Measurement of the Global Acidity of Solid Acids by ^{31}P MAS NMR of Chemisorbed Triethylphosphine Oxide

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Received: August 18, 1999; In Final Form: October 8, 1999

The bonding of triethylphosphine oxide (TEPO) to the acid site of a surface produces a systematic change in the phosphorus-31 isotropic chemical shift that is proportional to the acid strength of the adsorption site. The acidity of several amorphous solid acids of various strengths, several zeolites (HZSM-5, HY, TS-1, and H−Mordenite), and the crystalline solid 12-tungstophosphoric acid have been measured. A single parameter scale is developed utilizing the chemical shift of TEPO adsorbed on solid acids. Adsorption of TEPO onto Lewis acids demonstrates that this probe measures the global acidity of adsorption sites and is insensitive to the Brønsted or Lewis nature of the site. The significant difference between measuring acidity through the change in chemical shift of chemisorbed TEPO and those based on differential techniques is demonstrated for the case of 12-tunstophosphoric acid where a larger acidity is measured by TEPO than by calorimetry. The difference in acidity measured by these two experiments allows for the estimate of the energy needed to open the 12-tungstophosphoric acid lattice to include pyridine-sized molecules. Simple one pulse MAS NMR techniques are shown to be capable of measuring the global acidity of a wide variety of solid acids.

Introduction

The acidity of a system is often characterized by measuring spectral line shifts of an adsorbed probe molecule.[1] Techniques based on IR,[2−6] UV,[7] EPR,[8] and NMR have been developed. The shift of the spectral line is compared to the shift of the spectral line 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 as measured by that probe molecule. When several different spectral lines from a probe on one solid acid are observed, the additional spectral lines are taken to be additional acid sites with different strengths.[9] 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 be determined.

Several probe molecules have been used to study solid acids including 2-^{13}C acetone,[10−14] 4-^{13}C mesityl oxide,[15−18] and ^{15}N pyridine.[19−23] Unfortunately, due to the low population of probe molecules adsorbed on the acid sites of a surface, the low sensitivity of these nuclei requires either extensive signal averaging or the use of labeled materials. To avoid both of these problems, a probe including a more sensitive nucleus at or near the basic portion of the molecule is highly desirable. An ideal replacement probe would contain phosphorus-31. The gyromagnetic ratio and natural abundance of phosphorus-31 is much greater than either ^{13}C or ^{15}N resulting in an order of magnitude increase in the NMR signal that can be observed. The relative sensitivity of ^{31}P compared to ^{13}C and ^{15}N at natural abundance is approximately 700 and 2400, respectively.[24] The very high sensitivity allows for the detection of small amounts of phosphorus-containing compounds adsorbed on the surface of a solid without the use of expensive enriched samples.
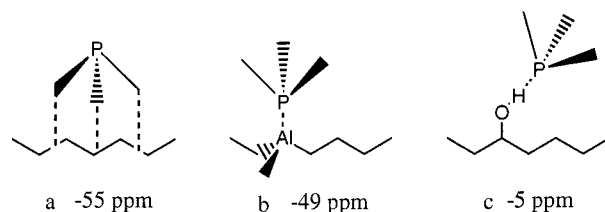
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Figure 1. The three chemical shifts of adsorbed trimethylphosphine (a) physisorbed (van der Waals forces only), (b) Lewis chemisorbed, and (c) Brønsted chemisorbed.

Over the past few years, the spectral probe molecule of choice for the study of solid acids by ^{31}P MAS NMR has been trimethylphosphine.[25−32] Coordination of trimethylphosphine to an acid site results in a characteristic shift of the spectral line that depends primarily on the Brønsted or Lewis nature of the acid site (Figure 1). The similar chemical shift of Lewis-bound and physisorbed trimethylphosphine results in difficulty for using this probe to unambiguously determine the presence and population of Lewis sites. Despite this shortcoming, trimethylphosphine has been widely used to determine the total population of Brønsted sites on a surface. The strong basicity of phosphines results in the formation of a protonated base upon coordination to any Brønsted site. The chemical shift of this characteristic system is about −5 ppm, with respect to 85% ortho phosphoric acid, and is largely invariant with the strength of the acid site. Results obtained using ^{15}N-labeled pyridine are similar to those with trimethyl phosphine in that the chemical shift is dependent on Lewis or Brønsted acidity of the solid. ^{15}N-pyridine also has some sensitivity toward the overall strength of the acid site, giving rise to two overlapping scales of acidity.[19−23]

While the basicity of trialkylphosphine oxides is on the same order of magnitude as trimethylphosphine, the removal of the phosphorus atom from the base site leads to a wide range of chemical shifts (δ^{31}P) that vary with the strength of the acid−
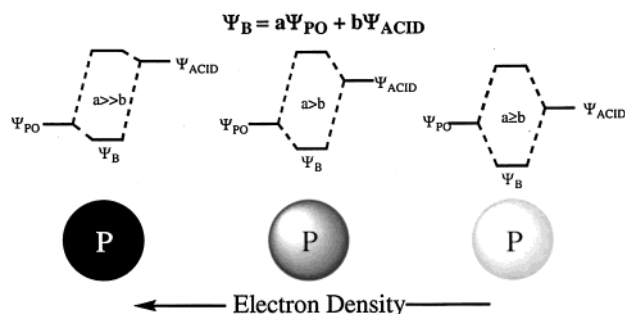
$$\Psi_B = a\Psi_{PO} + b\Psi_{ACID}$$

