

## Characterization of Acid Sites in Zeolitic and Other Inorganic Systems Using Solid-State $^{31}\text{P}$ NMR of the Probe Molecule Trimethylphosphine Oxide

Edward F. Rakiewicz,<sup>†</sup> Alan W. Peters,\* and Richard F. Wormsbecher

Washington Research Center, W.R. Grace and Company, 7500 Grace Drive, Columbia, Maryland 21044

Kevin J. Sutovich and Karl T. Mueller\*

Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, Pennsylvania 16802

Received: January 15, 1998; In Final Form: February 18, 1998

The ability to determine the types and concentrations of acid sites in zeolites and fluid-catalytic cracking systems is important for an increased understanding of structure/performance relationships in these materials. Currently, a variety of thermal methods exist that allow quantitative measurement of the Brønsted acid site concentration. In addition, numerous spectroscopic methods using probe molecules are available for qualitative and quantitative detection of both Brønsted and Lewis acid sites. In studies utilizing solid-state NMR spectroscopy, probe molecules containing  $^{31}\text{P}$  nuclei present substantial advantages over probes isotopically enriched with  $^{13}\text{C}$  and  $^{15}\text{N}$  nuclei. These advantages include increased sensitivity and chemical shift dispersion. While a number of phosphorus-based experiments have probed the interaction of trimethylphosphine with solid acid catalysts, initial studies of the more stable trimethylphosphine oxide (TMPO) have only been reported on amorphous silica–alumina surfaces. We now report the successful completion of TMPO studies of acid sites in several systems including  $\gamma$ -alumina; HY, USY, and dealuminated Y zeolites; and a silica–alumina catalyst with an aluminum concentration of 13%. Comprehensive and consistent assignments to particular types of sites are made for all resonance lines in the  $^{31}\text{P}$  MAS NMR signals from TMPO. Based on results from dehydroxylated  $\gamma$ -alumina, new chemical shift assignments are made for the TMPO/Lewis acid complex. The assignments of  $^{31}\text{P}$  resonances from molecules not directly associated with nearby  $^{27}\text{Al}$  nuclei (such as crystalline or physisorbed TMPO species) are supported using  $^1\text{H}/^{31}\text{P}/^{27}\text{Al}$  triple-resonance NMR methods. The concentrations of Brønsted acid sites from the NMR results are compared with concentrations obtained from isopropylamine/temperature-programmed-desorption measurements, and substantial agreement between the methods is found.

### Introduction

Acidic forms of high-surface-area materials are important for a number of catalytic reactions, including fluid-catalytic cracking of petroleum to produce useful fractions with a desired range of molecular weights. Important for understanding the chemistry associated with catalysis is the structural characterization and quantification of acid sites. Methods for the characterization and quantification of acidic sites in solids are well-documented in the literature,<sup>1–14</sup> and most of these approaches involve the loading of a weakly basic probe molecule onto the solid followed by spectroscopic and/or thermal characterization. One of the most commonly used techniques is pyridine/diffuse-reflectance IR spectroscopy (DRIFTS)<sup>1–3</sup> which measures the qualitative amounts of Lewis and Brønsted acid sites in a given material. Another common method used to characterize acid sites is isopropylamine/temperature-programmed desorption (IPA/TPD)<sup>10</sup> which provides a quantitative measure of Brønsted sites. However, this method is not capable of providing information on Lewis sites since it depends on the protonation of the IPA molecule and subsequent formation of propylene. A

need exists for methods that are both discriminating and quantitative with respect to populations of Lewis and Brønsted acid sites in catalytic systems.

Nuclear magnetic resonance (NMR) spectroscopy is a powerful analytic tool, providing quantitative measurement of populations of nuclei discriminated by their chemical shift and other parameters related to the local structural environment. A variety of solid-state  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR methods have been applied to the study of solid acidity. Many of the probe molecules used in these studies are amines such as *n*-butylamine,<sup>5</sup> pyridine,<sup>4</sup> and ammonia.<sup>7</sup> However, these studies are hampered by low sensitivity and/or limited chemical-shift ranges of the observed nuclei.  $^{13}\text{C}$  and  $^{15}\text{N}$  are the NMR-active isotopes used in these studies, and these species have natural abundances of 1.1% and 0.4%, respectively. Therefore, isotopic labeling is generally necessary. Both  $^{13}\text{C}$  and  $^{15}\text{N}$  also have moderate to low gyromagnetic ratios, and this further contributes to their low NMR sensitivity.

The use of phosphorus-containing bases in conjunction with solid-state  $^{31}\text{P}$  NMR<sup>6,8,9,12,13</sup> overcomes the most difficult experimental limitations associated with  $^{13}\text{C}$  and  $^{15}\text{N}$  studies. The  $^{31}\text{P}$  isotope is 100% abundant in nature, and it also has a larger gyromagnetic ratio than  $^{15}\text{N}$  and  $^{13}\text{C}$ . The large isotropic chemical shift range and full chemical shift anisotropy of  $^{31}\text{P}$

<sup>†</sup> Current address: PPG Industries, Inc. 4325 Rosanna Drive Allison Park, PA 15101.

\* To whom correspondence should be addressed.

provide a wealth of information on the local electromagnetic interactions of the nucleus and can therefore be applied directly in the study of phosphorus environments.

A number of studies of the acidity of zeolites and related oxides have been performed using trimethylphosphine (TMP) as a probe molecule for solid-state  $^{31}\text{P}$  NMR.<sup>6,9,12,13</sup> This relatively strong Lewis base ( $\text{p}K_{\text{a}} = 5.3$  in  $\text{H}_2\text{O}$ ) has shown substantial promise as a probe of acidic sites in solids. Formation of a protonated  $\text{TMPH}^+$  adduct is characterized by an isotropic chemical shift of approximately  $-3$  ppm relative to aqueous  $\text{H}_3\text{PO}_4$  and scalar coupling of approximately 500 Hz between  $^1\text{H}$  and  $^{31}\text{P}$  nuclei.<sup>15</sup> Lewis-bound TMP exhibits a considerable upfield shift relative to the Brønsted site, and, if an aluminum is involved in the bonding,  $^{31}\text{P}/^{27}\text{Al}$  scalar coupling results in a well-characterized multiplet pattern. Recently, Kao and Grey<sup>16,17</sup> have used  $^{31}\text{P}/^{27}\text{Al}$  transfer of populations in double resonance (TRAPDOR) NMR<sup>18</sup> to study the binding of trimethylphosphine on dehydroxylated zeolite HY, demonstrating the use of novel double-resonance NMR methods as probes of the binding of molecules on surfaces and in zeolites.

