Double Rotation and Magic-Angle Spinning NMR Study of an Ultrastable Y Zeolite

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Abstract: ^{27}Al double rotation (DOR) NMR is applied to a USY zeolite. It is shown clearly that a fraction of the tetrahedral aluminum species present suffers from second-order quadrupolar anisotropy. This is evident since DOR spinning sidebands of a tetrahedral species clearly appear. This shows the utility of the DOR method for studying highly distorted sites and/or nonframework aluminum sites in zeolites.

I. Introduction

Magic-angle spinning (MAS) is a routine NMR technique used for the study of zeolites. Normal MAS can average out many interactions experienced by a spin $-^1/_2$ nucleus such as chemical shift anisotropy and weak dipolar interactions, thus producing sharp lines that can be interpreted in a similar fashion to liquid-state NMR spectra. However, normal MAS cannot totally average out quadrupolar interactions experienced by spin $>^1/_2$ nuclei. This severely limits the ability to identify, in the solid state, molecular functionalities which involve quadrupolar nuclei. From second-order perturbation theory, the central transition of spin $>^1/_2$ nuclei (as for other transitions) is subject to field-dependent frequency shift and spectral broadening (powder averaging), which normal MAS cannot average to zero. The point of double rotation (DOR) NMR is to remove the anisotropic part (line-broadening part) of the second-order quadrupolar interaction by rendering it time dependent via the simultaneous rotation of the sample about two axes of specific direction relative to the Zeeman static field.[1]

In the past year we have made double rotation (DOR) NMR measurements in our lab on a variety of model compounds. We found that for many of the ^{27}Al containing model compounds, the DOR technique clearly improves the resolution of spectra of quadrupolar nuclei beyond what is achievable with MAS,[2] due to the removal of second-order quadrupolar anisotropy. In such cases, the improvements in resolution due to DOR are quite impressive. For less-well-ordered materials such as zeolites, the practical utility of the DOR method still remains largely to be determined.

The utility of the DOR technique for application to quadrupolar nuclei in "imperfect crystals" (e.g. ^{27}Al in zeolites) is quite often dependent on the strength of the quadrupolar interaction as compared to the spread in true shifts of the sites of interest. (By "true" shifts here we mean the resultant isotropic shift that includes the isotropic chemical shift and also the second-order quadrupolar isotropic shift.) If the observed line widths under MAS result mainly from a distribution of isotropic shifts, then DOR cannot possibly improve the resolution. However, if the line widths are dominated by second-order quadrupolar anisotropy, then DOR holds great promise as a means of finding unique resonances associated with particular lattice sites. It is shown here that a portion of the "tetrahedral region" in the ^{27}Al MAS spectra of our USY zeolite is dominated by second-order quadrupolar broadening. The DOR technique is able to average effectively the second-order quadrupolar anisotropy experienced by the ^{27}Al nuclei contributing to that region of the spectrum. This clearly shows the utility of the DOR technique for direct detection of previously unobserved distorted environments. This opens questions concerning assignment of newly detected resonances which will require some clever sample treatments and preparations to truly identify the nature of the responsible sites. From a purely practical standpoint, it at least provides another measurement to which the catalytic properties can be correlated.

We would like to restate that the above-mentioned interplay between the second-order quadrupolar interaction and dispersion of isotropic shifts appears to be the key parameter in ^{27}Al DOR NMR of zeolites. We have found many zeolites for which DOR is NOT effective in improving the resolution, and we conclude that shift dispersion is the key line-broadening mechanism in those cases. The general usefulness of the DOR technique for study of ^{27}Al in zeolites will unfold as more and more zeolites are examined.

II. Experimental Section

^{27}Al DOR NMR measurements were performed on 400- and 200-MHz spectrometers. Rotor synchronized techniques were used to suppress the odd order spinning sidebands.[3] The DOR probe used was home-built and follows closely the design of Wu.[4] ^{27}Al MAS NMR measurements were made with a Doty high-speed spinning probe (5-mm rotors) using a minimum spinning speed of 10 kHz. All shifts are referenced to $AlCl_3$(aq) at 0 ppm. The 90° pulse times were set on $AlCl_3$(aq) (15 μs for DOR and 9 μs for MAS) and then divided by 3 to give the proper pulse length for a 90° pulse on the central transition of ^{27}Al ($I + ^1/_2 = 3$). Recycle delays of 0.5 s were typically used.

In addition to the as-produced USY zeolite, a washed sample was also studied. The sample was washed three times in an EDTA solution at 50 °C to attempt to remove any nonframework aluminum. The washed catalyst was then dried in a vacuum oven at 120 °C.

