

## Determination of the $^{31}\text{P}$ – $^{27}\text{Al}$ $J$ -Coupling Constant for Trimethylphosphine Bound to the Lewis Acid Site of Zeolite HY

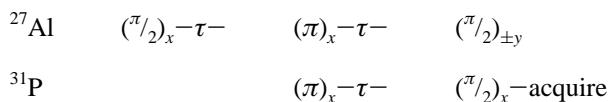
Hsien-Ming Kao and Clare P. Grey\*

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794-3400

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The exact nature of the Lewis acid sites in acidic zeolite catalysts remains unresolved. These sites have been extensively studied with probe molecules and NMR and IR techniques and are thought to be associated with the nonframework alumina clusters formed during the calcination or steaming process used to activate the zeolite.<sup>1,2</sup> Recent NMR experiments have proposed that these sites are due to both 4- and 5-fold-coordinated aluminum atoms.<sup>3</sup> It is difficult to observe these sites directly with one-pulse  $^{27}\text{Al}$  NMR methods, due to the large  $^{27}\text{Al}$  quadrupole coupling constants (QCCs) associated with these sites, which results in considerable line-broadening and a shift of the resonances out of the typical chemical shift range for  $^{27}\text{Al}$ . In addition, it is difficult to separate the broad resonances from those of other extraframework aluminum sites. We have observed these sites indirectly via dipolar coupling to adsorbed probe molecules (for example, monomethylamine and trimethylphosphine (TMP)).<sup>4,5</sup> In this paper, we report the indirect observation of these sites in dehydroxylated HY via  $J$ -coupling to the adsorbed probe molecule TMP. Homonuclear  $J$ -coupling NMR methods (COSY and INADEQUATE) have previously been used by Fyfe et al.<sup>6</sup> to establish the  $^{29}\text{Si}$ –O– $^{29}\text{Si}$  connectivities in zeolites. Recently, they demonstrated that coherence transfer via heteronuclear  $J$ -coupling between spin  $1/2$  and quadrupolar nuclei can be achieved in the solid state with INEPT and DEPT experiments.<sup>7</sup> These methods were used to determine a  $^{31}\text{P}$ – $^{27}\text{Al}$   $J$ -coupling constant of 268 Hz for  $\text{Ph}_3\text{P}$ – $\text{AlCl}_3$ .

Dehydroxylated HY was prepared by slowly heating, under vacuum, a small amount (approximately 0.3 g) of  $\text{NH}_4\text{Y}$  (Linde-LZY62, Si/Al = 2.6) to 600 °C and then maintaining the sample at 600 °C for a further 16 h (as described in ref 5). Approximately 20 TMP molecules per unit cell were then adsorbed at room temperature. A Si/Al ratio of 3.2 was determined for the dehydroxylated sample by  $^{29}\text{Si}$  MAS NMR. In addition, X-ray powder diffraction showed a considerable loss of crystallinity for this sample. All NMR experiments were carried out on a Chemagnetics CMX 360 spectrometer, with a tripled-tuned probe equipped with 7.5 mm zirconia rotors. The standard INEPT sequence, with appropriate phase cycling, was employed for the  $^{27}\text{Al}$   $\rightarrow$   $^{31}\text{P}$  INEPT experiments and is shown below:<sup>8</sup>



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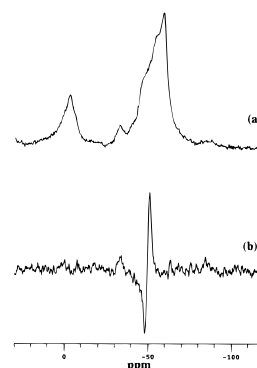
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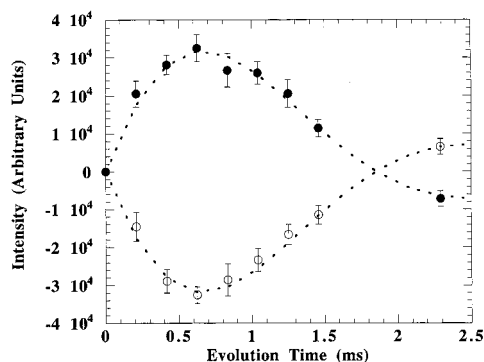
**Figure 1.** (a)  $^{31}\text{P}$  MAS NMR spectrum of TMP adsorbed in dehydroxylated zeolite Y. (b)  $^{27}\text{Al}$   $\rightarrow$   $^{31}\text{P}$  INEPT spectrum collected with an evolution time,  $\tau$ , of 0.625 ms and a spinning speed of 4.8 kHz and approximately 70 000 transients.