Figure 2. Overlap of the LUMO on the acid site with the HOMO of the base results in the formation of a molecular orbital. The component of the base molecular orbital in the adduct is reduced from the base alone, and as the strength of the acid site increases so will its share of the electrons in adduct bond. Also depicted is the lowering of electron density at the phosphorus center of a trialkylphosphine oxide as the adduct bond strength increases.

base interaction in solution.[33] The most prominently used trialkylphosphine oxides are triethylphosphine oxide (TEPO) and trimethylphosphine oxide (TMPO). Both have seen limited use as probes of solid acids.[26-27,29,34] The most well-known use of TEPO is as a probe of solvent acidity. Meyer and Guttman proposed the Acceptor Number scale based on $\delta^{31}P$ of TEPO extrapolated to infinite dilution in an acidic solvent.[4,28,33,35-36] This scale has been criticized for the observation that even neutral and basic solvents can have significant Acceptor Number values that have been attributed to van der Waals interactions and solvation effects.[36] While this and similar probe molecules have been used to distinguish multiple types of acid sites on the surface of several solids,[26,30,34] no attempt has been made to use TEPO to form a systematic scale of solid acidity. A scale based on the change in chemical shift of this probe would be advantageous due to the speed at which the characterization could be performed. Additionally, performing the experiment in the solid state rather than in solution will result in simplification of the parameters that influence $\delta^{31}P$ through the removal of effects related to solvation of the probe molecule.

The change in position of the spectral line through the chemisorption of a basic probe molecule onto an acidic site is primarily due to electronic changes in the probe molecule leading to a change in the local magnetic field about the nucleus.[33-36] Electron density is shifted from the base in favor of the acid site (Figure 2). Coordination of the phosphoryl oxygen of a trialkylphosphine oxide creates overlap between the electron deficient orbital on the acid site (LUMO), be it Brønsted or Lewis, and one of the orbitals on the oxygen that contains a lone pair of electrons (HOMO). The resulting adduct bond causes a loss of electron density from the probe that can be observed by a change in the ^{31}P NMR chemical shift. As the strength of a Brønsted acid site is increased, the acid site-probe adduct will begin to resemble an ion pair. However, once the base is fully protonated (acid site$^-$:H-probe$^+$) no further change in chemical shift will be observed by increasing the acidity of the site. Instead, the same chemical shift will be observed for any stronger acid sites, analogous to the leveling effect. A similar set of arguments can be made for the behavior of the phosphine oxide at a Lewis acid site. The phosphoryl oxygen atom acts as a bridge between the Lewis center and the phosphorus core. The strength of the acid site will be directly related to the strength of the adduct bond. In the case of an extreme interaction where electron transfer occurs, the reduced trialkylphosphine will be easily observed in the ^{31}P MAS NMR spectrum.

Moving the system to the solid state reduces some of the problems the Acceptor Number scale encountered (van der Waals forces and solvation effects). Solvation effects are eliminated, but the van der Waals effects will still be present. By comparing the shift of a phyisorbed base to that of a chemisorbed base, the contribution of the van der Waals forces to the chemical shift is reduced or removed.[26] The chemical shift of physisorbed TEPO has been observed to be approximately 50 ppm. By referencing the chemisorbed chemical shift to this value, the relative acidity of a solid acid site can be measured. The change in the chemical shift of TEPO has an excellent correlation with calorimetric measurements of acidity[37] except in the case of 12-tungstophosphoric acid.

Currently there is debate as to the acid strength of the crystalline solid acid 12-tungstophosphoric acid (HPW). Many reports have been issued with conflicting measurements of its acidity.[38-53] HPW is composed of large anions called Keggin units with a secondary structure composed of $H_5O_2^+$ counterions.[54-56] The Keggin unit is composed of four W_3O_{12} groups called W^3 triplets.[57] These triplets are linked by shared corners about a central PO_4 tetrahedron. The acidity of this solid is believed to come from the large size of this anion and from the high proton conductivities that spread any buildup of anionic charge throughout the solid.[58-60] For a probe to penetrate the crystalline HPW structure, the lattice must expand, which can be seen by comparing the lattice constants of HPW samples obtained from X-ray diffraction analysis before and after loading with the base pyridine.[51,62] Expansion of the lattice to incorporate a guest molecule requires energy, reducing the enthalpy observed by methods based on differential measurements of heats of adsorption and resulting in a lower estimation of acidity.

Recently, the acid sites of amorphous silica−alumina, various zeolties (HY, dealuminated HY, and USY), and γ-alumina were characterized with TMPO.[34] Several acid sites were distinguished on these materials, and the population of those sites was measured through spin counting experiments. It was also reported that this probe could differentiate Lewis and Brønsted sites. A small negative shift of the spectral line (compared to physisorbed trimethylphosphine oxide) on dry γ-alumina was observed. This feature disappeared upon exposure to water. It is known that water reduces both the Lewis acidity and basicity of γ-alumina. From these observations, the negative shift was taken to indicate the presence of Lewis acid sites. This trend of assigning shift ranges for Lewis or Brønsted bound phosphine oxides includes work by Baltusis et al.[26] and Lunsford et al.[29] However, each author has assigned a different region to the chemical shifts for the Lewis chemisorbed probe. TEPO has been previously used only twice for the characterization of solid acids: to identify two different acid sites on γ-alumina.[26-27]

Reported in this article is a new, single-step method for the determination of the global acidity of a solid acid. Chemisorption of the probes TEPO and TMPO result in a change in chemical shift that is dependent only on the strength of the acid site and not the Brønsted or Lewis nature of the site. We discuss the observed static acidity of HPW compared to acidity determined by calorimetric titration of this solid with pyridine. The chemical shift behavior of TEPO on solid neutrals and bases is also discussed.