III. Results and Discussion

Shown in Figure 1 are the ^{27}Al MAS and DOR spectra of USY zeolite collected in a 9.4-T field (the top spectra show all peaks without vertical expansion; the bottom spectra are expanded vertically). Notice in the MAS spectra of Figure 1 that there are clearly peaks at 60 ppm (tetrahedral) and at 0 ppm (octahedral). There is also a broad resonance that seems to be centered somewhere between 40 and 20 ppm. Also, note the asymmetry of the octahedral "peak". It has always been unclear how such

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(1) Samoson, A.; Lippmaa, E.; Pines, A. *Mol. Phys.* **1988**, *65*, 1013.

(2) Haddix, G. W.; Narayana, M.; Tang, S. C.; Wu, Y. *J. Phys. Chem.* **1993**, *97*, 4624.

(3) Samoson, A.; Lippmaa, E. *J. Magn. Reson.* **1989**, *84*, 410.

(4) Wu, Y.; Sun, B. Q.; Pines, A.; Samoson, A.; Lippmaa, E. *J. Magn. Reson.* **1990**, *89*, 297.

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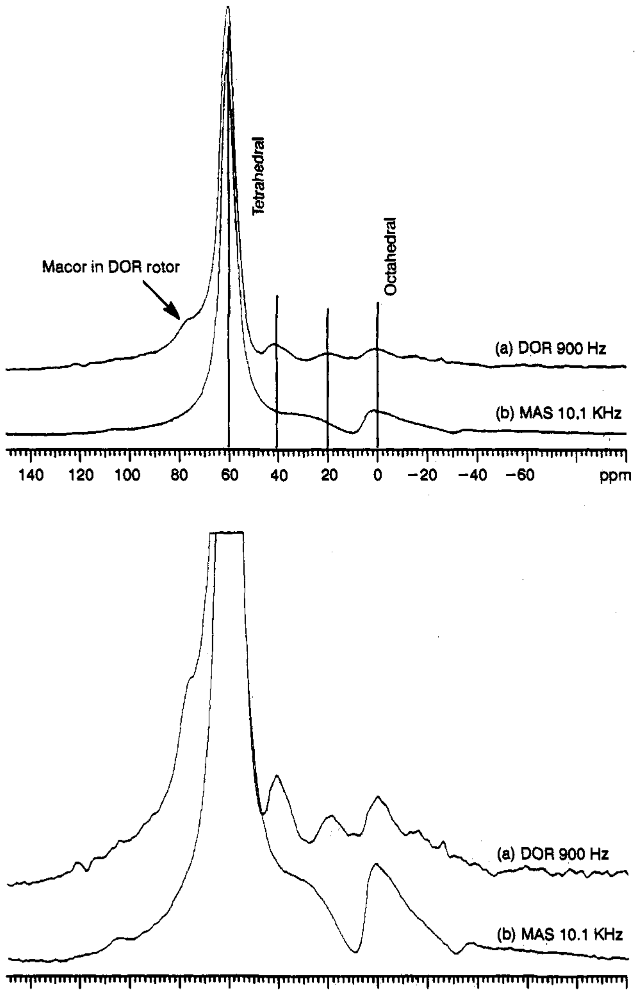

Figure 1. ^{27}Al DOR and MAS spectra of USY zeolite at 9.4 T (bottom shows vertical expansion): (a) DOR, outer rotor at 900 Hz; (b) MAS, 10.1 kHz.

broad "resonances" should be accounted for in ^{27}Al MAS spectra.[5] Many have postulated species with truly separate isotropic shifts, while others have postulated either essentially tetrahedral or octahedral sites that are somewhat distorted, thus lending some second-order quadrupolar anisotropy to the tetrahedral and/or octahedral peak.

Shown directly above the MAS spectra in Figure 1 are the DOR spectra with an outer rotor spinning speed of 900 Hz. The small downfield shoulder at ca. 80 ppm is due to macor pins used in the end of the DOR outer rotor as bearings. Since the odd numbered spinning sidebands are nulled, we expect spinning sidebands to appear at multiples of 1800 Hz (even sidebands) from the isotropic peaks. In the DOR spectrum, we see two small peaks between 60 and 0 ppm. The small peak at ca. 40 ppm is almost exactly 1800 Hz from the tetrahedral peak, suggesting it is a spinning sideband. The peak at ca. 20 ppm is not quite in the proper position to be cleanly identified as a sideband of either the 60- or the 0-ppm peak. To further study the origin of the peak at 40 and 20 ppm, the DOR outer rotor frequency was varied, and the peak positions were followed as a function of outer rotor spin rate (see Figure 2). The peak at 40 ppm is definitely a spinning sideband of the tetrahedral peak at 60 ppm. It appears that the peak at 20 ppm may be made up of an isotropic peak at about 20 ppm and also a component that is due to the second even sideband of the tetrahedral peak (3600-Hz separation with a DOR outer rotor frequency of 900 Hz).

