorotributylamine to form perfluorotributylaminium ions whose resonance signal

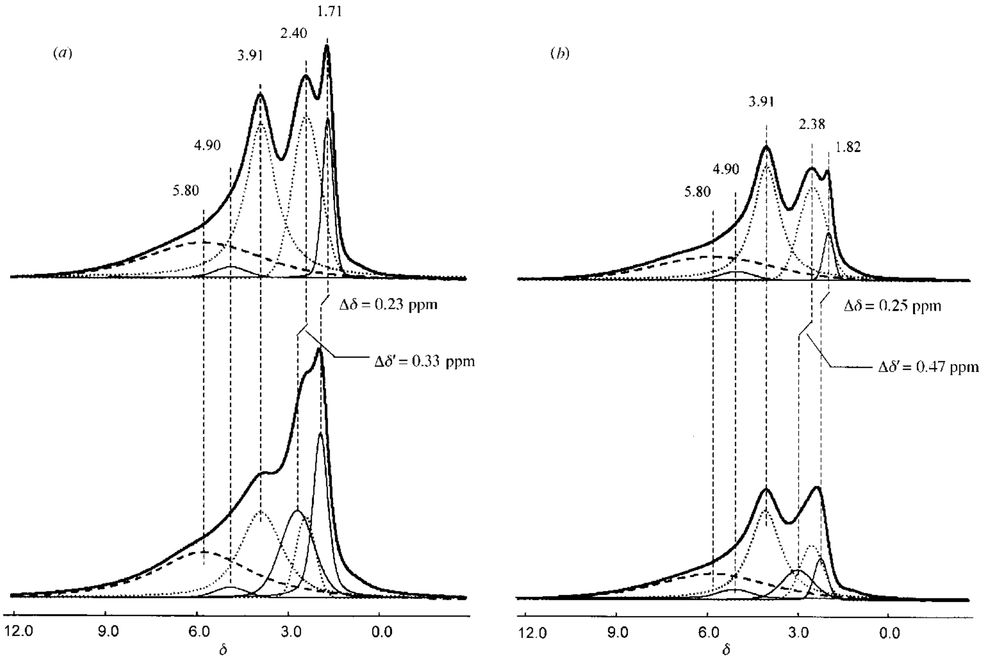

Fig. 2 ^1H MAS NMR spectra, with deconvolution, of (*a*) HZSM-5 zeolite and (*b*) 6 wt% Mo-HZSM-5, (top) before and (bottom) after adsorption of perfluorotributylamine, recorded at a resonance frequency of 400.1 MHz with a sample spinning rate of 8 kHz and 200 scans.

appears at about δ 6.0, while those at the internal surface are not accessible to perfluorotributylamine, so their chemical shift is unchanged. Based on these results, and after careful deconvolution of the obtained spectra, the concentration of Brønsted acid sites on the external surface of the zeolites can be calculated by (eqn. 1),

$$C_{\text{ext.surf.}} = (1 - A_1/A_2) \times 100\% \qquad (1)$$

where A_1 and A_2 denote the integral area of the peak at δ 3.9 after and before adsorption of perfluorotributylamine, respectively (quantitatively deconvoluted spectra are also shown in Fig. 2). According to eqn. (1), the concentration of Brønsted acid sites on the external surface for HZSM-5 zeolites (70 nm) is 32%, while that for the 6 wt% Mo-HZSM-5 is 9%. This result, combined with the fact that the peak intensity at δ 3.9 decreases after Mo-loading clearly demonstrates that the Brønsted acidic sites on the external surface of the HZSM-5 zeolite can also react with the molybdate ions during sample preparation.

In addition, the resonance position of silanols of the samples shifts from about δ 1.7 to about δ 2.0 after adsorption of perfluorotributylamine. This low-field shift of over 0.2 ppm confirms that a weak hydrogen bond between the SiOH and the N of perfluorotributylamine is formed due to its relatively high deprotonation energy (ΔE_{DP} = 1427 kJ mol^{-1}).[15] Thus most of the silanols of the given samples are located on the external surface, and not at the lattice defects of the internal surface in the zeolites. By reasonable deconvolution, the >0.3 ppm low-field shift of the non-framework Al resonance after adsorption of perfluorotributylamine demonstrates that some of the non-framework Al atoms exist on the external surface of the zeolites. Their concentration on the external surface can also be calculated *via* eqn. (1). Thus for HZSM-5 zeolites without Mo and with 6 wt% Mo, the concentrations are 65 and 51%, respectively. This also suggests that molybdate ions react with the non-framework AlOH groups on the external surface of the zeolites during sample preparation. From the above discussion, it is clearly demonstrated that there are at least three kinds of molybdenum species existing on the external surface of the HZSM-5 zeolite, *i.e.* Mo interacting with silanols, non-framework AlOH groups and Brønsted acidic sites on the external surface, respectively. These observations are consistent with the suggestion presented by Lunsford and co-workers[5,6] that impregnated Mo remains predominantly on the external surface of the zeolite, *via* studies comparing different preparation methods such as impregnation and solid state ion exchange. These Mo species are very likely associated with the activation of methane to form ethylene (and H_2) as the sole primary product, which aromatizes further on the Brønsted acidic sites to produce benzene and methylbenzene.[3]

In conclusion, this paper reports a feasible method for distinguishing the internal and external acidic sites in zeolites. After dehydration of the zeolites in a patented device capable of *in situ* sample pretreatments, and then adsorption of perfluorotributylamine as a probe, the Brønsted acidity distribution between the internal and external surfaces of the zeolites can be determined by ^1H MAS NMR spectroscopy. Meanwhile, the position of silanols and some non-framework Al species can also be identified.

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