Experimental Section

The solid acids and bases 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^{-1} and the molar mass of TEPO of 134.16 g mol^{-1} to the mass of the solid. For example, a TEPO loading of 0.74 mmol TEPO g^{-1} solid was obtained by combining approximately 100 mg of the TEPO solution to 200 mg of the solid. A volume of 2 mL of anhydrous pentane was also added to the samples to facilitate mixing. The slurries were allowed to equilibrate for twenty to thirty minutes with additional time for the zeolite samples. The samples were then dried in a vacuum oven maintained at 50 °C. Our preferred method, however, was to individually mix a small mass of TEPO dissolved in 4−5 mL anhydrous *n*-pentane or *n*-hexane with the solid, allowing twenty to thirty minutes for equilibrium to be established, and then treating the sample in the vacuum oven. TMPO was introduced to the sample in an analogous procedure except anhydrous tetrahydrofuran was used as the solvent.

The MAS spectrum of each sample was acquired on either a Varian Unity 500 MHz spectrometer operating at 202.270 MHz or a Bruker Avance 400 MHz spectrometer operating at 161.976 MHz. Both spectrometers were equipped with Jakobsen-style MAS probes operated at spinning speeds of 4−6 kHz (Unity) or 10−12 kHz (Avance). A simple one-pulse acquire sequence was employed with a pulse corresponding to the 90° flip angle of 22 μs (Unity) or 3.0 μs (Avance). A sample dependent recycle delay of 5 to 30 s was necessary to allow complete spin lattice relaxation between pulses. The spectra were referenced to an external 85% phosphoric acid standard.

Calorimetric tests of the solids were performed using the Cal-Ad method as documented elsewhere (see refs 73−74, 80−81 for examples).

Preparation of the Solids. Many of the solid acids used in this report were supported on a treated silica gel. The preparation of this silica gel can be found in ref 63. The preparation includes washing the silica with aqueous HCl, 30% hydrogen 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.[63]

Silica supported aluminum chloride,[64,65] (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) analogue, (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$_3$-SO$_3$, is also a strong Brønsted acid.[66] 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 a minimum of 20 h. The supported tungsten oxide 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 solid 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 γ-alumina was prepared by heating to 140 °C to remove physisorbed water.

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 weak acid sites. It has a surface area of approximately 400 m^2 g^{-1}.[67]

Zeolites HZSM-5 and H-Mordenite were prepared by ion exchanging the solids with 3 M ammonium chloride in deionized water. Both solids were then treated at 400 °C in flowing air

for 4 h and then for 12 h under vacuum. The furnace was then cooled and filled with dry nitrogen, and the samples were taken to an inert atmosphere glovebox where they were stored until used. Zeolite TS-1 was prepared by heating it to 200 °C in flowing air for 2 h and then in a vacuum for twelve. The furnace was cooled and transferred to the glovebox as described above.

The preparation of 12-tungstophosphoric acid (HPW) was followed as per the method of ref 62. Essentially, this method heats HPW hydrate in a vacuum at 200 °C for 4 h, followed by transfer, under vacuum or argon atmosphere, to an inert atmosphere glovebox.

The method of preparing the 1:1 adduct of TEPO with SbCl$_5$ was similar to one found in the literature for the preparation of a 1:1 adduct of SbCl$_5$ with triphenylphosphine oxide.[68] In separate vials 0.124 g of TEPO and 0.276 g SbCl$_5$ were dissolved in hot anhydrous CCl$_4$. After full dissolution, the hot CCl$_4$/TEPO solution was transferred by syringe to the vial containing the hot CCl$_4$/SbCl$_5$ solution. A clear white solution formed that contained a brown oil. The oil was extracted by syringe, allowed to cool, and the CCl$_4$ was evaporated. Both the solution and the oil yielded a white solid that was stable in air. The oil yielded the bulk of the solid, and this portion was used for the NMR studies. The same procedure was followed to produce the 1:1 adduct of TEPO with TaCl$_5$ (0.128 g TEPO and 0.309 g TaCl$_5$) and the 2:1 adduct with Al$_2$Cl$_6$ (0.305 g TEPO and 0.155 g Al$_2$Cl$_6$). The ^{1}H MAS NMR of 2:1 TEPO: Al$_2$Cl$_6$ showed only the ethyl protons.

Results and Discussion

A new solid acidity scale based on the change in the chemical shift of chemisorbed TEPO has been recently reported.[37] This scale is based on the change in ^{31}P MAS NMR chemical shift of TEPO from the shift of physisorbed TEPO, a $\Delta\delta$ value. The $\Delta\delta$ value is calculated by subtracting the chemical shift of physisorbed TEPO, estimated as 50.0 ppm, from the chemisorbed chemical shift (note: the spectra in the figures are reported as chemical shifts referenced to 85% phosphoric acid not as $\Delta\delta$ values). The $\Delta\delta$ values for many solid acids are reported in Table 1. By referencing all of the shifts to physisorbed TEPO the van der Waals component of the chemical shift is significantly reduced, making this an excellent, one-parameter measure of the donor−acceptor interaction between TEPO and the acid site.