When TMP is introduced in excess, the room-temperature dynamics of chemical exchange between bound species and the liquidlike TMP molecules complicate the identification and enumeration of acidic sites, and therefore the temperature must be lowered in order to investigate the binding. TMP is a highly flammable air-sensitive liquid at room temperature and requires great care in its handling. Studies on amorphous silica–alumina indicate that the use of trialkylphosphine oxides offers several advantages for the study of acidic binding sites.<sup>8</sup> These oxides are solids at room temperature, they are not susceptible to oxidation, and titration of the molecules onto acidic solids can be accomplished using solution-state chemistry. However, there are no comprehensive published reports describing the use of trialkylphosphine oxides to systematically study other interesting catalytic materials such as zeolites and aluminas.

In this paper we report our progress on the use of trimethylphosphine oxide (TMPO) and solid-state  $^{31}\text{P}$  NMR to study the acidic nature of solids, specifically zeolites and aluminas. The studies provide an unambiguous assignment of Lewis acid sites based on results from TMPO adsorbed directly onto a sample of dehydroxylated Catapal alumina. Samples containing Brønsted acid sites have also been characterized by  $^{31}\text{P}$  MAS NMR of TMPO probes. A sample of ultrastable Y zeolite was further characterized using triple-resonance  $^1\text{H}/^{31}\text{P}/^{27}\text{Al}$  NMR experiments to confirm a number of the specific assignments. Quantification of spectral intensities of resonances assigned to Brønsted sites is used to calculate the concentration of Brønsted acidity in the solids, and these results are compared with those obtained using IPA/TPD. A study of the  $^{31}\text{P}$  NMR spectra of TMPO in samples at various stages of rehydration also demonstrates the need for careful and consistent interpretation of experimental results.

## Experimental Section

A representative collection of a number of acidic solids was chosen for study. The samples are a dehydroxylated  $\gamma$ -alumina, a protonated form of NaY zeolite (HY), an ultrastable Y (USY) zeolite, a low-aluminum Y zeolite, and an amorphous silica–alumina sample containing 13% aluminum. A commercial sample of Catapal A alumina, obtained from Condea (Houston, TX), was calcined for 3 h at 705 °C to prepare the  $\gamma$ -alumina sample. The HY faujasite sample was prepared from NaY by ammonium sulfate exchange of the sodium, and the composition of the ammonium form is given in Table 1. A sample of USY

**TABLE 1: Summary of the Physical Properties of Samples in This Study**

	$\gamma$ -alumina	HY	USY	low-Al Y	silica–alumina
chemical analysis					
% $\text{Al}_2\text{O}_3$	100	21.81	21.82	9.23	12.78
% $\text{Na}_2\text{O}$	0	5.01	4.40	0.17	0.046
% $\text{SiO}_2$	0	72.94	73.80	90.46	86.95
Si/Al	0	2.8	2.9	8.3	6.8
nitrogen adsorption					
total surface area	201	874	744	731	497
zeolite surface area	NA	866	697	668	NA <sup>a</sup>
matrix surface area	NA	9	47	63	NA
X-ray diffraction					
unit cell (nm)	NA	2.466	2.4525	2.436	NA
no. of Al per unit cell	NA	54.14	38.59	19.58	NA
Si/Al	NA	2.55	3.98	8.80	NA

<sup>a</sup> NA = not applicable.

was prepared by hydrothermal dealumination of a sample of  $\text{NaNH}_4\text{Y}$  for 2 h at 700 °C. The low-aluminum Y was prepared by two cycles of hydrothermal dealumination followed by a low-pH (2.9) ammonium sulfate wash. The silica–alumina sample was prepared from a sodium silicate/sodium aluminate slurry by the addition of acid. The resulting gel was dried, and the sodium was removed by washing with ammonium sulfate solution, followed by a final drying of the sample. In all cases residual ammonia was removed by calcination at 650 °C before treatment with TMPO. The samples prepared for this study were characterized for atomic composition and other physical properties, and a listing of a number of relevant results is presented in Table 1.

Prior to characterization by solid-state NMR, samples were prepared following a uniform procedure for loading with TMPO. For each sample studied, approximately 0.8 g of solid was calcined at 600–800 °C for 4 h in a round-bottom flask. After lowering the oven temperature to 150 °C, the flask was capped with a rubber septum. A measured amount of a dry TMPO/ $\text{CH}_2\text{Cl}_2$  solution of known concentration was added to the flask via a gastight syringe, and the mixture was agitated overnight under  $\text{N}_2$  on a mechanical shaker. The solvent was removed under vacuum and the flask transferred into a glovebox where the product was placed into a vial and sealed. For analysis by solid-state NMR, the prepared solid samples were packed into dry MAS rotors of the Chemagnetics Pencil design. Either 5.0 or 7.5 mm rotors with sealed endcaps were used to hold the samples within the NMR probes.

For determination of the quantitative number of acid sites using NMR measurements, it is necessary to first measure the amount of phosphorus in a known mass of a particular sample. Phosphorus quantification was carried out by sample digestion followed by standard ICP analysis. A 0.1 g sample of the zeolite was dissolved in 10 mL of a 1:1:1 mixture of HF,  $\text{HNO}_3$ , and HCl until clear. A further 60 mL of a 5.3% boric acid solution was added to the cool solution, and the ICP analysis was carried out using matched phosphorus standards. To compare the NMR results with another, well-accepted method for analyzing the concentration of Brønsted acid sites, a slightly modified version<sup>19</sup> of the IPA/TPD method described by Kofke et al.<sup>10</sup> was used.

