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Identification of distinct Brønsted acidic sites in zeolite mordenite by proton localization and [^{27}Al]-^{1}H REAPDOR NMR

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[^{27}Al]-^{1}H REAPDOR (Rotational Echo Adiabatic Passage DOuble Resonance) NMR experiments distinguish structurally dissimilar Brønsted acid sites located in main 8 and 12 membered-ring channels of the zeolite mordenite.

In their protonic form, zeolites are extensively used as selective Brønsted acid catalysts, and the structural characterization of Brønsted acid environment has been a subject of considerable fundamental interest.[1] Structural variations among Brønsted acid environments ensue due to subtle geometrical variations within the acidic moiety Si–O(H$^+$)–Al$^-$. Dipolar interaction between the protons at the acidic sites and the framework aluminium in its immediate vicinity provides an effective way of studying the Brønsted acid environment. However, in magic angle spinning (MAS) experiments, often sought to characterize acid catalysts,[2,3] dipolar couplings are averaged to zero. Dipolar interaction between spin 1/2 (protons) and quadrupolar nuclei (aluminium, spin 5/2), within the Brønsted acidic environment, can be effectively recoupled under MAS by REAPDOR (Rotational Echo Adiabatic Passage DOuble Resonance),[4] a technique derived from the basic REDOR[5] and TRAPDOR[6] schemes. The REAPDOR pulse sequence involves the initial proton excitation, followed by the application of rotor synchronized π pulses twice per rotor period on these nuclei. In addition, an rf pulse of duration *ca.* half the rotor period τ_R is applied in the middle of the sequence to the ^{27}Al nuclei to cause a partial adiabatic population inversion.[7] Since the application of this pulse reintroduces only the dipolar interaction among ^{27}Al-^{1}H spin pairs, the signal dephasing due to an exclusive Al–H dipolar interaction can be measured in the REAPDOR experiment and quantified in terms of the inter-nuclear distance ($r_{\mathrm{Al-H}}$).[8]

The aim of this communication is to show that the experimental strategy of using [^{27}Al]-^{1}H REAPDOR NMR for Brønsted acid sites characterization is facilitated by proton localization and observation in mildly calcined mordenite (MOR), an acid catalyst which is extensively used in heterogeneous catalysis. There are four crystallographically non-equivalent tetrahedral framework Al sites in the structure of mordenite[9] and the acidic protons bound to these T-sites can be localized as two distinguishable species NH$_4^+$ and H$^+$ in the proton MAS spectrum, owing to the fact that the different topographical location of these T-sites in mordenite gives rise to acid sites of different strengths. Upon a mild calcination of NH$_4^+$-MOR, ammonia is selectively desorbed[10] from the weakly bound sites so that the acidic protons are localized in the form of NH$_4^+$ and H$^+$ species, which can be distinguished in the proton MAS spectra of the [^{27}Al]-^{1}H REAPDOR experiment.

We have prepared a NH$_4^+$/H$^+$-MOR sample by first converting Na-mordenite (Si/Al = 10.5 from ^{29}Si MAS NMR) into NH$_4^+$ form by repeated ion exchange in NH$_4$NO$_3$, followed by drying at 80 °C and mild calcination at 280 C for 8 h in the presence of flowing dry air. NMR experiments were performed at the Larmor frequency of 400 MHz (^{1}H) and 104.2 MHz (^{27}Al) on a Bruker ASX-400 spectrometer using a double resonance MAS probehead equipped to spin 4 mm zirconia rotors. [^{27}Al]-^{1}H REAPDOR experiments were carried out at three different spinning speeds (ν_R = 5, 10 and 14.925 kHz) using rf fields of 34.7 kHz and 41 kHz for ^{1}H and ^{27}Al, respectively. The REAPDOR dephased spectrum $S(N\tau_R)$, *versus* the total dephasing time $N\tau_R$, was measured by sequentially stepping up the number of rotor periods by two and applying an ^{27}Al rf pulse of duration $\tau_R/2$ in the middle of the sequence. In each case, a reference $S_0(N\tau_R)$ spectrum was recorded by omitting the ^{27}Al rf pulse. ^{27}Al triple quantum (3Q) MAS spectrum[11] was recorded with the t_1 rotor synchronized[12] three-pulse z-filter sequence[13] using rf fields of 200 kHz for the first two hard pulses and 5 kHz for the last 'central transition' selective $\pi/2$ pulse.