The comparison of the $\Delta\delta$ scale to calorimetric measures of acidity results in a linear relationship (Figure 3). Fitting the data points from both scales resulted in a straight line with an excellent r^2 value of 0.986. The use of a second-order (or higher) polynomial results in a better fit ($r^2 = 0.988$); however, within experimental error it cannot be distinguished from a first-order fit, leading to a choice of the linear fit. The correlation of $\Delta\delta$ to the Cal-Ad and slurry calorimetry scales is not fortuitous. Both experiments measure the extent of interaction of a basic probe molecule with a solid acid site. Stronger acid sites will cause greater interactions with the probe, decreasing the electron density about the central phosphorus atom in TEPO or increasing the enthalpy of interaction with pyridine. The chemical shift of TEPO will consistently increase with the acid strength until oxygen atom transfer or full protonation occurs. In the case of oxygen atom transfer, chemical shifts similar to that expected for triethylphosphine should be observed. In the case of full protonation, no further increase in the chemical shift will occur, as the conjugate acid of TEPO, HTEPO$^+$, can no longer easily donate electron density.

The derivation of a relationship between the change in chemical shift and enthalpy of adsorption is not known.

TABLE 1: Δδ Scale

acid or adduct	Δδ
(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
1:1 TEPO:TaCl5	51.3[a]
	46.3[a]
	~42.2[a,b]
	41.8[a]
	38[a]
HPW	45.8
1:1 TEPO:SbCl5	41.7[c]
	37.5
supported sulfated tungsten oxide	41.7
HZSM-5	
site 1	39
site 2	7
2:1 TEPO:Al$_2$Cl$_6$	36.6
sulfated silica gel	35.9
tungstic acid hydrate	
site 1	27.6
site 2	13.4
H-Mordenite[d]	25.6
silica gel	6.0
sol−gel	4.5
NaCl*6H$_2$O	2.7
NaOH	−1.2

[a] Various solids with different acidities. [b] Identified through the spinning sidebands. [c] This is a minor peak with less than 10% of the total intensity. [d] TEPO can probably only access the large cavities where the weaker of two acid sites can be found.
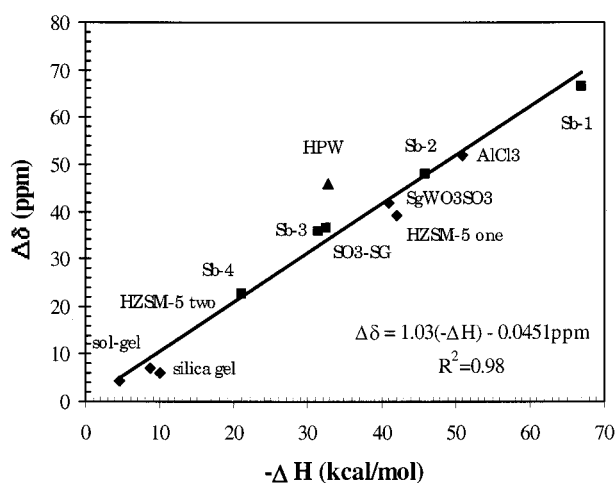

Figure 3. The correlation between calorimetry and Δδ. The acids are: sol−gel, a low acidity silica solid; silica gel, a typical silica gel; HZSM-5 one and two, the acid sites of zeolite HZSM-5; Sb-1 through Sb-4, the four acid sites of silica supported antimony pentachloride; SO3−SG, sulfuric acid washed silica gel; SgWO3SO3, silica supported sulfated tungsten oxide; HPW, 12-tungstophosphoric acid; AlCl3, silica supported aluminum trichloride. The ◆ points are enthalpies derived from the Cal-Ad method, while the ■ are derived from slurry calorimetry alone. The ▲ represents 12-tungstophosporic acid. The line was fit without 12-tungstophosphoric.

However, there are two empirical methods to justify a relationship between the two values. The first comes from Drago's E and C method (ECW).[69] ECW is a σ-bonding-only scale that uses two parameters to describe the donor−acceptor interaction between two molecules (eq 1)[70]

$$\Delta\chi = E_aE_b + C_aC_b - W \qquad (1)$$

The nature of $\Delta\chi$ can be enthalpies of reaction, spectral shifts, rate constants, etc. The first set of parameters, E_a and E_b, represent the electrostatic component of the interaction, while the second set, C_a and C_b, represent the covalent component. The W term accounts for any barrier that must be overcome to allow the acid and base to interact, such as the breaking of a dimer. The ECW model indicates that the same factors that lead to an evolution of an enthalpy of interaction will lead to a proportional change in the spectral parameters[69]

$$E_aE_b + C_aC_b \propto E_aE_b{}^* + C_aC_b{}^* \qquad (2)$$

where the * indicates the equation for the spectral parameters.