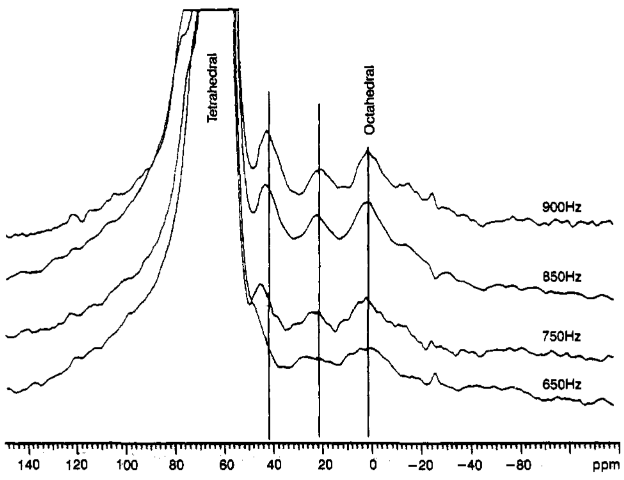

Figure 2. ^{27}Al DOR spectra collected with varying outer rotor spin frequencies at 9.4 T: (a) 900 Hz; (b) 850 Hz; (c) 750 Hz; (d) 650 Hz.

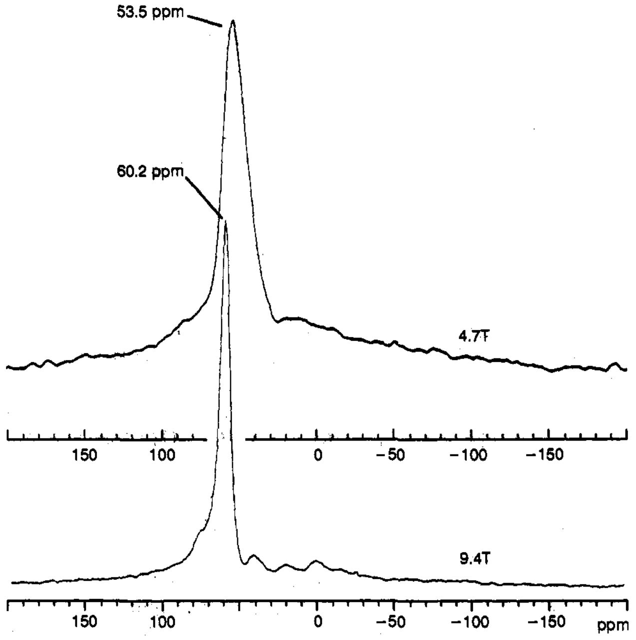

Figure 3. ^{27}Al DOR spectra collected at different magnetic fields (outer rotor spin frequency = 900 Hz): (a) 4.7 T; (b) 9.4 T.

Figure 3 compares DOR spectra of the zeolite collected at two different magnetic fields. Clearly, the spectrum collected at 9.4 T has better resolved peaks at 20 and 40 ppm. These peaks are not discernible in the 4.7-T spectrum. It is also interesting to note the shift of the 60-ppm peak upon the field change. At 9.4 T the tetrahedral peak is centered at 60.2 ppm, but at 4.7 T it occurs at 53.5 ppm. This is a clear indication that the position of the main tetrahedral peak maximum is being affected by the second-order quadrupolar interaction. (The chemical shift stated in ppm is independent of magnetic field.) Given these two shifts, the true chemical shift of the main tetrahedral species can be estimated to be 62.4 ppm by use of the following equation.

$$\sigma_{\text{true}} = \frac{s_{\text{hi}}(\omega_{0\text{hi}}/\omega_{0\text{lo}})^2 - s_{\text{lo}}}{(\omega_{0\text{hi}}/\omega_{0\text{lo}})^2 - 1} \qquad (1)$$

In eq 1, σ_{true} is the true chemical shift (in ppm); s_{lo} and s_{hi} are the observed shifts at the low and high fields, respectively (in ppm); and $\omega_{0\text{lo}}$ and $\omega_{0\text{hi}}$ are the Larmor frequencies of the nucleus of interest at the low and high fields, respectively. It should also be noted that a rough estimate of the value for ω_Q (quadrupolar coupling constant) can also be found from the observed shifts at

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(5) Engelhardt, G.; Michel, D. *High-Resolution Solid-State NMR of Silicates and Zeolites*; Wiley: New York, 1987; p 274.