Two sets of experiments were performed. In the first, the  $\pi/2$  and  $\pi$  pulses were applied synchronously with the rotor period (i.e.,  $\tau = (n/\nu_r - \pi/2)$ , where  $\nu_r$  is the spinning speed and  $n$  is an integer). Experiments were also performed where the pulses were applied asynchronously with the rotor period. An  $^{27}\text{Al}$  radio frequency strength of 55 kHz, measured with aqueous aluminum sulfate, was used to excite the  $^{27}\text{Al}$  spins. The  $^{31}\text{P}$   $\pi/2$  pulse lengths of 5  $\mu\text{s}$  and repetition times of 1 s were employed. Since the aluminum quadrupolar coupling constant for the Lewis acid sites bound to TMP was known to be large ( $\sim 11$  MHz),<sup>5</sup> the  $^{27}\text{Al}$   $\pi/2$  and  $\pi$  pulse lengths of approximately one-third of those determined for the liquid were used (i.e., 2 and 4  $\mu\text{s}$ , respectively).

The  $^{31}\text{P}$  MAS NMR spectrum of TMP adsorbed on dehydroxylated HY (Figure 1a) shows resonances at  $-3$  ppm and in the range of  $-30$  to  $-60$  ppm. These are assigned to the protonated trimethylphosphonium cation,  $\text{TMPH}^+$  ( $-3$  ppm), which results from reaction of the TMP with the Brønsted acid sites and sites due to TMP bound to the Lewis acid sites created in the dehydroxylation process ( $-30$  to  $-60$  ppm). A number of different resonances have been observed in the  $-30$  to  $-60$  ppm spectral region by previous workers; these resonances arise from different Lewis acid sites and/or from multiplet structure due to  $^{31}\text{P}$ – $^{27}\text{Al}$   $J$ -coupling.<sup>9,10</sup> We previously assigned the resonance at  $-60$  ppm to physisorbed or weakly bound TMP, on the basis of a minimal  $^{31}\text{P}/^{27}\text{Al}$  TRAPDOR NMR effect seen (at  $-150$  °C) for this resonance and the mobility, at room temperature, of the TMP molecules bound to this site. The resonance at  $-46$  ppm showed a significant  $^{31}\text{P}/^{27}\text{Al}$  TRAPDOR NMR effect at  $-150$  °C, which allowed us to assign this site to TMP directly bound to aluminum atoms (i.e., an aluminum Lewis acid site). The resonance at approximately  $-55$  ppm is due to a subset of TMP molecules in rapid exchange between the physisorbed TMP ( $-60$  ppm) and Lewis acid sites ( $-46$  ppm). This process is frozen out at  $-150$  °C and only the  $-60$  and  $-46$  ppm resonances are observed.<sup>5</sup>

A  $^{27}\text{Al}$   $\rightarrow$   $^{31}\text{P}$  INEPT spectrum obtained with  $\tau = 0.625$  ms with rotor-synchronized  $\pi/2$  and  $\pi$  pulses is shown in Figure 1b. The dispersive nature of the INEPT signal is clearly apparent in the FID (i.e., the signal intensity is 0 at the beginning of the FID). Only the resonance at approximately  $-49$  ppm in the one-pulse spectrum gives rise to a significant INEPT signal, consistent with the assignment of this resonance to an aluminum Lewis acid site directly bound to the phosphine molecule. The resonance is due to coherence transfer from the ( $1/2$ ,  $-1/2$ ) Zeeman levels of the  $^{27}\text{Al}$  spins coupled to the  $^{31}\text{P}$  nuclei. We have previously obtained an estimate for the QCC of aluminum