Solid-state  $^{31}\text{P}$  MAS and  $^1\text{H}/^{31}\text{P}$  CPMAS NMR spectra were obtained on both a Chemagnetics CMX Infinity 400 and a Chemagnetics CMX 200 spectrometer operating with  $^{31}\text{P}$  Larmor frequencies of 161.880 or 81.025 MHz, respectively. Typical spinning speeds of 5–8 kHz were used, and nominal 90° pulses were 4  $\mu\text{s}$  in length. Recycle delays of 10–30 s were necessary to allow full recovery of equilibrium magnetiza-

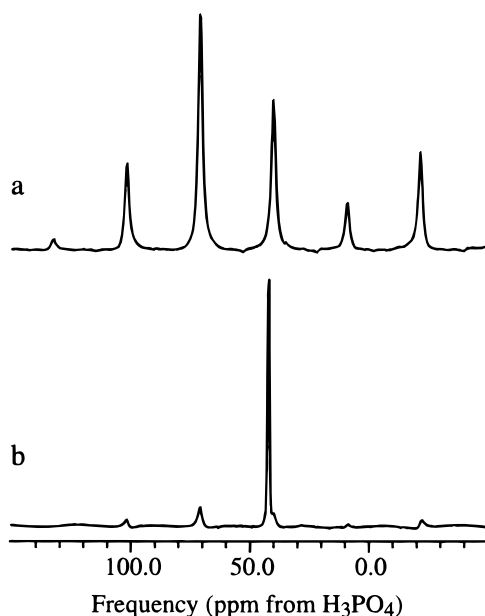
tion. The number of scans collected for each spectrum varied between 500 and 10 000, and the  $^{31}\text{P}$  chemical shifts were referenced to an external sample of solid phosphomolybdic acid (Fisher Scientific Co.) which was assigned a shift value of  $-6$  ppm with respect to aqueous 85%  $\text{H}_3\text{PO}_4$ .

Solid-state NMR experiments were also performed on a home-built 400 MHz NMR spectrometer utilizing a Tecmag Libra system for pulse programming and signal digitization. The static magnetic field strength of the spectrometer is 9.4 T, corresponding to resonance frequencies for the  $^1\text{H}$ ,  $^{31}\text{P}$ , and  $^{27}\text{Al}$  species of 399.995, 161.927, and 104.229 MHz, respectively. Spectra were acquired using a Chemagnetics 5.0 mm triple-resonance CPMAS NMR probe with rotor frequencies between 5 and 10 kHz. The rotor frequencies were stabilized to  $\pm 2$  Hz using an active-feedback-spin-rate controller system from Chemagnetics. Solid-state rotational-echo double-resonance (REDOR)<sup>20</sup> experiments were performed utilizing  $^{31}\text{P}$  and  $^{27}\text{Al}$  spin pairs,<sup>21,22</sup> with initial cross-polarization from  $^1\text{H}$  spins in this triple-resonance  $^1\text{H}/^{31}\text{P}/^{27}\text{Al}$  REDOR experiment. Triple-resonance TRAPDOR experiments<sup>18</sup> were also performed in a similar manner. The use of proton polarization as the initial source of the signal allows for a shorter recycle delay in the triple-resonance experiments (compared to  $^{31}\text{P}/^{27}\text{Al}$  double-resonance), since the  $T_1$  values for the protons are considerably shorter than relaxation times for the  $^{31}\text{P}$  nuclei. A TRAPDOR NMR signal is obtained as the difference of the signals from two separate NMR experiments: The first is a spin-echo MAS signal obtained from the  $^{31}\text{P}$  spins after initial cross-polarization from the  $^1\text{H}$  nuclei. In a second experiment, the  $^{31}\text{P}$  spin-echo is formed in an analogous manner, but during this time a long radio-frequency pulse is applied at the Larmor frequency of the  $^{27}\text{Al}$  nuclei. The interaction between the nuclear electric quadrupole moment of the  $^{27}\text{Al}$  nuclei and local gradients in the electric field causes a time-dependent change in the spin energy levels under MAS conditions, and the long radio-frequency pulse causes mixing and scrambling of coherences among these energy levels. If  $^{31}\text{P}$  nuclei are close in space to the  $^{27}\text{Al}$  nuclei (usually within 5 Å), there is a substantial dipole–dipole interaction between the heteronuclei, and the result of the time-dependent modulation in  $^{27}\text{Al}$  energy levels is the dephasing of the  $^{31}\text{P}$  spin-echo signal. The signal will only be diminished for  $^{31}\text{P}$  close in space (dipole-coupled) to  $^{27}\text{Al}$  spins, and therefore the TRAPDOR difference signal will display only resonances from  $^{31}\text{P}$  nuclei close to  $^{27}\text{Al}$  nuclei. Spectral editing of the resonances in the REDOR experiment occurs in a similar manner, except that in REDOR experiments rotor-synchronized  $180^\circ$  pulses are applied to the heterospins during the formation of the spin-echo signal.

## Results

### Crystalline and “Hydrated” Trimethylphosphine Oxide.

A sample of crystalline TMPO (purchased from Alfa and recrystallized from a solution in dry  $\text{CH}_2\text{Cl}_2$ ) was analyzed by  $^{31}\text{P}$  MAS NMR, and a wide sideband pattern is observed corresponding to a large  $^{31}\text{P}$  chemical shift anisotropy (Figure 1a). The parameters describing the chemical shift anisotropy were determined from a Herzfeld–Berger analysis of the spinning sideband pattern.<sup>23,24</sup> The measured parameters are  $\Delta\sigma = -170.9$ ,  $\eta = 0.44$ , and  $\sigma_{\text{iso}} = 39.4$ . In our studies of solid acids, any crystalline TMPO present will show a similar pattern if the crystalline material is contained within a bulk crystalline phase. Comparison of calculated sideband intensity patterns at a given spinning speed will allow positive identification of this phase.