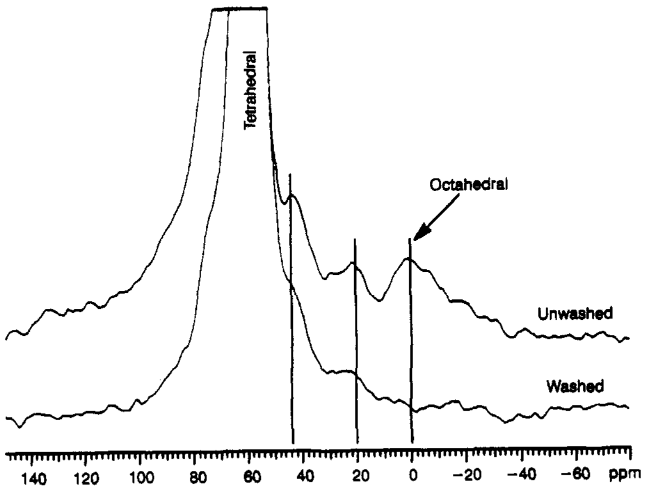

Figure 4. ^{27}Al DOR spectra for washed and unwashed USY zeolite at 9.4 T (outer rotor spin frequency = 800 Hz): (a) unwashed; (b) washed.

different fields using the following equation:

$$s_{\text{hi}} - s_{\text{lo}} = -\frac{1}{30}\omega_{\text{Q}}^2\left(1 + \frac{\eta^2}{3}\right)\left(I(I+1) - \frac{3}{4}\right)\left(\frac{1}{\omega_{0\text{hi}}^{\ 2}} - \frac{1}{\omega_{0\text{lo}}^{\ 2}}\right) \times 10^6 \quad (2)$$

where

$$\omega_{\text{Q}} = \frac{3e^2qQ}{2I(2I-1)h} \quad (3)$$

η is the asymmetry parameter ($0 \leq \eta \leq 1$), and I is the spin of the nucleus ($^5/_2$ for ^{27}Al). Equation 2 can be rearranged and solved for the value of $\omega_{\text{Q}}^2(1 + \eta^2/3)$. Then by assuming that η is either 0 or 1, ω_{Q} can be bracketed. In this case the value of ω_{Q} is found to be between 0.261 and 0.301 MHz for the main tetrahedral peak.

It should also be pointed out that the "peaks" at 60 ppm and between 40 and 20 ppm of the MAS spectrum are unlikely to result from a *single* anisotropic line shape representative of a *single* tetrahedral Al species experiencing a well-defined quadrupolar interaction. This is clear from the simple fact that the overall line shape between 90 and 10 ppm of the MAS spectrum will never fit properly to a single powder pattern. The fact that the DOR results in spinning sidebands shows that the intensity between about 40 and 10 ppm in the MAS spectrum is at least partially due to tetrahedral Al. If the peak at 20 ppm in the DOR spectrum could be confidently assigned to be a sideband also, then all of the intensity between 40 and 10 ppm of the MAS spectrum could be attributed to tetrahedral Al. In any case it is fairly clear from this work that there is clearly *some* distorted tetrahedral Al giving rise to spectral intensity in the 40- to 10-ppm region of ^{27}Al MAS spectra at 9.4 T. This obviously has ramifications for the fitting of ^{27}Al MAS spectra of these zeolites. It is evident now that broad "peaks" that have been attributed to nonframework Al are not solely due to distinct species with different isotropic shifts. The most plausible scenario is that there is a distribution of quadrupolar interactions for both the tetrahedral and octahedral geometries. This distribution along with the second-order quadrupolar anisotropy associated with the distorted sites gives rise to the broad lines generally observed under MAS. The inherent line widths of true isotropic peaks and spinning sidebands observed under DOR arise from the distribution of sites, and no amount of spinning will remove this.

We attempted to wash any "nonframework" Al from the zeolite using the EDTA solution. We hoped that in this manner we might be able to identify the 20-ppm peak as either a unique site or a spinning sideband by studying any relative changes between the intensity of the 20-ppm peak and that of the 40-ppm spinning sideband upon washing. Shown in Figure 4 is a comparison of the DOR spectra of the washed and unwashed zeolite. It appears that the wash has removed the majority of the octahedral Al (ca. 0 ppm). The intensity of the spinning sideband (near 40 ppm) has apparently dropped, suggesting loss of some highly distorted tetrahedral Al, and it appears that the peak at 20 ppm has dropped in intensity also. Unfortunately, correlation between the loss of the spinning sideband intensity at 40 ppm and the 20-ppm peak really tells us very little about the nature of the 20-ppm peak. It could be a spinning sideband of a tetrahedral species, or it could be a unique species (an isotropic peak) that was removed via the wash.

IV. Conclusion

In spite of the uncertainty in the origin of the 20-ppm peak, the DOR result is still of great importance as it without a doubt shows that the tetrahedral Al atoms in the sample are subject to second-order quadrupolar broadening that can be attacked using DOR. The uncertainty about the true identity of the 20-ppm peak could possibly be cleared up if (a) we could spin our DOR outer rotor considerably faster, (b) we could develop a means of removing even order spinning sidebands, or (c) we could perform the measurement at higher field. The appearance of spinning sidebands and/or separate resonances under DOR clearly opens the door for further strides in characterization of zeolites using NMR.

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