^{1}H MAS spectrum presented in Fig. 1-A, displays three proton resonances ($\Delta\nu$ ~ 100 Hz), readily assigned to Brønsted acid protons of Si–O(H$^+$)–Al$^-$ and Si–O(NH$_4^+$)–Al$^-$ types (3.2 and 6.7 ppm, respectively), and SiOH hydroxyl protons at the defect sites (1.4 ppm).[14,15] This resonance does not interfere with the REAPDOR measurement for the acidic protons. The faster REAPDOR fraction ($\Delta S/S_o = 1 - S/S_o$) for the 6.7 ppm signal (Fig. 1-B, curve-1) envisages a stronger dipolar interaction for the Si–O(NH$_4^+$)–Al$^-$ Brønsted acid environment, while the slower response noticed for the 3.2 ppm signal (curve-2) envisages a weaker dipolar interaction at the Si–O(H$^+$)–Al$^-$ sites. The Al–H dipolar interaction for this environment was noticed in a [^{27}Al]-^{1}H TRAPDOR experiment performed on H$^+$-MOR.[16]

In order to quantify the corresponding Al–H dipolar interaction (D), theoretical REAPDOR dephasing curves were calculated using PULSAR,[17] a general purpose density matrix based computer program developed to simulate the time evolution of spin system undergoing MAS and experiencing

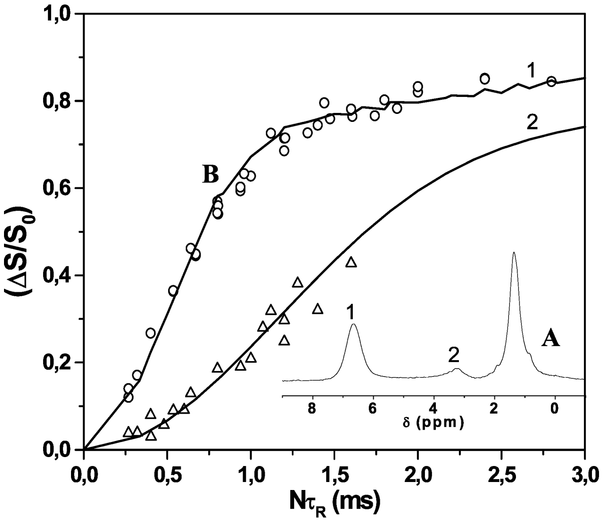

Fig. 1 (A) ^{1}H MAS spectrum of NH$_4^+$/H$^+$-MOR. **(B)** ^{27}Al-^{1}H REAPDOR response ($1 - S/S_o$) from 5, 10 and 14.925 kHz experiments corresponding to the NH$_4$ (δ = 6.7 ppm) (○) and H$^+$ (δ = 3.2 ppm) resonance (△) as a function of the total dephasing time $N\tau_R$. The theoretical REAPDOR curves shown were calculated using the following values: ν_r = 14.925 kHz, ν_{1H} = 34.7 kHz, ν_{1Al} = 41 kHz, δ_{CSA} = 5 ppm, D = 510 Hz (curve 1) and 215 Hz (curve 2). Curves (B1) and (B2) correspond to peaks (A1) and (A2), respectively.

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various spin interactions subjected to rf pulses and delays. For the calculation of the REAPDOR response, we consider an isotropic reorientation of the NH_4^+ group.[18] This was independently verified by ^{14}N echo experiments where quadrupolar echoes could not be generated due to the isotropic averaging of the quadrupolar interactions. The best agreement between the experimental points (Fig. 1-B) and the theoretical REAPDOR calculations is obtained for D = 510 Hz with the consideration that we have an isolated spin pair because we are observing the protons and the four protons of NH_4^+ group are equivalent. From the REAPDOR response we can thus estimate that the average location of protons (on the nitrogen atom) is at a distance $r_{\text{Al–H}}$ = 396 ±5 pm from the aluminium atoms in the Brønsted acidic environment Si–O(NH_4^+)–Al$^-$. Similarly, for the weaker Al–H$^+$ dipolar interaction observed for the 3.2 ppm signal, theoretical REAPDOR dephasing curves can be fitted (Fig. 1B) with a dipolar interaction D = 215 Hz, which corresponds to an Al–O–H distance of 525 pm. This too small dipolar coupling (and thus too long distance with respect to the classical 340–350 pm value) is attributable to the large mobility of protons when localized as Si–O(H$^+$)–Al$^-$ acidic sites.[19]

