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RESEARCH NOTE

Simultaneous Quantification of Brønsted- and Lewis-Acid Sites in a USY Zeolite

Kevin J. Sutovich,*,† Alan W. Peters,† Edward F. Rakiewicz,†,1 Richard F. Wormsbecher,†
Susan M. Mattingly,* and Karl T. Mueller*,2

*Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, Pennsylvania 16802;
and †Washington Research Center, W. R. Grace and Company, 7500 Grace Drive, Columbia, Maryland 21044

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In this report, experimental methods and calculation procedures are described for direct and simultaneous quantification of the Brønsted- and Lewis-acid site concentrations in a sample of USY zeolite. The concentrations of both types of acid sites are characterized by solid-state ^{31}P MAS NMR spectroscopy of trimethylphosphine oxide probe molecules. The errors associated with the area measurements in the NMR spectrum, and hence the errors in the concentration measurements reported, are estimated with Monte Carlo simulations applied with spectral line-fitting and deconvolution procedures. © 1999 Academic Press

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A number of experimental methods are readily available for the characterization and quantification of acid sites in solids. These include thermal methods, temperature-programmed desorption (TPD), and microcalorimitry which are all either selective for Brønsted sites (1) or do not distinguish clearly between Lewis- and Brønsted-acid sites. Infrared techniques, depending on the probe used, can have the same difficulty. Even if a band is identifiable as due to an interaction with a Lewis site, relative quantification is often difficult. Therefore the simultaneous quantification of both types of sites in a solid acid is an important goal, with the ultimate desire being an understanding of the relationship of atomic-level structure to catalytic activity and selectivity.

Studies utilizing solid-state NMR spectroscopy of probe molecules containing NMR-active ^{31}P nuclei have demonstrated the use of the wide ^{31}P chemical shift dispersion for the identification of Lewis and Brønsted sites (2–6). Since the quantification of spectra from spin-1/2 nuclei is relatively straightforward, these results are in principle quantitative measures of acid site concentrations. The use of ^{31}P as a reporting nucleus for solid acidity has been demonstrated using a number of ^{31}P-containing compounds, with most promising results reported using trimethylphosphine (TMP) as the probe. However, TMP is a dangerous liquid at room temperature, and there are difficulties in handling TMP and in preparing solid acid standards for the quantitation step.

Studies of the more stable trimethylphosphine oxide (TMPO) have been reported on amorphous silica–alumina surfaces (3, 7), and recently we reported the successful completion of ^{31}P magic-angle spinning (MAS) NMR studies of TMPO complexed with acid sites in γ-alumina, a number of Y-type zeolites, and a silica–alumina catalyst system (8). For these samples, comprehensive and consistent assignments to particular types of sites are made for all resonance lines in the ^{31}P MAS NMR spectra. Based on results from dehydroxylated γ-alumina, a new chemical shift assignment (37 ppm with respect to 85% phosphoric acid) was reported for a TMPO–Lewis-acid complex. Brønsted sites occur with a shift of 50 ppm and higher, and other forms of TMPO are also detected and characterized in the spectra. The assignments of ^{31}P resonances from molecules not directly associated with nearby ^{27}Al nuclei (such as crystalline or physisorbed TMPO species) were supported using ^{1}H/^{31}P/^{27}Al triple-resonance NMR methods. The concentrations of Brønsted-acid sites as calculated from the NMR results were comparable with concentrations obtained from isopropylamine/temperature programmed desorption (IPA/TPD) measurements. The most important results from this previous study were the positive identification of the chemical shift of a Lewis site–TMPO complex (different from the reported shifts of earlier studies), and the ability to quantify the number of acid sites after titration with TMPO. However, in the previous study the only measurement

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[1] Current address: PPG Industries, Inc., 4325 Rosanna Drive, Allison Park, PA 15101.

[2] To whom correspondence should be addressed. E-mail: ktm2@psu.edu.

of a Lewis site occurred in a standard γ-alumina sample, and no quantification of Lewis site concentrations was reported.

In this work we report further studies of acid sites in an ultrastable Y zeolite (USY). We demonstrate that for a USY sample treated with TMPO and carefully protected from aqueous attack, the concentrations of two different Brønsted-acid sites and one unique Lewis-acid site are quantifiable from ^{31}P MAS NMR results. We describe the deconvolution of the spectral lineshapes as well as an estimation of the errors in concentrations derived from these fittings. The concentrations of the Brønsted acid sites are compared with results obtained from IPA/TPD measurements, and the differences in the values measured by these two complementary methods are briefly discussed.