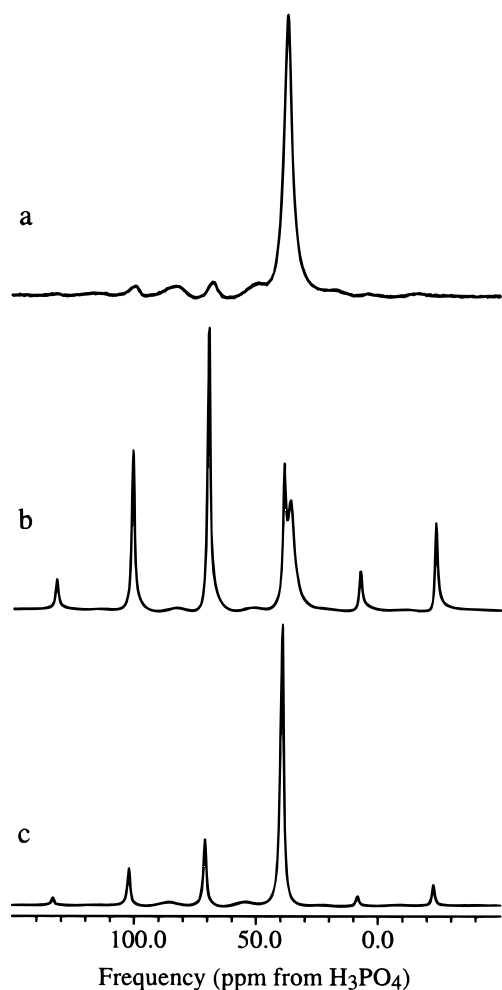


**Figure 1.** (a) The single-pulse solid-state  $^{31}\text{P}$  MAS NMR spectrum of crystalline TMPO. The isotropic peak appears at 39 ppm, along with a well-defined set of spinning sidebands. (b) The single-pulse solid-state  $^{31}\text{P}$  MAS NMR spectrum of crystalline TMPO with the addition of approximately 1  $\mu\text{L}$  of water to the sample rotor. A new isotropic resonance appears at 41 ppm. Sample spinning rates in both spectra are 5.0 kHz.

Addition of a small amount (approximately 1  $\mu\text{L}$ ) of water to solid TMPO contained within an NMR rotor produces a new  $^{31}\text{P}$  resonance at 41 ppm, lacking a broad sideband pattern, as shown in Figure 1b. The characteristic pattern from crystalline TMPO also remains, representing the fraction of the sample unaffected by the water.

When a small amount of TMPO is dissolved in excess deionized distilled water (pH 7), the  $^{31}\text{P}$  resonance from TMPO appears at 53 ppm. A single peak also appears at 53 ppm in a slightly basic solution and also when the solution has a starting pH of 6. This single peak at 53 ppm remains until the pH of the initial solution is dropped below a pH of 1. Eventually, the resonance moves downfield, reaching 83 ppm in a concentrated (12 M) HCl solution. For comparison, the chemical shift of TMPO in DMSO is 37 ppm while that of TMPO in chloroform is reported as 38 ppm.<sup>6</sup>

**Catapal Alumina.** The first acidic sample investigated was a dehydroxylated Catapal alumina with two different loadings of TMPO per gram of solid. This form of alumina ( $\gamma$ -alumina) is a representative source of Lewis acid sites, as hydroxyl groups are removed from the surface during high-temperature treatment.<sup>25</sup> The heat treatment to above 700  $^\circ\text{C}$ , as described above, is sufficient to remove over 90% of surface hydroxyl species.<sup>25</sup> The solid-state  $^{31}\text{P}$  MAS NMR spectra from a sample of  $\gamma$ -alumina loaded with 0.78 and 2.3 mmol of TMPO/g of solid are shown in Figure 2. At low TMPO loading (Figure 2a), there is a major signal in the spectrum at 37 ppm. At higher loading (Figure 2b) a second peak appears with an isotropic chemical shift of 39 ppm and a wide sideband pattern matching that of crystalline TMPO. The close correspondence of the wide pattern to that observed from crystalline TMPO demonstrates that crystalline TMPO readily forms in these systems in a bulk phase. The  $^{31}\text{P}$  NMR spectra of both TMPO/alumina samples also show the presence of a broad minor signal (with a discernible sideband pattern) at approximately 53 ppm, while all other peaks in the spectrum correspond to spinning sidebands of the resonances at 37 and 53 ppm.

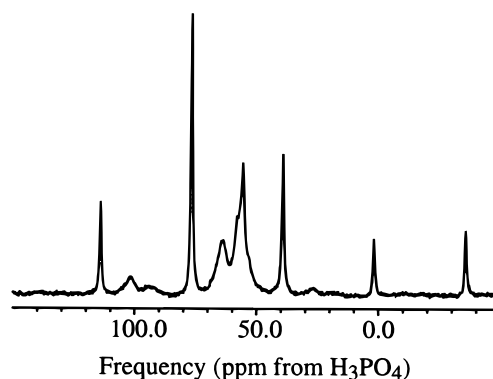


**Figure 2.** Single-pulse solid-state  $^{31}\text{P}$  MAS NMR spectra of Catapal alumina samples with: (a) 0.78 mmol of TMPO/g of solid, (b) 2.3 mmol of TMPO/g of solid, and (c) 2.3 mmol of TMPO/g of solid after exposure to an atmosphere with 25% relative humidity for 1 h. Sample spinning rates in all spectra are 5.0 kHz.

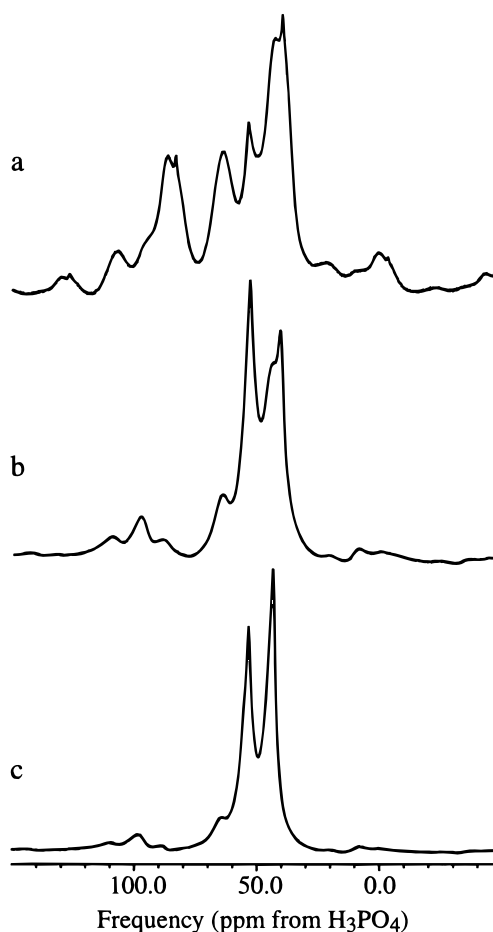
The effect of the introduction of water to the TMPO/alumina system was accomplished by exposing the sample with 2.3 mmol of TMPO/g of solid to a controlled atmosphere with 25% relative humidity. The  $^{31}\text{P}$  MAS NMR spectrum (Figure 2c) shows two distinct features: a broad resonance at around 53 ppm and an isotropic peak with a wide sideband pattern. The relative sideband intensities, *but not the intensity of the isotropic peak*, match the intensities of the sidebands in the crystalline pattern of Figure 1. The enhanced isotropic peak at 39 ppm in the pattern must therefore be the sum of resonances from both crystalline TMPO and  $^{31}\text{P}$  in a different environment than the crystalline sample. The resonance at 37 ppm is absent in the spectrum acquired after rehydration.