Our observations thus show that the non-equivalent tetrahedral Al sites at the Brønsted acid environments could be distinguished by ^{27}Al-[^{1}H] REAPDOR due to the large difference in the dipolar dephasing behavior when proton localization has been achieved in the manner we have done. Additionally, evidence from an independent ^{27}Al triple quantum MAS experiment on NH_4^+/H$^+$-MOR is presented in Fig. 2. Two tetrahedral ^{27}Al resonances [Al^{IV}(I), Al^{IV} (II)] are clearly resolved along the isotropic dimension (δ_{ISO}) of the 3Q-MAS sheared spectrum. No clue about the multiplicity of tetrahedral Al sites is provided in the ^{27}Al MAS spectrum (top of Fig. 2). The absence of octahedral aluminium is also evidenced. From a graphical analysis[20] of 3Q-MAS data we estimate the isotropic chemical shift (δ_{CS}) and quadrupole interaction parameter ($P_Q = C_Q(1 + \eta_Q^2/3)^{1/2}$, where $C_Q = e^2qQ/h$ is the quadrupole coupling constant and η_Q is the asymmetry parameter) to be 45 and 35 ppm and 1.9 and 5.6 MHz for the two aluminium environments.

Mordenite is a large pore zeolite with straight 12 (650 × 700 pm) membered ring (MR) main channels, interconnected through small 8 (260 × 570 pm) MR channels. As mentioned above, there are four crystallographically unique tetrahedral sites (T_1–T_4) in mordenite (space group *Cmcm*).[9] The interconnections of the 12 and 8 MR channels are through T_1 and T_2 sites which are part of 5-MR T-units, while T_3 and T_4 are part of 4-MR T-units, and they are located in large and small pore channels, respectively. Thus, based on their siting, the T-sites may be grouped into two distinct tetrahedral environments, namely, $T_{1,2}$ and $T_{3,4}$. The identity of these non-equivalent Al sites is fully revealed in the 3Q-MAS spectrum of NH_4^+/H$^+$-mordenite. The larger P_Q value for Al^{IV}(II) implies a stronger electric field gradient at this Al site, allowing us to identify and assign the Brønsted acidic environments Si–O(NH_4^+)–Al$^-$ and Si–O(H$^+$)–Al to the two isotropic aluminium resonances in the 3Q-MAS spectrum. Independent ^{1}H-^{27}Al 3Q-t$_2$-REDOR experiments support these assignments.[21]

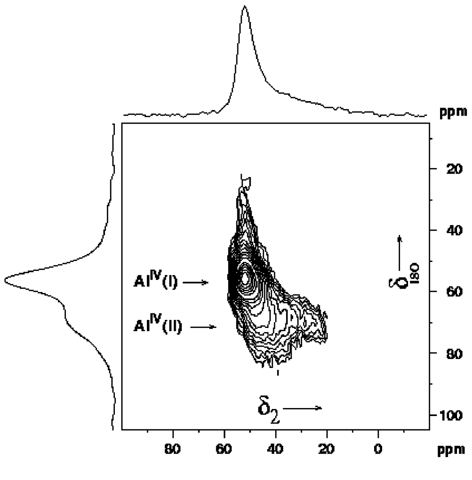

Fig. 2 ^{27}Al 3Q-MAS spectrum of NH_4^+/H$^+$-MOR. The anisotropic projection onto the δ_2 axis (top), which gives the classical MAS spectrum, displays only one broad tetrahedral resonance. On the contrary, the isotropic projection onto the δ_{ISO} axis (left) shows two different tetrahedral resonances [Al^{IV}(I), Al^{IV}(II)], identified as the Brønsted acid sites Si–O(H$^+$)–Al$^-$ and Si–O(NH_4^+)–Al$^-$, respectively.

It is pertinent to mention that corroborated evidence for the presence of two distinct Brønsted acid environments located in large pore (main) and small pore (side pockets) channels of mordenite is provided by previous FT-IR studies.[10,22,23] Further, similar observations, using FT-IR studies, were also made in zeolites ZSM-12[10] and NCL-1,[24] both having large pore unidimensional channels like mordenite.

We have shown that [^{27}Al]-^{1}H REAPDOR NMR is a potentially useful technique to study Brønsted acid environments in zeolites. By localizing acidic protons as NH_4^+ and H$^+$, we are able to distinguish the structurally different Brønsted acid sites located in the main 12 MR and 8 MR channels of mordenite. Further, REAPDOR measurements aid in the determination of Al–H distance for these distinct sites. The non-equivalence among the Brønsted acid environments is also revealed by ^{27}Al triple quantum MAS experiments.

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