A sample of framework-dealuminated Y zeolite was prepared by hydrothermal dealumination of a sample of $NaNH_4Y$ for 2 h at 700°C. The USY had a surface area of 744 m^2/g and a unit cell size of 2.452 nm. The elemental composition was 4.4% sodium oxide, 21.8% alumina, and the balance was silica. Prior to characterization by solid-state NMR, the sample was prepared as described in Ref. (8). The TMPO was introduced dissolved in a dry CH_2Cl_2 solution of known concentration, and the mixture was agitated overnight under N_2 on a mechanical shaker before removal of solvent. A 5.0-mm rotor with sealed endcaps was used to hold and spin the TMPO-loaded USY sample within the MAS NMR probe. The ^{31}P chemical shifts are referenced to an external sample of solid phosphomolybdic acid (Fisher Scientific) which was assigned a shift value of −6 ppm with respect to aqueous 85% H_3PO_4. A standard Bloch decay spectrum at 9.4 T magnetic field was acquired, with a signal averaging of 1272 experiments, radiofrequency excitation pulses of 4 μsec in length (corresponding to approximately 30° pulses), a spinning speed of 7 kHz, and a recycle delay of 10 s between scans. Spectra were accumulated with longer relaxation delays (up to 60 s) and no changes were observed in relative spectral intensities. Therefore the spectra obtained under the above conditions should be quantitative.

Bulk phosphorus quantification was carried out by sample digestion followed by ICP analysis. The NMR results were compared with the results of a modified version (9) of an IPA/TPD method for determination of Brønsted-acid concentrations described by Kofke *et al.* (1). It is assumed that all phosphorus measured in the ICP analysis is also measured in the ^{31}P MAS NMR experiment. Dynamic-exchange effects, a problem with TMP and other probe molecules that are not solids at room temperature, are minimized due to the lack of a rapidly exchangeable set of probe molecules. Peaks from crystalline TMPO are detected only after titration of the acid sites, and sharp resonances appear with a recognizable MAS sideband pattern (8).

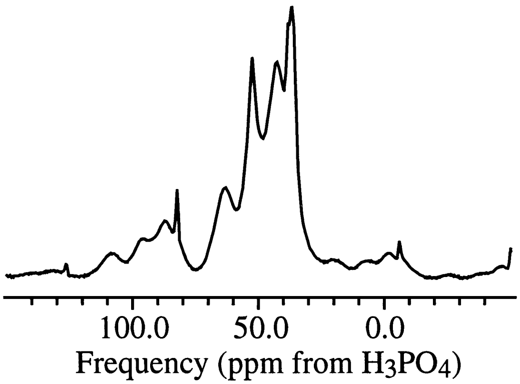

FIG. 1. Full ^{31}P MAS NMR spectrum at 9.4 T for a USY zeolite loaded with 1.9 mmol TMPO/g solid.

The ^{31}P MAS NMR spectrum of a sample of USY loaded initially with 3.00 mmol TMPO/g of solid (1.9 mmol/g of solid by ICP analysis) is shown in Fig. 1. A broad resonance at 63 ppm is detected, along with a resonance at 53 ppm, and both are assigned to Brønsted-acid sites. Confidence in the assignment of the peak at 53 ppm depends upon total exclusion of water from this system both during the loading of TMPO and throughout the analysis by ^{31}P MAS NMR. The strong peak at 43 ppm is due to physisorbed TMPO, and the peak at 39 ppm with a sharp sideband pattern is due to crystalline TMPO. The presence of the crystalline TMPO peak confirms that this sample is past the titration point of the acid sites that readily form complexes with the TMPO. The peak at 37 ppm (more easily seen in the expanded view of Fig. 2a) does not display a strong sideband pattern, and it occurs at the same chemical shift value as the Lewis-acid site in γ-alumina. This peak is therefore also assigned to a TMPO–Lewis-acid complex in the USY sample.

A deconvolution of the isotropic resonances is shown in Fig. 2b. Fits of all lines in the spectrum (including the spinning sidebands) were obtained with GRAMS/32 software (10), using the CurveFit routine which employs an algorithm based on the Levenberg–Marquardt method of nonlinear least squares fitting. Mixed Lorentzian–Gaussian lineshapes were allowed, providing the greatest flexibility and quality of fits. Integration of the spectral areas of all peaks, including the spinning sidebands, gives 298 μmol/g of Brønsted acidity contributing to the resonance at 63 ppm, 378 μmol/g of Brønsted acidity at 53 ppm, and 165 μmol/g of Lewis acidity from the resonance at 37 ppm.

A full error analysis, incorporating spectral intensities from each of 20 lines used in the overall fit is extremely difficult. The error in concentrations reported has therefore been estimated by characterization of the error in the areas of the five isotropic peaks seen in Fig. 2. Error characterization was conducted by first subtracting the sum of the deconvoluted peaks in the center cluster region from the actual data. These residuals (shown as the difference spectrum of Fig. 2c) represent the error of the best fit using the peak shapes, positions, intensities, and widths returned by the curve fitting routine.

