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NMR Characterization of Bronsted Acid Sites in Faujasitic Zeolites with Use of Perdeuterated Trimethylphosphine Oxide

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Characterization of active sites in solid-acid catalyst systems is enhanced by performing a suite of ^{31}P magic-angle spinning (MAS) NMR experiments on samples treated with a fully deuterated form of trimethylphosphine oxide (TMPO).[1] Zeolites are excellent catalysts for a wide host of chemical reactions and have been the object of extensive study and research.[2] Bronsted acid sites in zeolites are thought to be essential for the catalytic activity and have been studied by techniques including NMR, FTIR, NH_3-temperature programmed desorption, and isopropylamine-temperature programmed desorption.[3] Studies with fully deuterated TMPO (TMPO-d_9) allow simultaneous probing of ^{1}H species specifically associated with the zeolite host, rather than introduced into the sample in methyl groups that are part of nondeuterated TMPO.

Zeolite Y has a faujasite structure, is used extensively as a fluid cracking catalyst[4] in petroleum refining, and provides an excellent demonstration of the enhanced information obtained in these experiments. In the conventional model, Bronsted acidity arises from bridging hydroxyl groups of which there are two main forms: protons associated with either the supercage (O(1)) or sodalite cage (O(3)) oxygen atoms.[5] These two different groups produce two bands in the infrared spectrum, and are also distinguished uniquely in ^{1}H MAS NMR spectra.[6]

The basicity[7] of TMPO coupled with the large chemical shift range of ^{31}P is a recognized advantage for studying subtle differences in “acid strength” by producing large changes in the frequency of resonance.[8] Figure 1a shows the ^{31}P MAS spectrum of HY loaded with 3 mmol/g of TMPO-d_9. There are three main peaks at +65, +55, and +41 ppm, and a broad peak at +40 ppm. The ^{31}P isotropic peak from TMPO in solution shows a monotonic downfield shift with increasing pH,[9] and hence the first two peaks are tentatively assigned to TMPO-d_9 complexed to Bronsted acid sites. The +41 ppm peak corresponds to excess crystalline TMPO-d_9. Figure 1b shows the $^{1}H/^{31}P$ cross-polarization NMR spectrum from the same sample. A comparison indicates that the +65 and +55 ppm peaks have appreciable cross-polarization signal, as does the broad peak at +40 ppm. The peak from crystalline TMPO-d_9 does not appear in the CP spectrum. Hence the use of TMPO-d_9 allows direct probing of sites associated with ^{1}H by defining the source of the ^{31}P signal as the ^{1}H species that are part of the catalyst materials.

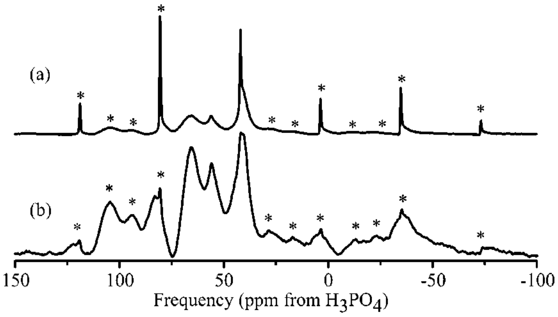

Figure 1. (a) The ^{31}P MAS spectrum of zeolite HY loaded with 3.0 mmol/g TMPO-d_9 reports on all ^{31}P nuclei in the sample. (b) The $^{1}H/^{31}P$ CPMAS spectrum of the same sample is dominated by ^{31}P nuclei near the ^{1}H nuclei.

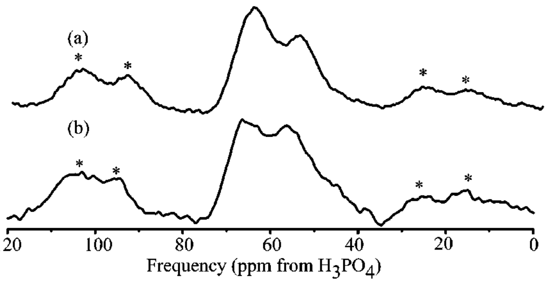

Figure 2. (a) $^{31}P/^{27}Al$ TRAPDOR difference spectrum of HY (2.5 mmol/g TMPO-d_9) revealing two resonances at +65 and +55 ppm. (b) The $^{1}H/^{31}P/^{27}Al$ CP-TRAPDOR spectrum confirms that these peaks arise from ^{31}P nuclei close to both ^{27}Al and ^{1}H.