Literature precedence has established a second link between acidity measured by enthalpies of interaction and changes in chemical shift. It can be shown that acidity is proportional to strength of the acid−base bond formed (eq 3)[14,30,35,36,71−76]

$$-\Delta H_{acid-base} \propto acid-base\ bond\ strength \qquad (3)$$

The change of chemical shift of TEPO or 2-^{13}C acetone is also proportional to the bond strength of the donor−acceptor pair formed in solution (eq 4)[39−41,43,50,70]

$$\Delta\delta^{31}P, \Delta\delta^{13}C \propto acid-base\ bond\ strength \qquad (4)$$

These two equations allow the relationship between chemical shift, a spectral parameter, and enthalpy of interaction, a thermodynamic parameter, to be written

$$\Delta\delta^{31}P, \Delta\delta^{13}C \propto acid-base\ bond\ strength \propto -\Delta H_{acid-base} \qquad (5)$$

This relationship allows for a correlation between the Δδ and pyridine calorimetry scales.

The Δδ scale is a global acidity scale: it measures acidity without regard for the type of acid site to which the probe is bound. The total donor−acceptor interaction is the primary contribution to the observed change in chemical shift. The ^{31}P MAS NMR spectra of TEPO on the solid acid (silica gel)$_n$-Sb^{V}Cl$_3$ demonstrates this phenomenon.[37] This solid contains four types of acid sites, at least one of which is a Lewis site as determined by pyridine adsorption IR.[77] Additionally, the Δδ of the four acid sites observed all correlate with differential heats of pyridine adsorption obtained from slurry calorimetry. Additional evidence for a global measurement of acidity comes from TEPO adsorbed on a series of Lewis acids. The spectrum of the adducts formed between TEPO and tantalum pentachloride (TEPO:TaCl$_5$) is presented in Figure 4: the five peaks are believed to be several different forms of the TEPO:TaCl$_5$ adduct. Each adduct (TEPO:TaCl$_5$, :SbCl$_5$, and :Al$_2$Cl$_6$) has a positive Δδ at a different chemical shift. By changing the loading of TEPO on TaCl$_5$, a new shift can be observed. The variation in shift is attributed to a nearest-neighbor effect. In samples with less than a 1:1 TEPO:TaCl$_5$ ratio, induction effects that will increase the acidity of the acid site are likely to be observed. Two different loadings of TEPO on TaCl$_5$ demonstrate this effect (Table 2).

For completeness, the chemical shift of TEPO adsorbed onto basic solids (NaOH, CaO, KOH, and unactivated γ-Al$_2$O$_3$) and neutral sodium chloride was studied. At low loadings a small, positive Δδ was observed due to interaction with weak Lewis acid centers (Na$^+$, Ca^{2+}, K$^+$), but at very high loadings on the basic solids a negative shift was observed (Table 3). A similar shift was not observed for the sodium chloride sample at high loading. It is believed that the cause of the shift is an acid−
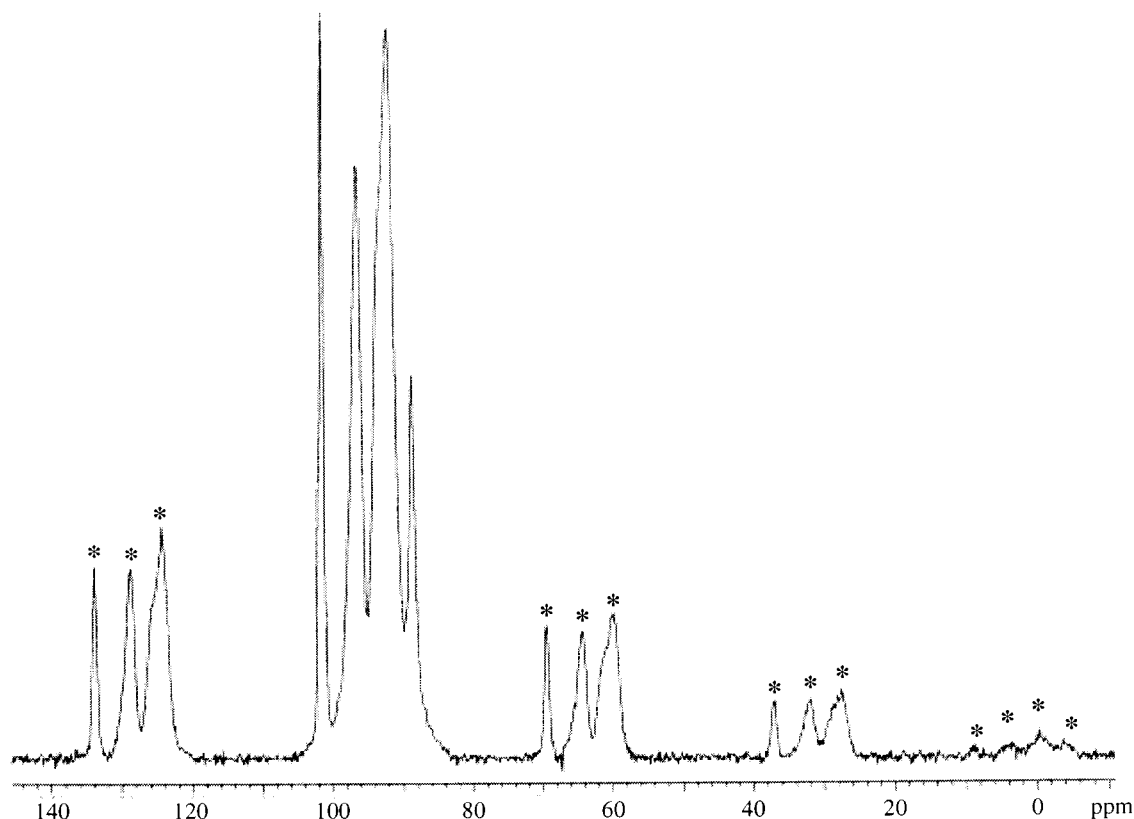
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Figure 4. Phosphorus-31 MAS NMR of TEPO adsorbed on TaCl$_5$. The four lines observed are each a different solid form of the adduct with different bonding between the metal and the phosphine oxide. A fifth spectral line can be identified through the spinning sidebands (*).