**Zeolite HY.** The  $^{31}\text{P}$  NMR spectrum of a sample of zeolite HY loaded with 2.70 mmol of TMPO/g of solid is shown in Figure 3. Isotropic resonances appear in three distinct regions of the spectrum. The first is a sharp peak at 39 ppm, with the same well-defined sideband pattern as seen in the crystalline TMPO and nonhydrated TMPO/alumina samples. Broader resonances are observed at 65 ppm and around 55 ppm, with small but measurable spinning sidebands at this moderate (6 kHz) rotational frequency.

**Steam-Calcined Zeolite HY (USY).** In the  $^{31}\text{P}$  MAS NMR spectrum of a sample of steam-calcined HY impregnated with a moderate loading of base (2.70 mmol of TMPO/g of solid),

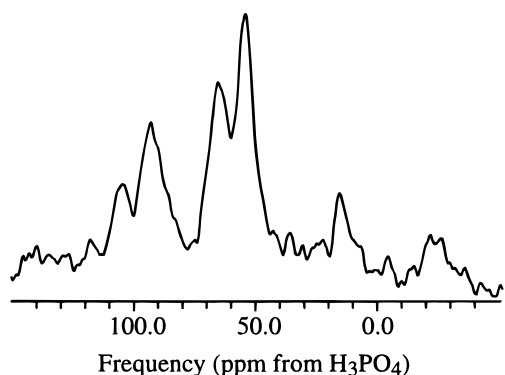


**Figure 3.** Single-pulse solid-state  $^{31}\text{P}$  MAS NMR spectrum of HY sample containing 2.70 mmol of TMPO/g of solid. The sample spinning rate is 6.0 kHz.

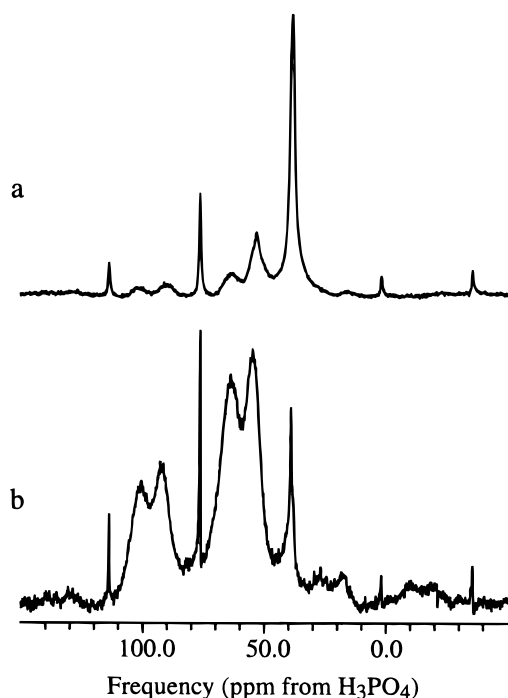


**Figure 4.** Single-pulse solid-state  $^{31}\text{P}$  MAS NMR spectra of a USY sample containing 2.70 mmol of TMPO/g of solid: (a) prior to exposure to atmosphere, (b) after exposure to an atmosphere with 25% relative humidity for 1.5 h, and (c) after hydrating in a saturated atmosphere for 2 h.

a wide band of signals appears (Figure 4a). Each signal has a measurable sideband pattern, but the overlap and spectral crowding precludes direct comparison with the crystalline TMPO signal of Figure 1a. Isotropic peaks are observed at 65, 55, 44, and 39 ppm. After the sample was gradually exposed to a controlled atmosphere (20% relative humidity) for 2 h, the peak at 65 ppm decreased in intensity, while the peak at 55 ppm increased in relative intensity (Figure 4b). After the sample was placed in a saturated atmosphere (100% relative humidity) for 1 h, the  $^{31}\text{P}$  MAS spectrum (Figure 4c) shows no resonance at 39 ppm and an increase in relative intensity for the peak at



**Figure 5.**  $^1\text{H}/^{31}\text{P}/^{27}\text{Al}$  triple-resonance TRAPDOR spectrum of USY after treatment with 2.70 mmol of TMPO/g of solid. The difference spectrum shown was obtained with 10 rotor cycles on each side of the  $180^\circ$  refocusing pulse and a spinning speed of 6.25 kHz.

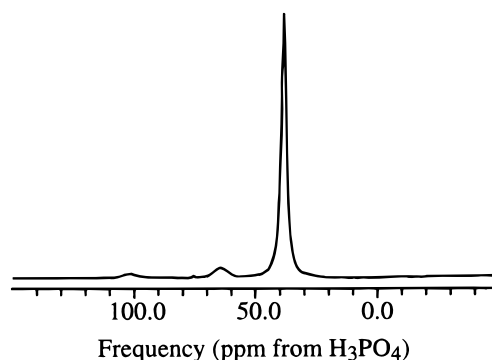


**Figure 6.** Solid-state  $^{31}\text{P}$  MAS NMR spectra of a dealuminated Y zeolite with 2.74 mmol of TMPO/g of solid: (a) single-pulse spectrum; (b)  $^1\text{H}-^{31}\text{P}$  CPMAS spectrum acquired with a contact time of 3 ms. The sample spinning rate is 6.0 kHz.