In previous work on catalyst systems, a suite of double- and triple-resonance NMR methods were brought to bear for additional and corroborative structural information, and must be used to further characterize these resonances.[8] TRAnsfer of Populations via DOuble Resonance (TRAPDOR)[10] is a rotor synchronized NMR experiment designed to probe connectivities between spin-$^{1}/_{2}$ and quadrupolar nuclei. In these systems, TRAPDOR experiments with ^{31}P and ^{27}Al determine which of the four peaks in the ^{31}P spectrum arise from nuclei close to ^{27}Al. The traditional model for a Bronsted site is a bridged hydroxyl group between silicon and aluminum and the results of this experiment (Figure 2a) indicate that only the +55 and +65 ppm peaks arise from ^{31}P nuclei associated with such bridging hydroxyl units. Figure 2b is the spectrum resulting from a $^{1}H/^{31}P/^{27}Al$ CP-TRAPDOR experiment where an initial cross polarization step was performed from protons, again showing the absence of ^{27}Al interacting with the +40 ppm peak. These two experiments (CP and TRAPDOR) provide strong evidence that the two downfield peaks (+55 and +65 ppm) are indeed TMPO interacting with Bronsted acid sites (bridging an Al−O−Si), while the +40 ppm peak arises from ^{31}P nuclei with ^{1}H nuclei nearby, but no aluminum atoms in close proximity.

The +40 ppm peak is tentatively assigned to silanol sites, which can also associate with TMPO. However, the TRAPDOR experiment is sensitive to the quadrupolar coupling constant (qcc) of the ^{27}Al and large values of qcc could also be responsible for the lack of any loss of signal intensity (dephasing).[10] By our model, though, the small change of chemical shift indicates that the +40 ppm peak is TMPO complexed to a very weak acid site (such as a silanol).

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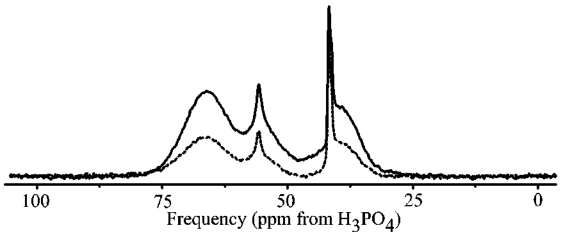

Figure 3. Comparison of the full echo S_0 (—) and reduced echo S_f (- - -) signals from a ^{31}P/^{1}H REDOR experiment for HY loaded with 2.5 mmol/g TMPO-d_9 indicating dipolar coupling to ^{1}H nuclei for the peaks at +65, +55, and +40 ppm.

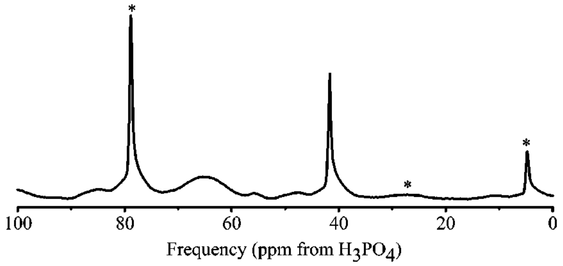

Figure 4. The ^{31}P MAS NMR spectrum for HNaY loaded with 3 mmol/g TMPO-d_9 indicates that the +55 ppm peak is significantly reduced, due to trapping of Na^+ species in the sodalite cages.

Rotational Echo DOuble Resonance (REDOR)[11] is also a double resonance NMR technique that probes dipolar couplings between spin-$^1/_2$ heteronuclei. In favorable cases, internuclear distances are extracted by using this experiment. ^{31}P/^{1}H REDOR experiments were carried out on zeolites loaded with TMPO-d_9 and results are shown in Figure 3. This experiment correlates further the isotropic chemical shift of the ^{31}P with the degree of proton transfer, which could be unambiguously measured by extracting the internuclear distance between the ^{1}H nuclei and the phosphorus. The results of Figure 3 show that the +65, +55, and +40 ppm peaks show dephasing, while there is no change in signal intensity for the crystalline peak. The full dephasing curves for the different peaks qualitatively agree with the above hypothesis but it was impossible to extract internuclear distances when performing the experiments at room temperature. This is thought to be due to molecular motion, which attenuates the dipolar coupling.[12] Further experiments should be attempted at lower temperatures to confirm this hypothesis.

The two main forms of Bronsted acid sites in faujasites are associated with either supercage or sodalite cages within the structure.[5] To further identify these sites in the ^{31}P MAS spectrum, a starting material of NaY was exchanged with a 1:3 solution of NH_4NO_3:$NaNO_3$ (75% degree of cation exchange as measured by ICP analysis) and then heat treated.[6] The calcined sample was reacted with TMPO-d_9 and the ^{31}P MAS NMR results are shown in Figure 4. It can very clearly be seen that the intensity of the +55 ppm peak has been drastically reduced. The +55 ppm peak is then assigned to TMPO interacting with protons associated with the sodalite cages, since the Na^+ ions are smaller than the NH_4^+ ions and there is a preferential replacement of Na^+ ions (with NH_4^+ ions) in the larger supercage, leading to a smaller concentration of Bronsted acid sites associated with the sodalite cages. A more extensive discussion of these results and comparisons to other measurements from IR and ^{1}H NMR spectroscopy are provided in the Supporting Information.[9]