TABLE 2: Inductive Effect in Lewis Haloacids

compound	compound observed	chemical shift (ppm)	$\Delta\delta$ (ppm)
1:1 TEPO:SbCl$_5$	TEPO:SbCl$_5$	87.5	37.5
		91.7	41.7
2:1 TEPO:Al$_2$Cl$_6$	TEPO:AlCl$_3$	86.6	36.6
		88.0	38
		91.8	41.8
1:1 TEPO:TaCl$_5$	various TEPO:TaCl$_5$	~92.2	~42.2
	crystals	96.3	46.3
		101.3	51.3
	TEPO:TaCl$_5$	101.6	51.6
1:10 TEPO:TaCl$_5$	TEPO:TaCl$_5$−TaCl$_5$	110.2	60.2

TABLE 3: $\Delta\delta$ Value of TEPO on Several Bases

system	$\Delta\delta$ (ppm)
NaOH	−1.36
KOH	−0.90
	−1.66
CaO	−0.56
	−1.63
γ-alumina	−1.35

base interaction between the TEPO and the basic sites of the solid. In this case, TEPO is acting as a very weak acid and accepting a small amount of electron density from the basic site. Figure 5 is the spectrum of TEPO adsorbed on potassium hydroxide.

Static vs Differential Measures of Acidity. Measuring the chemical shift of a chemisorbed probe molecule results in a static measurement of acidity. This static interaction is a measurement of the acidity of the site that a molecule experiences while bound to it. Differential heats of adsorption may indicate a different acidity than such a static measure depending on the acid under study. The acidity of 12-tungstophosphoric

acid has been measured calorimetrically both in solution[74] and in the solid state (Table 4).[61] Most results indicate that HPW is a powerful solid acid; however, there is much dispute over the true strength of this solid. The Cal-Ad acidity of the strongest site is 32.7 kcal mol^{-1}, the expected $\Delta\delta$ is therefore 33.6 ppm. The observed $\Delta\delta$ of HPW is 45.8 ppm (predicted enthalpy of 44.5 kcal mol^{-1}), much greater than the expected value. The $\Delta\delta$ scale predicts that HPW is a much stronger acid than measured by the Cal-Ad technique.

The source of this discrepancy between calorimetry and $\Delta\delta$ can be readily accounted for with an understanding of the nature of the two experiments. The heat measured from slurry calorimetry is the heat of interaction of the base with the acid site less the heat required to displace a solvent molecule from the acid site and, in this case, less the heat required to open the lattice for the basic probe to enter (Figure 6). The heat of interaction of the base with the acid site contains contributions from both donor−acceptor interactions and van der Waals forces. It can be shown that with the correct choice of basic probe and solvent, the van der Waals component can be removed from the measured enthalpy by the displacement of the solvent molecule.[70, 73]

