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PRIORITY COMMUNICATION

A Solid Acidity Scale Based on the ^{31}P MAS-NMR Shift of Chemisorbed Triethylphosphine Oxide

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The change in chemical shift of a chemisorbed probe molecule is an informative tool for the characterization of solid acids. This work demonstrates that the phosphorus-31 isotropic chemical shift of the probe triethylphosphine oxide (TEPO) can be used to identify the acidity of multiple acid sites on a surface. The difference in the phosphorus-31 chemical shift of chemisorbed TEPO with respect to physisorbed TEPO, $\Delta\delta$, establishes a scale of solid acidity that can be validated by comparison to enthalpies of calorimetric methods. A linear correspondence is observed for the strong solid acid (silica-gel)$_n$Sb^{V}Cl$_3$ with four acid sites and with enthalpies of -66, -46, -33, and -21 Kcal/mol for interaction of the solid acid with pyridine in a cyclohexane slurry that correlate with $\Delta\delta$ values of 66, 48, 36, and 22 ppm, respectively.

Key Words: **acidity scale; solid acidity; triethylphosphine oxide; Cal-Ad.**

Solid acidity is often characterized by measuring spectral line shifts of a chemisorbed probe molecule. Techniques based on IR (1), UV (2), and NMR have been developed. The shift of the spectral line is compared to the shift of the same probe molecule on other solid acids with different acidity to generate a scale of relative acidity. A relatively larger shift of the spectral line indicates higher acidity. When several different spectral lines from a probe on one solid are observed, the additional spectral lines are taken to be additional acid sites with different strengths (3). By monitoring the changes in intensity of the different spectral lines as the total amount of adsorbed probe is varied, the amount of each acid site present in the solid can often be determined. In this communication, we demonstrate that the isotropic phosphorus-31 chemical shift of the probe molecule triethylphosphine oxide (TEPO) can serve as a highly sensitive indicator of solid acidity. The method is simple and convenient, yet provides accuracy and resolution, especially when more than one type of acid site is to be distinguished.

Phosphorus-31 magic angle spinning (MAS) NMR is well suited for solid acid characterization. The large magnetogyric ratio and 100% natural abundance of phosphorus-31 allows detection of very small amounts of probe molecules, which is advantageous when attempting to observe the limited number of acidic sites present on the surface of a solid acid. Previously reported phosphorus-31 MAS-NMR studies over the past decade have focused primarily on trimethylphosphine as the adsorbate probe of choice. Trimethylphosphine has been used to identify the number of different sites on the solid, the density of each site, and the nature of each site as either Lewis or Brønsted (3). Unfortunately, the small variation of the phosphorus-31 chemical shift of trimethylphosphine in solids of wide ranging acidity limits the utility of this probe for the determination of acidity (4). For Brønsted acids the range of acidity correlates with chemical shifts over a 5 ppm range, with an error in measurement of 0.5 ppm. For Lewis acids, the range is covered in only 3 ppm, with an error of measurement of 1 ppm. The most promising use of trimethylphosphine is for the determination of the site densities of the Lewis and Brønsted sites on the surface. However, the inability to accurately quantify acidity using trimethylphosphine has motivated us to search for a more sensitive and versatile phosphorus-31 NMR probe for solid acid characterization.

Liquid acids have been previously characterized using TEPO, upon which the acceptor number scale is based (5). Here we demonstrate that the phosphorus-31 isotropic chemical shift of TEPO can identify the relative acidity in a series of solid acids with known acidity. Previous studies (6) demonstrated the ability of chemisorbed trialkylphosphine oxides to distinguish multiple acid sites on the surface of several solids (6) and also attempted to qualify the nature of the acid site as Brønsted or Lewis in nature by the position of the chemical shift (6a, 6c). However, there is a discrepancy between the location of each of these regions (6a, 6c).

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The origin of the phosphorus-31 chemical shift of chemisorbed TEPO is the shift of electron density from the basic probe to the acid site (7). The interaction of the TEPO oxygen atom with the acid site gives rise to a lengthening of the phosphorus–oxygen bond. Evidence for the weakening of this bond can be obtained from the IR investigation of solvent acidity. The phosphorus–oxygen stretching frequency of TEPO can be seen to decrease, indicating a weakening of the bond, as the acidity of the solution it is dissolved in increases (8). Positive charge develops at the phosphorus center, and negative charge builds up at the acid site (7). The stronger the acid site, the greater the shift of electron density and the greater the charge build up. Chemical shifts characteristic of phosphines were not observed, an indication that oxygen atom transfer does not occur.