Finally, Figure 5, parts a and b, presents the ^{31}P MAS spectra of a different zeolite HY sample (now with Si/Al = 6) loaded with 0.5 and 1 mmol/g TMPO-d_9. As can be seen from the expanded scale, TMPO-d_9 provides even greater resolution among Bronsted acid sites at low loadings in this sample. The loss of resolution at higher loadings is possibly explained by exchange of TMPO-d_9 in this zeolite where the overall acid site density is lower. There are also indications that the +55 ppm resonance comprises a relatively narrow peak with a small chemical shift anisotropy (CSA) and a broad peak with a larger CSA, deduced through a comparison of the widths of the spinning sidebands with the isotropic resonance. It is unknown whether the complexity observed at low loadings is due to the preparation of the zeolite as synthesized, or represents more fundamental differences in acid-site structure. Preliminary results also indicate that TMPO-d_9 provides excellent resolution in the zeolite ZSM-5.[13] Three Bronsted sites are observed, consistent with recent crystallographic reports where three cation positions for cesium have been identified.[14]

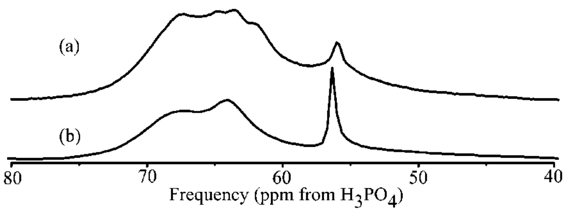

Figure 5. (a) The ^{31}P MAS NMR spectrum of HY (Si/Al = 6) loaded with 0.5 mmol/g of TMPO-d_9 showing the resolution of at least 5 isotropic resonances. (b) At higher loadings (1 mmol/g TMPO-d_9) there is a noticeable loss of resolution.

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Supporting Information Available: Procedures for the synthesis of TMPO-d_9 and calcination protocols for zeolites, details of NMR experiments and graphs related to the discussion above, and extended discussions mentioned in the text (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Baltusis, L.; Frye, J. S.; Maciel, G. E. *J. Am. Chem. Soc.* **1987**, *109*, 40.
(2) Corma, A. *Chem. Rev.* **1995**, *95*, 559.
(3) (a) Freude, D.; Hunger, M.; Pfeifer, H.; Schwieger, W. *Chem. Phys. Lett.* **1986**, *128*, 62. (b) Freude, D.; Hunger, M.; Pfeifer, H.; Scheler, G.; Hoffmann, J.; Schmitz, W. *Chem. Phys. Lett.* **1984**, *105*, 427. (c) Echoufi, N.; Gelin, P. *Catal. Lett.* **1996**, *40*, 249. (d) Yin, F.; Blumenfeld, A. L.; Gruver, V.; Fripiat, J. J. *J. Phys. Chem. B* **1997**, *101*, 1824. (e) Gorte, R. J. *Catal. Lett.* **1999**, *62*, 1.
(4) Peters, A. W. In *Studies in Surface Science and Catalysis*; Magee, J. S., Mitchell, M. M. J., Eds.; Elsevier: New York, 1993; Vol. 76, p 183.
(5) Czjzek, M.; Jobic, H.; Fitch, A. N.; Vogt, T. *J. Phys. Chem.* **1992**, *96*, 1535.
(6) Jacobs, W. P. J. H.; Dehaan, J. W.; Vandeven, L. J. M.; Vansanten, R. A. *J. Phys. Chem.* **1993**, *97*, 10394.
(7) (a) Haake, P.; Cook, R. D.; Hurst, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 2650. (b) Hunter, E. P.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1988**, *27*, 413. (c) NIST Chemistry WebBook http://webbook.nist.gov/chemistry/.
(8) Rakiewicz, E. F.; Peters, A. W.; Wormsbecher, R. F.; Sutovich, K. J.; Mueller, K. T. *J. Phys. Chem. B* **1998**, *102*, 2890.
(9) See Supporting Information.
(10) Grey, C. P.; Vega, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 8232.
(11) Gullion, T.; Schaefer, J. *J. Magn. Reson.* **1989**, *81*, 196.
(12) Kao, H. M.; Liu, H. M.; Jiang, J. C.; Lin, S. H.; Grey, C. P. *J. Phys. Chem. B* **2000**, *104*, 4923.
(13) Mueller, K. T.; Karra, M. D. In *Northeastern Corridor Zeolite Association 1999 Meeting*; University of Pennsylvania: Philadelphia, PA, 10 December 1999.
(14) Olson, D. H.; Khosrovani, N.; Peters, A. W.; Toby, B. H. *J. Phys. Chem. B* **2000**, *104*, 4844.

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