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**Figure 2.** The intensities of the both peaks of the dispersive INEPT resonance, plotted as a function of  $\tau$ . The experimental data (points) were fit with the function  $I(\tau) = C \sin(2\pi J\tau) \exp(-\tau/T_2)$  (dashed line) where  $J = 270$  Hz,  $T_2 = 2.5$  ms, and  $C$  is a constant.

atoms associated with this Lewis acid site of approximately 11 MHz, and the QCC is so large that only the  $(1/2, -1/2)$  states of  $^{27}\text{Al}$  are excited by the initial  $\pi/2$  pulse. The experiment was repeated for different values of  $\tau$  with both rotor-synchronized and asynchronous sequences. A significant reduction in the intensity of the INEPT signal was observed in the non-rotor-synchronized experiment, presumably due to a decrease in the buildup of the  $I_x S_z$  coherence, prior to the  $^{27}\text{Al} \rightarrow ^{31}\text{P}$  magnetization transfer, caused by an interference between the  $J$ - and dipolar-coupling dephasing mechanisms. The average dipolar coupling is 0 during the evolution time  $\tau$  in the synchronous experiment. Additional evidence that the INEPT signal results from a  $^{31}\text{P}$ - $^{27}\text{Al}$   $J$ -coupling mechanism is obtained from the variation of the signal with  $\tau$  (Figure 2). An increase in signal intensity is observed with increasing  $\tau$  until a maximum is reached at approximately 0.625 ms. The signal then decreases in magnitude, inverting in sign between 1.25 and 2.29 ms. In theory, a maximum signal intensity for two coupled spin- $1/2$  nuclei is predicted when  $\tau = 1/(4J)$ , assuming that the spin-spin relaxation time ( $T_2$ )  $\gg 1/J$ . However, for short  $T_2$  values, which is expected to be the case for  $^{27}\text{Al}$  nuclei with large QCCs, the maximum may occur for shorter values of  $\tau$ , and thus, the whole INEPT curve was fit assuming a sinusoidal evolution of the signal intensity  $I(\tau)$  for both peaks in the INEPT signal and an exponential decay due to  $T_2$  (i.e.,  $I(\tau) \propto \sin(2\pi J\tau) \exp(-\tau/T_2)$ ). Values for the magnitude of  $^{31}\text{P}$ - $^{27}\text{Al}$   $J$ -coupling constant and  $T_2$ , of  $270 \pm 10$  Hz and 2.5 ms, respectively, were obtained. A series of experiments was also performed on the TMP- $\text{AlCl}_3$  complex formed in zeolite NaX, to confirm the validity of our approach. The  $^{31}\text{P}$ - $^{27}\text{Al}$   $J$ -coupling and  $^{27}\text{Al}$  QCC can be directly obtained from the  $^{31}\text{P}$  and  $^{27}\text{Al}$  NMR spectra, respectively, and are similar to those obtained for the TMP- $\text{AlCl}_3$  complex in HY.<sup>10</sup> Again, the  $^{27}\text{Al} \rightarrow ^{31}\text{P}$  INEPT curve could only be fit if a nonzero  $T_2$  decay was included. Finally, refocused INEPT experiments were not successful for the Lewis acid complex in NaX, presumably due to the short  $^{27}\text{Al}$   $T_2$  values in this system.

The combination of the second-order quadrupolar interaction and the dipolar coupling can, for large QCCs, result in significant changes in the spacings between the peaks in the  $J$ -coupling manifolds of  $I = 1/2$  and  $S > 1/2$  coupled spins.<sup>11</sup> However, since we only observe INEPT signals from  $I = 1/2$  ( $^{31}\text{P}$ ) nuclei coupled to the  $(1/2, -1/2)$  Zeeman levels of the quadrupolar nucleus, and these are affected equally, this mechanism will not affect the magnitude of the measured  $J$ -coupling.