EXPERIMENTAL

The solid acid samples were loaded with TEPO by combining a known mass of 1.0 M TEPO in anhydrous pentane solution with a known mass of the solid. The loading is determined by the ratio of the moles of TEPO, determined by using a solution density of 0.679 g/ml and the molar mass of TEPO of 134.16 g/mol, to the mass of the solid acid. For example, a TEPO loading of 0.74 mmol TEPO/g solid was obtained by combining approximately 100 mg of the TEPO solution with 200 mg of the solid acid. A volume of 2 ml of anhydrous pentane was also added to the samples to facilitate mixing. The resulting slurries were allowed to equilibrate for 15–20 min before drying in a vacuum oven maintained at 50°C. Alternatively, a small mass of TEPO can be dissolved in 4–5 ml of anhydrous pentane, and this solution is then mixed with the solid acid and allowed to equilibrate before treatment in the vacuum oven. The MAS-NMR spectrum of each sample was acquired at 202.270 MHz on a Varian Unity 500 MHz spectrometer equipped with a 5 mm Jakobsen style MAS probe operated at spinning speeds of 4–6 KHz. A simple one pulse acquire sequence was employed with a 22 μs pulse corresponding to the 90° flip angle. A recycle delay of 30 s was employed to allow complete spin lattice relaxation between pulses. The spectra were referenced to an 85% phosphoric acid external standard.

Equation [1] is used to determine $\Delta\delta$ from the spectra:

$$\Delta\delta\ (\text{ppm}) = \delta^{31}P\ (\text{ppm}) - 50.0\ \text{ppm}. \qquad [1]$$

The 50.0 ppm shift corresponding to physisorbed TEPO was assigned the value $\Delta\delta = 0$.

All of the solid acids used in this report (except 2:1 TEPO:Al_2Cl_6 and the sol-gel sample) were supported on treated silica gel. The preparation of this silica gel can be found in reference (9). The preparation includes washing the silica with aqueous HCl, 30% peroxide, and deionized water followed by a heat treatment. This preparation procedure is believed to increase the number and strength of silanol sites on the silica surface (9).

Silica-supported aluminum chloride (10, 11), (silica-gel)$_n$ $Al^{III}Cl_2$, is a strong Brønsted acid that was prepared by refluxing the silica gel described above with anhydrous aluminum chloride in carbon tetrachloride. This solid was prepared and stored under an inert atmosphere. The antimony (V) analog, (silica-gel)$_n$$Sb^{V}Cl_3$, was prepared in an identical manner, except trichloromethane was used as the solvent.

Silica-supported sulfated tungsten oxide, (silica-gel)$_n$ WO_3SO_3, is also a strong Brønsted acid (12). The preparation of this solid was performed in two steps. The first step was refluxing tungsten hexachloride with silica gel for 24 h. The solid was then collected and dried in a 140°C oven for 1 day. The solid was cooled to room temperature and then washed with 1 M sulfuric acid. It was activated at 200°C in flowing air prior to use.

The sulfated silica gel was prepared by washing silica gel with 1 M sulfuric acid. This solid was activated at 200°C in flowing air prior to use.

The sol-gel sample was prepared by hydrolyzing tetraethyl ortho silicate in the presence of a catalytic amount of HCl at 80°C. The resulting gel was crushed and calcined at 400°C. This solid was found to have a very small number of very weak acid sites. It had a surface area of approximately 400 $m^2\ g^{-1}$.