44 ppm. The ratio of peak intensities at 65 and 55 ppm remains approximately constant after the initial rehydration procedure.

The original TMPO/USY sample (before hydration) was also characterized using a  $^1\text{H}/^{31}\text{P}/^{27}\text{Al}$  triple-resonance TRAPDOR NMR experiment. The results of this experiment (Figure 5) demonstrate which phosphorus resonances arise from complexes where the TMPO molecules are in close proximity to aluminum atoms. Resonances are observed in the TRAPDOR difference spectrum at 65 and 55 ppm, while no TRAPDOR intensity is seen at 44 and 39 ppm. Therefore, the peaks at 65 and 55 ppm must arise from  $^{31}\text{P}$  nuclei in spatial proximity to  $^{27}\text{Al}$  nuclei. REDOR experiments were also performed, and the REDOR effect for the sites at 65 and 55 ppm was approximately the same, indicative of similar  $^{31}\text{P}/^{27}\text{Al}$  distances.

**Low-Aluminum Y Zeolite.** Solid-state  $^{31}\text{P}$  NMR spectra of a low-aluminum Y sample loaded with 2.74 mmol of TMPO/g of solid are shown in Figure 6. As in the HY and USY samples, signals appear at 65 and 55 ppm. Although the two signals in the 40 ppm region are not resolved in Figure 6a, the low



**Figure 7.** Single-pulse solid-state  $^{31}\text{P}$  NMR spectrum of an amorphous silica-alumina (13% Al) with 2.5 mmol of TMPO/g of solid. The sample spinning rate is 6.0 kHz.

intensity of the spinning sidebands and the absence of the broad peak in the CP spectrum (Figure 6b) indicates once again that there are actually two peaks present, similar to the observation from the rehydrated Catapal aluminum spectrum (Figure 2c).

**Silica-Alumina (13% Al).** The solid-state  $^{31}\text{P}$  MAS NMR spectrum for the silica-alumina sample with 2.5 mmol of TMPO/g of solid is shown in Figure 7. A large  $^{31}\text{P}$  signal with few or no spinning sidebands appears at 41 ppm. An additional broad peak appears at 63 ppm, similar to that observed in the faujasite samples.

## Discussion

**Lewis Acid Sites.** The isotropic chemical shift for a TMPO/Lewis complex in acidic solids has been reported by Baltusis et al. as 53 ppm based on a spectrum of TMPO on amorphous silica-alumina (75% silica, 25% alumina by weight). They also reported a similar shift of 58 ppm for  $^{31}\text{P}$  from a solution of 1:1 TMPO/ $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$  measured at  $-60^\circ\text{C}$ .<sup>8</sup> In our studies, a dehydroxylated sample of Catapal alumina was chosen as a representative solid acid containing a predominant population of Lewis acid sites. Figure 2a displays a strong resonance at 37 ppm from TMPO adsorbed onto a Catapal alumina. Therefore, we assign this resonance at 37 ppm, with a minor sideband pattern, to TMPO/Lewis acid sites.

In this same sample, the assignment of the minor peak at 53 ppm is not as clear. According to Peri,<sup>25</sup> as hydroxyl groups are removed from the surface of alumina, the underlying aluminum cations become exposed to the surface and form Lewis sites. The hydroxyl groups that remain on the surface could, in principle, behave as weak proton donors. Further insight is gained by exposing the sample containing the higher loading of 2.3 mmol of TMPO/g of solid to the atmosphere and again examining the  $^{31}\text{P}$  MAS NMR signal. The peak at 37 ppm disappears from the spectrum, along with its associated sideband pattern. Based on our assignment of this resonance to Lewis-bound TMPO molecules, this result is expected given the high sensitivity of Lewis sites to aqueous attack. The signature signal for crystalline TMPO is still present, with an isotropic chemical shift of 39 ppm and the same CSA pattern, but with the difference that the peak at 39 ppm is of improper intensity. Therefore, another peak must be contributing to the signal at 39 ppm, and this peak does not have a strong pattern of spinning sidebands. Therefore, we assign this narrower resonance to either "solution-like" TMPO formed in the presence of water (see below) or physisorbed TMPO which would be weakly bound and undergoing rapid exchange with more mobile species. Importantly, the broad resonance at 53 ppm is still present, indicative of sites not affected by partial rehydration

of the sample. As shown below, we identify this resonance with  $\text{H}^+$  complexed (Brønsted-bound) TMPO species.

**Brønsted Acid Sites.** The  $^{31}\text{P}$  NMR signal from TMPO in association with the Lewis acid sites on the surface of a dehydroxylated alumina shows a resonance at 37 ppm. Moving to studies of systems with potential Brønsted acid sites, a peak at 65 ppm in the  $^{31}\text{P}$  MAS NMR spectrum of TMPO has been reported and assigned in the literature to a Brønsted acid site by Baltusis et al. in their study of an amorphous silica–alumina sample (as described above).<sup>8</sup> It is also reported<sup>26</sup> that the spectrum of TMPO in contact with  $\text{H}^+$  resin reveals a  $^{31}\text{P}$  resonance with an isotropic shift of 72 ppm. Our study of TMPO dissolved in 12 M HCl also confirms a large downfield shift (83 ppm) for protonated TMPO. Therefore, the assignment of a peak at 65 ppm to a Brønsted complex is unambiguous. The form of this site is presumably a  $\text{TMPOH}^+$  species attached to a bridging oxygen, similar to the  $\text{TMPH}^+$  species associated with Brønsted acid sites in previous studies.<sup>6</sup> Further, in aqueous solution with an excess of water and a pH above 1, a single  $^{31}\text{P}$  resonance appears at 53 ppm representing the average chemical shift for  $^{31}\text{P}$  in a TMPO molecule undergoing rapid exchange of an acidic proton in solution. This should be compared to an isotropic shift of 37 ppm from TMPO in DMSO and 38 ppm reported for TMPO in  $\text{CDCl}_3$ <sup>6</sup> where no protonation equilibrium is possible.