The reduction of the measured enthalpy by opening the lattice cannot be accounted for without a measure of the lattice energy of the initial and final states. The reduction of the exothermic energy by the opening of the lattice will lower the measured acidity of the solid by the amount of energy required to open the lattice. While the initial adsorption of TEPO contains all of these energetic steps, the measure of the acidity by ^{31}P MAS NMR occurs after all of these processes have been completed. The $\Delta\delta$ is a measure of the static interaction of TEPO with the acid site after the lattice is opened and the molecule is fully adsorbed at the site. The difference between the enthalpy
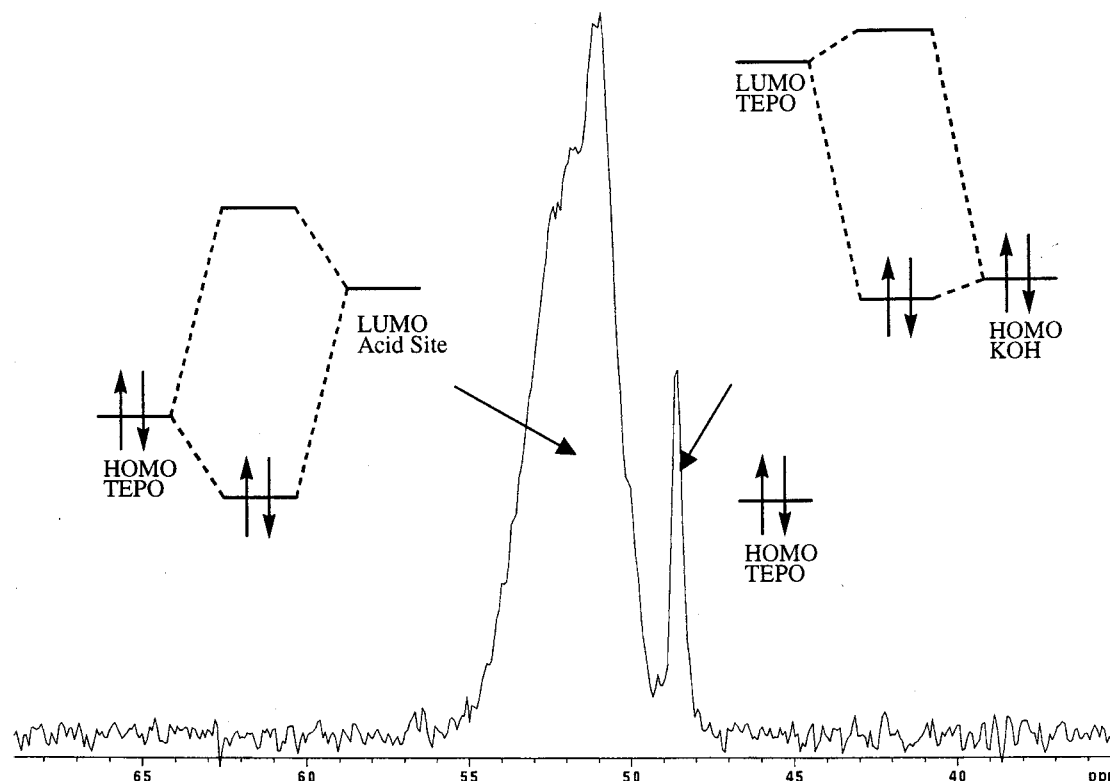
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Figure 5. Phosphorus-31 MAS NMR of TEPO on potassium hydroxide. The small peak at around 48.5 ppm represents TEPO interacting with a basic site. Molecular orbital diagrams representing the interactions are presented.

TABLE 4: Cal-Ad Results for 12-Tungstophophoric Acid (HPW) in Acetonitrile Solution and as a Solid Slurried in Cyclohexane

	HPW dissolved in acetonitrile[74]			solid HPW in cyclohexane slurry[61]		
site	$-\Delta H$ (kcal mol^{-1})	density[a] (mmol g^{-1})[b]	K[c]	$-\Delta H$ (kcal mol^{-1})	density[a] (mmol g^{-1})[b]	K[c]
1	21.0	0.33	2.1×10^3	32.7	0.079	3.7×10^5
2	11.8	0.33	2.4×10^2	19.6	0.16	2.9×10^3
3	18.6	0.33	4.1×10^1			

[a] All of the protons are available for titration in solution; however, only about 25% of the protons of solid HPW are available for reaction. [b] To convert from mmol g^{-1} to [mmol site (mmol H$_3$PW)$^{-1}$] multiply each value by 2.880 g mmol^{-1} H$_3$PW. [c] Equilibrium constant for adsorption.

estimated from the change in chemical shift of TEPO and the enthalpy measured by the Cal-Ad method leads to an estimated energy of 11.8 kcal mol^{-1} required to open the HPW lattice to include a pyridine-sized molecule.

Triethylphosphine Oxide in Zeolites. Previous measurements of TMPO in zeolites HY and dealuminated HY have been carried out by Zalewski et al.[30] and Rakiewicz et al.[34] and of zeolite USY by Rakiewicz et al.[34] These authors report that the shift observed is very sensitive to the type of acid site to which the probe is adsorbed. We extend their observations of phosphine oxide behavior to include the measurement of zeolites HZSM-5 and H-Mordenite with TEPO and zeolite TS-1 with trimethylphosphine oxide.

The ^{31}P MAS NMR spectrum of 0.1 mmol g^{-1} TEPO on zeolite HZSM-5 demonstrates the presence of two acid sites. The structure of HZSM-5 is large enough to allow complete penetration by the probe into the intersections and channels after an equilibration time.[79] The first acid site is a low population strong site that has been assigned as a Brønsted site through pyridine IR adsorption and Cal-Ad.[73] The second site has been shown to be a weaker hydrogen bonding site of significantly larger population. The acidities determined for these two sites are in good agreement with results from calorimetric measurements (Table 5).

TABLE 5: Cal-Ad and $\Delta\delta$ Results for HZSM-5

	site 1	site 2
$-\Delta H_{ave}$ (kcal mol^{-1})[a]	42.1 ± 0.8	8.6 ± 3.8
population (mmol g^{-1})[a]	0.0415 ± 0.0057	0.53 ± 0.01
K[a]	$4.9 \pm 2.3 \times 10^6$	$2.3 \pm 2.0 \times 10^6$
$\Delta\delta$ (ppm)	39 ± 1.0	7.0 ± 0.5
predicted enthalpy[b](kcal mol^{-1})	38 ± 1.1	6.8 ± 0.7

[a] Values from ref 81. [b] Using the correlation established in Figure 3: $\Delta\delta = 1.03 (-\Delta H) - 0.0451$ ppm.

The spectra of TEPO adsorbed on H-Mordenite shows the presence of only one acid site. The $\Delta\delta$ value for this moderate strength site is 25 ppm. TEPO cannot penetrate the small channels of H-Mordenite where additional strong acid sites reside.