The final solid, 2:1 TEPO:Al_2Cl_6, was prepared by mixing two equivalents of TEPO with anhydrous Al_2Cl_6 in hot carbon tetrachloride. A minimum amount of carbon

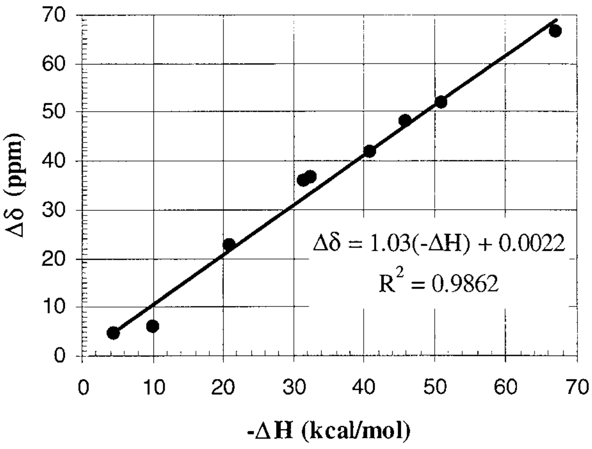

FIG. 1. The acidity determined by pyridine adsorption slurry calorimetry of several solid acids is plotted against the change in the isotropic phosphorus-31 chemical shift of triethylphosphine oxide. The solid acids are a high surface area/low acidity sol-gel; a silica gel that has been treated with hydrochloric acid and hydrogen peroxide; sulfuric acid washed silica gel; the four sites found for silica supported antimony (V) chloride, (silica-gel)$_n$$Sb^{V}Cl_3$; and the strong site of silica supported aluminum chloride, (silica-gel)$_n$$Al^{III}Cl_2$.

tetrachloride was used to dissolve both reactants prior to mixing. The precipitate was a white solid that formed needlelike white crystals upon cooling. The solvent was removed, and the solid was loaded into the NMR rotor.

RESULTS AND DISCUSSION

The change in chemical shift of TEPO has been measured on a variety of solid acid standards. These solid acids were chosen to test the $\Delta\delta$ scale over a wide range of acid strengths arising from both Lewis or Brønsted sites. Table 1 summarizes the $\Delta\delta$ value of several amorphous solid acids. The scale is a relative measure of acidity, with increasing $\Delta\delta$ values indicating increasing acid strength.

The acidity of the solid acids were also measured by either slurry calorimetry or the Cal-Ad method as described elsewhere (9, 10, 12). Figure 1 shows the plot of the new acidity scale, $\Delta\delta$, against acidity measured through these techniques. A linear trend is observed, demonstrating a correlation between the two observables. The validity of measuring acidity by either technique is therefore established. As an example of the ability of phosphorus-31 NMR of chemisorbed TEPO to resolve multiple acid sites within the same solid we present the spectrum (Fig. 2) of TEPO adsorbed on (silica-gel)$_n$Sb^{V}Cl$_3$ (13). We have recently discovered that this compound has an activity greater than (silica-gel)$_n$Al^{III}Cl$_2$, a solid that is thought to be on the verge of solid super acidity (11). Four sites are observed for (silica-gel)$_n$Sb^{V}Cl$_3$ in both the NMR and calorimetry data. This solid contains both Lewis and Brønsted sites as determined by Fourier transform infrared spectroscopy of adsorbed pyridine. Other acids shown in this plot include