In solid acids, peaks in the 50–55 ppm range are seen as a minor component in the TMPO/alumina sample and as major components in the spectra from TMPO in association with HY, USY, and dealuminated Y zeolites. In previous studies, these peaks have been assigned to Lewis-complexed or possibly physisorbed TMPO species.<sup>14</sup> Since TMPO is a solid at room temperature, we do not expect a large amount of free TMPO in the unhydrated samples. A peak at 53 ppm is a major constituent of the spectrum from HY, and this sample of HY zeolite is not expected to possess an appreciable amount of Lewis acidity due to the minimal amount of nonframework aluminum in the sample. Solid-state  $^{27}\text{Al}$  MAS NMR (not shown) confirms the lack of substantial amounts of NMR-visible octahedrally coordinated aluminum atoms with moderately sized quadrupolar-coupling constants.

The assignments of the resonances at 37 ppm to a Lewis acid site and at 53 ppm to a Brønsted site are further supported by consideration of chemical shift perturbations observed in TMP and TMPO binding experiments. The chemical shift of  $^{31}\text{P}$  in liquidlike TMP (the major form of TMP at room temperature when in excess in zeolite systems) is reported as  $-67$  ppm when in association with acidic solids, while that of neat TMP is  $-63$  ppm.<sup>6</sup> A large change is observed in the TMP  $^{31}\text{P}$  NMR chemical shift upon complexation to a Brønsted site ( $\Delta\delta = 65$  ppm) forming  $\text{TMPH}^+$ .<sup>6</sup> In  $\text{TMPH}^+$ , the proton is directly bonded to the phosphorus and should result in a larger change of the electronic environment (and hence  $^{31}\text{P}$  chemical shift values) compared to  $\text{TMPOH}^+$ , where the proton is one bond removed from the phosphorus. The chemical shift of crystalline TMPO, the major form of TMPO at room temperature, is 39 ppm, and the largest shift we measure for a protonated TMPO molecule has a chemical shift difference of 44 ppm. Using a similar argument for the Lewis sites,  $\Delta\delta$  for the TMPO system should again be much smaller than the value obtained when considering TMP, which is reported in the literature as 11 ppm.<sup>6</sup> This would not be the case for a  $^{31}\text{P}$  peak from TMPO at 53 ppm ( $\Delta\delta = 14$  ppm), although when observed previously in TMPO/silica–alumina this peak was assigned to a TMPO/Lewis acid complex.<sup>8</sup> In fact, we measure an *upfield* shift of the

TMPO resonance when coordinated to Lewis sites in the Catapal alumina sample. We have also shown that an enhancement of a peak at 53 ppm (but with a noticeably different spinning sideband pattern) occurs upon partial rehydration of zeolite samples. This is indicative of at least a partial contribution to this peak of signals from TMPO molecules in rapid motion and closely associated with water in the system.

However, not all TMPO molecules in contact with water contribute resonances at 53 ppm. The most striking example occurs when a small amount of water is added to a sample of crystalline TMPO, and an isotropic peak arises at 41 ppm. Recent *ab initio* quantum mechanical calculations<sup>27</sup> may explain and illuminate the difference in  $^{31}\text{P}$  chemical shift observed when comparing TMPO dissolved in an excess of water and a pure TMPO sample with a small amount of water present. In systems with isolated water molecules, the minimum surface potential calculated for the oxygen atom in water is made significantly more negative (by about  $20 \text{ kcal mol}^{-1}$ ) if two molecules of TMPO form a complex with each water molecule. In this energetically preferred orientation, the P–O double bonds are each also involved in hydrogen bonding with the water. When water is present in excess, the complexation and therefore local electromagnetic environment will differ. The  $^{31}\text{P}$  chemical shift will undergo a change, which our studies show is approximately 12–14 ppm downfield.

Consistent with previous results obtained using trimethylphosphines as probes,<sup>6</sup> our work shows that there are at least two different types of Brønsted complexes formed when probe molecules are added to acidic materials. Although there are many factors that influence the  $^{31}\text{P}$  chemical shift in these complexes, one possible explanation may be that there are varying degrees of proton transfer to the TMPO that would result in variations of the proton–oxygen bond length of the complex. Assuming this to be the case, it may be possible to relate the chemical shift of the TMPO/Brønsted complex with the strength of the acid site. For instance, if we assume that a shift value of 72 ppm measured for TMPO in contact with  $\text{H}^+$  resin represents a TMPO/Brønsted complex with a very short H–O bond, we can then tentatively assign the signals with chemical shifts of 65 and 55 ppm to TMPO/Brønsted complexes with longer H–O bonds. Preliminary results obtained in our laboratories studying TMPO adsorbed onto ZSM-5 zeolites show additional, and supposedly more tightly bound, Brønsted acid sites giving rise to chemical shift values of 75 ppm.

The spectra from a rehydrated USY system also contain peaks tentatively attributed to physisorbed and mobile TMPO species. These assignments are corroborated with  $^1\text{H}/^{31}\text{P}/^{27}\text{Al}$  REDOR and TRAPDOR NMR experiments. The experimental TRAPDOR results (Figure 5) clearly demonstrate that the phosphorus nuclei in the two TMPO/acid site complexes (65 and 55 ppm) are coupled via a through-space direct dipolar interaction to aluminum atoms. The signals attributed to physisorbed (43 ppm) and crystalline (39 ppm) TMPO do not appear in the spectrum, demonstrating that they are not closely associated with aluminum species.