Zeolite TS-1 is a very weakly acidic zeolite.[81] The acidity of TS-1 arises from defect sites resulting in tricoordinate Ti^{4+}. The acidity of this solid was measured with trimethylphosphine oxide (with chemical shift referenced to 85% phosphoric acid). Two overlapping spectral lines were observed. From a short study of the behavior of trimethylphosphine oxide on various solid acids (Figure 7), the change in the chemical shift of trimethylphosphine oxide can be roughly compared to the $\Delta\delta$ values for TEPO, but with a chemical shift for the physisorbed probe
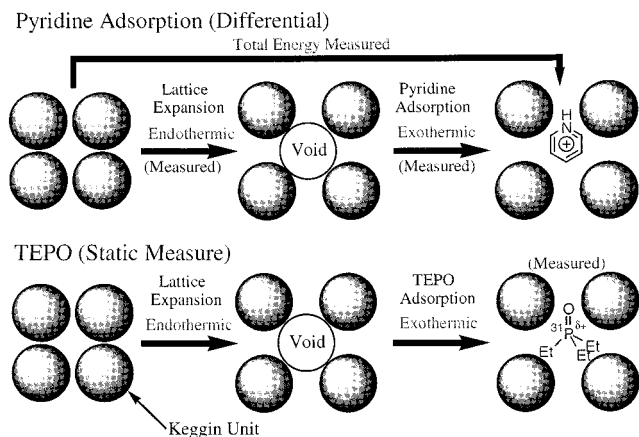
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Figure 6. A comparison of two different methods of measuring solid acidity. The top scheme demonstrates the energy changes measured during differential calorimetry of 12-tunsgstophosporic acid (HPW) with pyridine. The first step is the endothermic opening of the lattice to accommodate the probe molecule. The second step is the exothermic enthalpy for adsorption of the probe. The total energy measured is the sum of both of these steps. The lower scheme is for the measurement of the chemical shift of chemisorbed triethylphosphine oxide. Only the interaction between the probe and the acid site is measured. Note: The nature of the phosphorus−oxygen bond in trialkylphosphine oxides is not understood.[78] Due to the short length of this bond measured through crystallography and other means, this bond has been characterized as a double bond. However, calculations have shown that it is possible to represent the bonding as a single bond with a full positive charge at the phosphorus and a full negative charge at the oxygen. The work here cannot add to this debate and the choice to describe the phosphorus−oxygen bond as a double bond throughout this article is for clarity only.
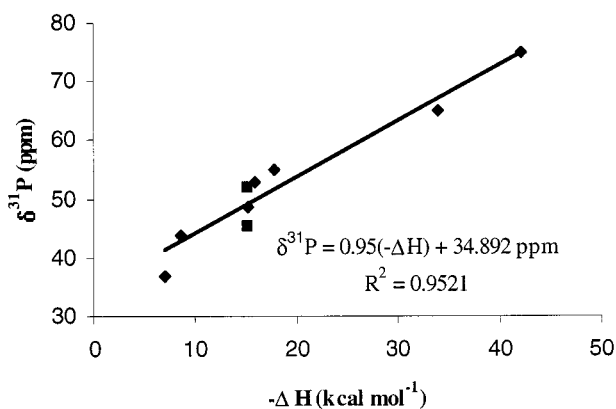

Figure 7. The chemisorbed chemical shift of trimethylphosphine oxide compared to calorimetric measures of acidity of several solid acids. The two chemical shifts of trimethylphosphine oxide interacting with zeolite TS-1 (represented by ■) were averaged together to estimate the shift of the acid site found by Cal-Ad for this solid. The Cal-Ad method cannot separate two sites that have similar acidity. The chemical shifts reported by Rakiewicz et al. (ref 54) for zeolite HY were used for this solid. The other solids include HZSM-5 and silica gel.

of ∼30−34 ppm. This assumption leads to the conclusion that the acidity of TS-1 is very mild and arises from previously reported titanium sites scattered throughout the structure (there are twelve possible substitution positions that can be occupied to different extents by titanium in TS-1) and possibly from surface silanols.

Conclusions

The basic probe molecule triethylphosphine oxide is capable of measuring the acidity of solid acids using simple one pulse ^{31}P MAS NMR. The shift of TEPO has been shown to correlate

well with acidities measured with Cal-Ad or slurry calorimetry. The nature of the acid site, as Lewis or Brønsted, does not affect the shift of TEPO. The value of measuring acidity through several techniques has been demonstrated by a comparison of the acidity measured by differential heats of adsorption to the static method involving ^{31}P MAS NMR to determine a "lattice penetration" energy for pyridine into HPW. Reports of a Lewis acid region observed for TMPO have been shown to be inappropriate for TEPO. Small, negative $\Delta\delta$ values have been demonstrated to be interactions with basic sites. Overall, this is a powerful, accurate, and fast tool for characterizing and exploring solid acidity.

Triethylphosphine oxide is an ideal probe for the measurement of the global acidity of solid acids. It is capable of identifying different strength acid sites on the surface. However, simple one-pulse experiments are incapable of identifying the nature of the acid site. TEPO lacks the chemical shift ranges dependent upon the nature of the acid site observed for TMP. It has been demonstrated here and elsewhere[34] that the population of acid sites can be determined with phosphine oxides. The combination of all of these traits makes phosphine oxides ideal for the characterization of solid acids.

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