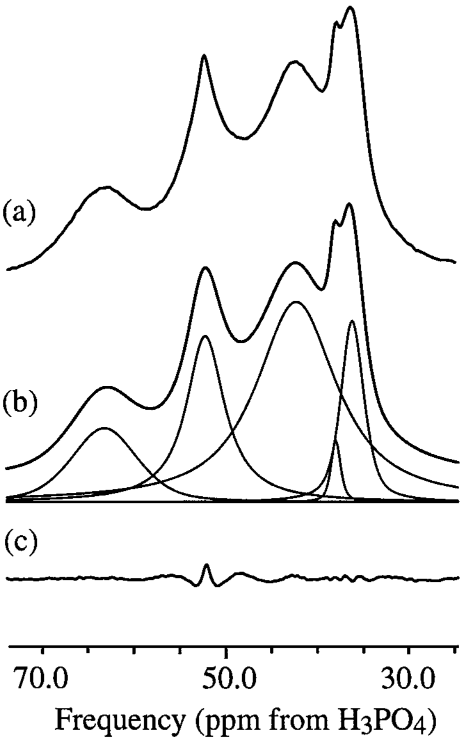

FIG. 2. (a) Expanded view of the ^{31}P MAS spectrum clearly showing the upfield resonance (at 37 ppm) assigned to a TMPO/Lewis-acid complex. (b) Separate lines obtained from spectral deconvolution of the isotropic resonances are shown along with their sum (top spectrum). (c) The difference spectrum for the isotropic resonances compares the sum of the deconvoluted spectrum and the actual spectrum, forming the set of residuals for Monte Carlo estimation of errors in the reported acid site concentrations.

If the residuals truly represent the "noise" or random uncertainty present in the data set, Monte Carlo (MC) sampling is an effective method for estimating the error in the relative areas of the peaks (11, 12). The uncertainty is first characterized to determine the noise distribution, and this noise distribution (here assumed as Gaussian in nature) serves as the basis for the MC sampling. The errors placed on the overall measurements are propagated by standard methods, and the uncertainty in the areas of the peaks arising from the two Brønsted sites at 63 and 53 ppm are estimated at less than 1% after 5000 Monte Carlo iterations. The same Monte Carlo simulations also place an estimate of less than 1% on the error in the reported area of the peaks associated with the Lewis sites. The peak with the largest relative error is the small peak from the crystalline TMPO, representing a concentration of less than 50 μmol/g with an uncertainty of 3%.

Under the assumptions that the spectral deconvolutions provide an accurate separation of the resonances from the ^{31}P species associated with Lewis- or Brønsted-acid sites, the errors in the concentrations reported are also on the order of a few percent or less. However, other systematic errors could substantially change the confidence placed upon these results. For example, the lineshapes used were chosen for maximum flexibility, in order to provide the best fit spectral analysis, and this leads to a direct minimization of the residuals that are analyzed in order to produce random Gaussian noise for the Monte Carlo analysis. Further, observations have also been made regarding the lack of mobility among the TMPO molecules, leading to the assumption that the observed resonances can account for all of the phosphorus in the sample. If this is not the case, then the reported acid site concentrations are systematically biased toward an overcounting of the sites. Also, if titration with TMPO does not provide full coverage of the acid sites, then the reported values may be systematically lower than the total number of acid sites available in this sample. Therefore, it is correct to report these concentrations as those measurable with TMPO titration of acid sites. Comparison with results from IPA/TPD analysis, or other independent methods for measuring acid site concentrations, is then informative.

The amount of Brønsted acidity measured by IPA/TPD analysis for this USY sample is 560 μmol/g, and this should be compared to the total Brønsted acidity of 676 μmol/g calculated using TMPO as a probe for ^{31}P MAS NMR analysis. One possibility for the differences in these numbers is that the sites counted by the resonance at 53 ppm in the TMPO analysis may not all be active for cracking IPA during the TPD experiment. Based on studies of aqueous TMPO solutions at different solvent pH values (8), the position of the ^{31}P resonances from protonated TMPO species tend to move downfield as the degree of proton transfer increases. Therefore, the resonance at 63 ppm is most likely due to stronger protonic acid species. The weaker protonic species, giving rise to the peak at 53 ppm, may have reduced acidic strength or activity in these materials, at least with respect to the cracking of isopropylamine. Any water present in this system will also cause an increase in the intensity of signal at 53 ppm, and this systematic error would need to be taken into account if water was not carefully excluded from the system.

TMPO is a useful acidity probe in solid acid systems such as zeolites. This probe molecule forms several types of complexes characterized by different chemical shifts from association with protons and proton donors as well as with Lewis-acid sites. The amount of each type of complex, including the complex with Lewis-acid sites, can be quantified based on deconvolution and integrated ratios from ^{31}P MAS NMR spectra. In a USY zeolite system, both Lewis- and Brønsted-acid site populations were quantified concurrently yielding concentrations of 165 and 676 μmol/g, respectively. Error analysis by Monte Carlo simulation of approximate spectra is shown to be useful for estimating random errors in deconvolutions of the complex spectra. Based on fitting of the MC simulated NMR spectra, the errors in the concentrations are estimated at less than 1% of the reported values. The possible identity and contributions of systematic errors, and their effects on the quantification of acid sites, have also been discussed.

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