**Brønsted Site Quantification.** The results in this study suggest that the chemical shift range for TMPO/Brønsted acid complexes is from approximately 50 to 75 ppm. If these assignments are made in a dry atmosphere and then used to calculate absolute concentrations of Brønsted sites, the Brønsted acid site concentrations as measured by  $^{31}\text{P}$  NMR should compare favorably with measurements from other analytic methods such as IPA/TPD. Assigning all resonances between 50 and 70 ppm to Brønsted acid sites, and calculating the

**TABLE 2: Summary of the Brønsted Acid Site Concentrations Measured with IPA/TPD and  $^{31}\text{P}$  NMR**

sample	Brønsted site concn from IPA/TPD ( $\mu\text{mol/g}$ ) <sup>a</sup>	Brønsted site concn from $^{31}\text{P}$ NMR ( $\mu\text{mol/g}$ ) <sup>b</sup>
HY	1750	1458
USY	520	662
low-Al Y	610	824
silica–alumina	310	327

<sup>a</sup> Error estimated at  $\pm 10\%$  of reported value. <sup>b</sup> Error estimated at  $\pm 5\%$  of reported value.

concentration of acid sites per gram of material from the phosphorus concentrations measured with ICP analysis, the concentrations of Brønsted acid sites were calculated and are reported in Table 2. For comparison, the IPA/TPD results are also provided in Table 2. For the HY sample, the concentration by NMR is measured as 83% of the concentration measured by IPA/TPD. This sample contained the largest number of Brønsted sites per gram in our studies. The results for the USY and dealuminated Y samples are also in relatively close agreement. Finally, in the silica–alumina sample, the numbers obtained by NMR and IPA/TPD are the same, within the experimental error of both techniques.

## Conclusion

We have demonstrated that it is indeed possible to use solid-state  $^{31}\text{P}$  NMR of the probe molecule TMPO to determine the types and amounts of acid sites on a variety of zeolitic and amorphous materials. The concentrations of Brønsted sites determined by this method are in good agreement with those determined via IPA/TPD. The  $^{31}\text{P}$  NMR chemical shift range for Brønsted complexes was determined to be 50–75 ppm. Contrary to previous reports, we report that the chemical shift of a TMPO/Lewis acid complex is 37 ppm based on our studies of dehydroxylated alumina. The quantitation of Lewis acid strengths and sites is important for an increased understanding of the catalytic nature of these systems, and the newly assigned signal can in principle be used to determine the amount of Lewis acidity in a given material. This is the subject of current studies in our group. Further studies of  $^{27}\text{Al}/^{31}\text{P}$  distances (as well as  $^1\text{H}/^{31}\text{P}$  interactions) at Brønsted acid sites are also in progress.

**Acknowledgment.** The authors wish to thank J. Swain for conducting the IPA/TPD experiments, A. Nadjadi for his

assistance in sample preparation, J. Burnham for her ICP work, and Dr. J. Frye for his helpful discussions and reports of unpublished data. This report is also based upon work supported by the National Science Foundation under Grant DMR-9458053 and an Arnold and Mabel Beckman Foundation Young Investigator Award to K.T.M.

## References and Notes

- (1) Basila, M. R.; Kantner, T. R.; Rhee, K. H. *J. Phys. Chem.* **1964**, *68*, 3197–3207.
- (2) Hughes, T. R.; White, H. M. *J. Phys. Chem.* **1967**, *71*, 2192–2201.
- (3) Eberly, P. E., Jr. *J. Phys. Chem.* **1968**, *72*, 1042–1047.
- (4) Liang, S. H. C.; Gay, I. D. *J. Catal.* **1980**, *66*, 294–300.
- (5) Dawson, W. H.; Kaiser, S. W.; Ellis, P. D.; Inners, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 6780–6781.
- (6) Lunsford, J. H.; Rothwell, W. P.; Shen, W. *J. Am. Chem. Soc.* **1985**, *107*, 1540–1547.
- (7) Majors, P. D.; Raidy, T. E.; Ellis, P. D. *J. Am. Chem. Soc.* **1986**, *108*, 8123–8129.
- (8) Baltusis, L.; Frye, J. S.; Maciel, G. E. *J. Am. Chem. Soc.* **1986**, *108*, 7119–7120.
- (9) Baltusis, L.; Frye, J. S.; Maciel, G. E. *J. Am. Chem. Soc.* **1987**, *109*, 40–46.
- (10) Kofke, T. J. G.; Gorte, T. J.; Kokotailo, G. T.; Farneth, W. E. *J. Catal.* **1989**, *115*, 265.
- (11) Peters, A. W. Instrumental methods of FCC catalyst characterization. In *Fluid Catalytic Cracking: Science and Technology*; Magee, J. S., Mitchell, M. M., Jr., Eds.; Elsevier: New York, 1993; Vol. 76, pp 183–221.
- (12) Sheng, T.-C.; Gay, I. D. *J. Catal.* **1994**, *145*, 10–15.
- (13) Sang, H.; Chu, H. Y.; Lunsford, J. H. *Catal. Lett.* **1994**, *26*, 235–246.
- (14) Maciel, G. E.; Ellis, P. D. NMR Characterization of Silica and Alumina Surfaces. In *NMR Techniques in Catalysis*; Bell, A. T., Pines, A., Eds.; Marcel Dekker: New York, 1994; Vol. 55, pp 231–309.
- (15) Lunsford, J. *Top. Catal.* **1997**, *4*, 91–98.
- (16) Kao, H.-M.; Grey, C. P. *Chem. Phys. Lett.* **1996**, *259*, 459–464.
- (17) Kao, H.-M.; Grey, C. P. *J. Am. Chem. Soc.* **1997**, *119*, 627–628.
- (18) van Eck, E. R. H.; Janssen, R.; Maas, W. E. J. R.; Veeman, W. S. *Chem. Phys. Lett.* **1990**, *174*, 428–432.
- (19) Juskelis, M.; Peters, A. W.; Slanga, J. P.; Roberie, T. G. *J. Catal.* **1992**, *138*, 391.
- (20) Gullion, T.; Schaefer, J. J. *Magn. Reson.* **1989**, *81*, 196–200.
- (21) Fyfe, C. A.; Mueller, K. T.; Grondey, H.; Wong-Moon, K. C. *Chem. Phys. Lett.* **1992**, *199*, 198–204.
- (22) Fyfe, C. A.; Mueller, K. T.; Grondey, H.; Wong-Moon, K. C. *J. Phys. Chem.* **1993**, *97*, 13484–13495.
- (23) Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021–6030.
- (24) Eichele, K.; Waylishen, R. E. HBA 1.2 Dalhousie University, 1997.
- (25) Peri, J. B. *J. Phys. Chem.* **1965**, *69*, 211–220.
- (26) Frye, J. S., personal communication.
- (27) Kariuki, B. M.; Harris, K. D. M.; Philp, D.; Robinson, J. M. A. *J. Am. Chem. Soc.* **1997**, *119*, 12679–12680.