Coherence transfer to the resonance at  $-32$  ppm is also observed, suggesting that the TMP giving rise to this resonance is bound to an aluminum atom. Furthermore, the  $J$ -coupling for this site appears to be significantly larger, an inversion in the signal being observed for evolution times as little as 1.25 ms suggesting a very large  $J$ -coupling constant in excess of 400 Hz. However, the signal-to-noise obtained in these experiments for this relatively weak signal prevents further analysis: further work is needed to improve the signal-to-noise of these experiments, possibly by treating the materials under conditions where the intensity of this resonance is maximized. The observation of an INEPT signal was surprising, given that we were unable to observe a significant  $^{31}\text{P}/^{27}\text{Al}$  TRAPDOR effect for this resonance. This suggests that this resonance may be due to a TMP molecule bound to an Al site with a very large QCC.

The  $J$ -coupling between two nuclei will depend on the degree of s-orbital contribution to the P-Al bond. This will depend on a variety of factors which include the electronegativity and steric bulk of the groups bound to the phosphorus atom of the phosphine group and the coordination number and electronegativity of the atoms bound to the aluminum atom.<sup>12</sup> The  $^{31}\text{P}$ - $^{27}\text{Al}$   $J$ -coupling has been observed in solution for a variety of tetrahedral  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ , and  $\text{Al}(\text{BH}_4)_3$  Lewis adduct complexes, with increasing values of 248, 265, and either 263 or 280 Hz for the TMP- $\text{AlBr}_3$ , TMP- $\text{Al}(\text{BH}_4)_3$ , and TMP- $\text{AlCl}_3$  complexes, respectively, where two different values were independently determined for the  $\text{AlCl}_3$  complex in two different solvents.<sup>13-16</sup> More recently, two TMP- $\text{AlCl}_3$  coordination complexes were detected after adsorption of TMP on a mixture of  $\text{AlCl}_3$  and zeolite HY or NaHY, in which the  $\text{AlCl}_3$  molecule coordinated to one and two TMP molecules.<sup>10</sup>  $^{31}\text{P}$ - $^{27}\text{Al}$   $J$ -coupling constants and internuclear distances of 299.5 Hz and 2.58 Å and 260 Hz and 2.96 Å were determined for the two adducts, respectively. The decrease in  $J$ -coupling from the tetrahedral to the 5-fold-coordinated complex is in agreement with the decrease in the proportion of s-character of the P-Al bond with increased aluminum coordination number. The  $^{31}\text{P}$ - $^{27}\text{Al}$   $J$ -coupling constants for the  $\text{AlCl}_3$ - $\text{PPh}_3$  complexes are 190 and 268 Hz in solution and in the solid state, respectively.<sup>7,14</sup> From the limited literature that is available, it is noticeable that the  $^{31}\text{P}$ - $^{27}\text{Al}$   $J$ -coupling constants determined in solution are typically smaller than those determined in the solid state for the same complex. This may be due to the occurrence of exchange processes in solution. Thus, comparing our measured value for the Lewis acid site in HY (270 Hz), with  $J$ -couplings determined for the same ligand in the solid state, the  $J$ -coupling is intermediate between the values obtained for the 4- and 5-fold-coordinated TMP- $\text{AlCl}_3$  complexes. Given the increased electronegativity of oxygen over chlorine, we can then tentatively assign the aluminum in the TMP-Lewis acid adduct to a 5-fold site; this suggests that the Lewis acid site comprises a tetrahedrally coordinated aluminum site. Further studies are in progress to measure the  $J$ -coupling in a greater variety of Lewis acid complexes to correlate the measured  $J$ -coupling with both the aluminum coordination number and the strength of probe molecule binding.

**Acknowledgment.** Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation National Young Investigator program (DMR-9458017) for support of this research. The solid state NMR spectrometer was purchased with a grant from the National Science Foundation (CHE-9405436).

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