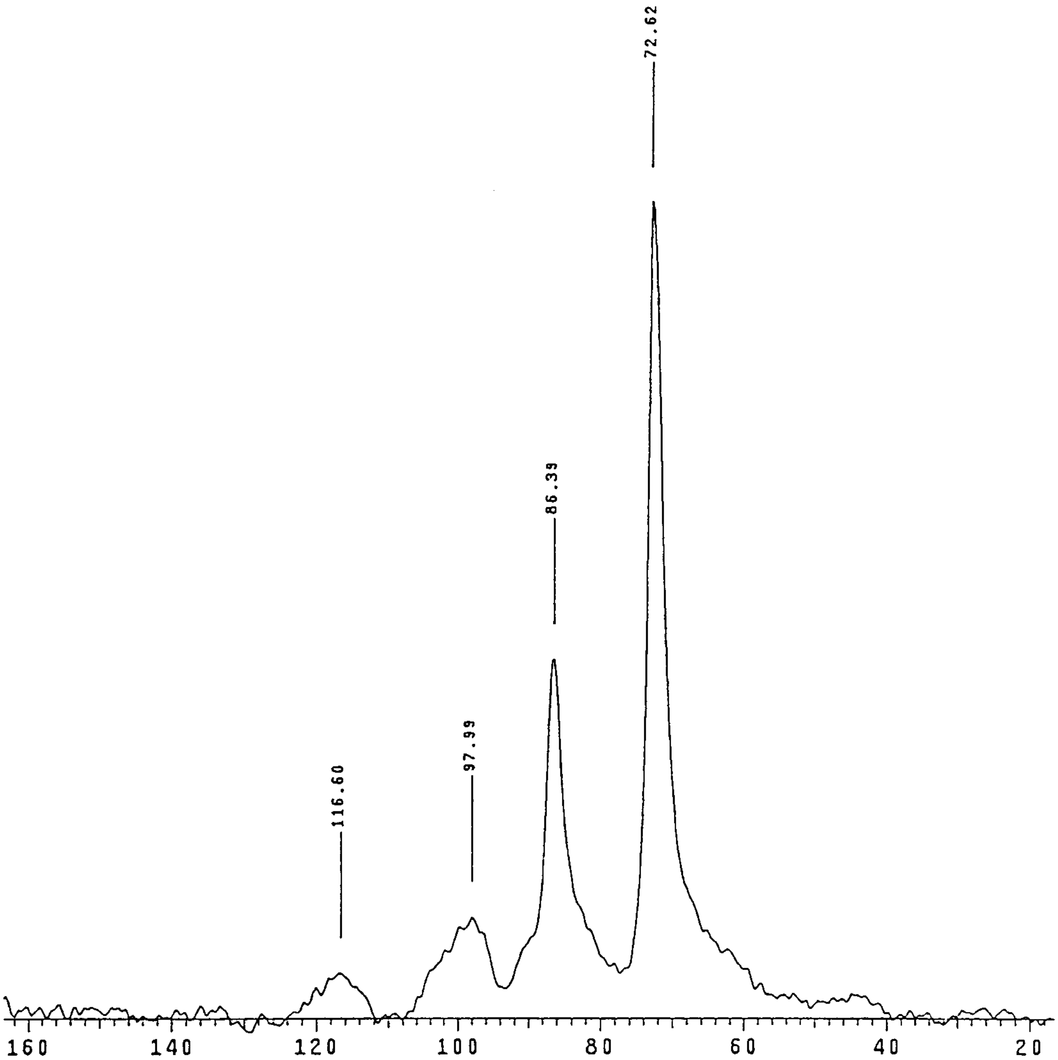

FIG. 2. The phosphorus-31 magic angle spinning NMR spectra of triethylphosphine oxide chemisorbed on a silica supported antimony (V) chloride solid acid, (silica-gel)$_n$Sb^{V}Cl$_3$. The peaks at 116.6, 97.99, 86.39, and 72.62 ppm each correspond to a different acid site detected by pyridine adsorption slurry calorimetry.

TABLE 1

Acid		$\Delta\delta$
(silica-gel)$_n$Sb^{V}Cl$_3$	Site 1	66.6
	Site 2	48.0
	Site 3	36.4
	Site 4	22.6
(silica-gel)$_n$Al^{III}Cl$_2$		52.0
Supported sulfated tungsten oxide		41.7
2 : 1 TEPO : Al$_2$Cl$_6$		36.6
Sulfated silica gel		31.5
Silica gel		6.0
Sol-gel		4.5

a specially treated silica gel (9), a low acidity/high surface area sol-gel silica, (silica-gel)$_n$Al^{III}Cl$_2$ (10), sulfated tungsten oxide (12), and a sulfated silica gel.

The activity of solid acids is also known to increase with increasing $-\Delta H$ as determined from either calorimetry or Cal-Ad. Increasing $\Delta\delta$ is therefore an indication of increasing activity toward acid catalyzed reactions.

Work is in progress to add more solid acids such as several zeolites, sulfated zirconia, and 12-tungstophosphoric acid and to include molecular modeling of the interaction in order to improve the accuracy and fundamental interpretation of this phosphorus-31 NMR method.

CONCLUSION

With this Communication, a new method for the characterization of solid acids is introduced. This method is based on one pulse MAS-NMR and can be used to qualify the acidity of multiple acid sites on a surface. The chemical shift of TEPO is not directly dependent upon the nature of the acidic site, but only on the total acid–base interaction. The phosphorus-31 NMR of TEPO has a resolution of 1.0 ppm over a range of 66 ppm and can discriminate a wide range of acidities. This will be a valuable new method for studying solid acidity and intermolecular interactions.

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