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Measurement of Surface Acidity by ^{31}P NMR of Adsorbed Trimethylphosphine: Application to Vapor Deposited SiO_2 on Al_2O_3 Monolayer Catalysts

Tai-Cheng Sheng* and Ian D. Gay†

**Department of Chemistry, Shandong University, Jinan, Shandong, 250100, China; and †Department of Chemistry, Simon Fraser University, Burnaby, British Columbia V5A 1S6, Canada*

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Experimental procedures for quantitative estimation of surface acid by ^{31}P NMR of adsorbed phosphines are discussed. These procedures are illustrated by application to a commercial silica–alumina cracking catalyst, and are applied to a series of silica on alumina monolayer catalysts prepared by chemical vapor deposition. The monolayer catalysts show a maximum in Brønsted acidity for a deposition of 8 SiO_2 groups per nm^2 of Al_2O_3 surface. The evolution of Brønsted acid concentration as a function of amount of deposited silica can be accounted for by a simple kinetic model.

INTRODUCTION

Trimethyl phosphine (PMe_3) is a useful NMR probe of acid sites on solid surfaces. As previous workers have shown (1–3), the ^{31}P resonance of the protonated phosphine is well separated from those of Lewis-bound and physically adsorbed phosphine. The latter two resonances are somewhat less well separated.

The authors of (2) and (3) have explored the problem of quantitative measurements of acid sites, and have exhibited some of the problems which can arise due to steric effects, and adsorption thermodynamics. We explore these questions further in the context of SiO_2 on Al_2O_3 monolayer catalysts prepared by chemical vapor deposition (4, 5). The authors of (5) have observed the spectrum of PMe_3 on one such catalyst, but have not attempted a quantitative evaluation. These catalysts are of interest in that they permit the development of a controlled level of Brønsted acidity on the catalyst surface.

EXPERIMENTAL

The following commercially available solids were used: SiO_2—Davison high purity silica gel, grade 923, 484 m^2/g; Al_2O_3—Harshaw γ-Al_2O_3 grade Al-3945 E, 225 m^2/g; silica–alumina cracking catalyst Davison type 980, 25% Al_2O_3, 400 m^2/g. The last was of the same lot as used in previous investigations in this laboratory (6).

Our initial attempts to prepare SiO_2 on Al_2O_3 monolayer catalysts following the static procedure of (4) led to products of poorly reproducible characteristics. We have therefore devised a fluidized-bed method of preparing these catalysts. A sample of 0.5 g of Al_2O_3, ground and sieved to 60–80 mesh was placed on a fritted glass disk in a vertical Pyrex tube of 2 cm i.d. The bed of alumina was fluidized by a flow of dried nitrogen at 500 ml/minute. The solid was first dried by heating to 400°C in the flowing N_2 for 1 h. After drying the temperature was adjusted to 320°C, and the N_2 flow was diverted to pass through an upstream reservoir of $Si(OCH_3)_4$ maintained at 0°C. The Si-containing vapor flow was continued for variable lengths of time. The sample was then cooled in flowing N_2 to room temperature, transferred to a crucible, and calcined in air for 3 h at 500°C. Transmission infrared spectroscopy of pressed disks of the catalysts (7) showed no C–H stretching bands, indicating complete decomposition of the methyl orthosilicate. The amount of silica deposited was determined from the weight gained, in comparison with a sample that was treated only in nitrogen. The results of our preparations are summarized in Table 1.

NMR measurements were carried out on a home-built instrument operating at 3.5 T, which produces a resonance frequency of 60.4 MHz for ^{31}P. NMR samples were prepared on a vacuum line, and sealed in 5-mm-o.d. glass tubes. These could be spun at the magic angle, using a previously described spinner (8). Chemical shift anisotropies were rather low, and spinning speeds of 1.8 to 2.4 kHz were used. Quantitative measurements were made using 90° pulses to excite the spectra, and some observations were also made by cross-polarization. In both cases, protons were decoupled with a 50-kHz decoupling field. Chemical shifts were referenced to 85% H_3PO_4. Both reference and experimental samples were in the form of long

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TABLE 1

Amount of SiO_2 Deposited on Al_2O_3, as Function of Time of $Si(OCH_3)_4$ Flow

Time	SiO_2/nm^2
10 min	1.3
30 min	4.2
1 h	8.2
4 h	12.3
11 h	17.5

cylinders inclined at the magic angle, thus no susceptibility correction is required.

The total amount of phosphine in each sample was determined by gas volumetric measurements when the sample was prepared. The uncertainty of this amount ranges from about 5% at the lowest coverages used, to 2% at the highest coverages. The relative amount of phosphorous in each peak of the spectrum was determined from the relative areas of the integrated spectra. The accuracy of the relative area determinations varies with the relative size of the peaks, and with the signal-to-noise ratio. From repeated measurements we estimate an uncertainty of ±5% when peak area ratios do not exceed 10 : 1. This condition applies to all of our measurements except for the monolayer catalyst of lowest SiO_2 level. For this sample, ratios ranged up to 20 : 1, and a 10% uncertainty estimate is more realistic. Since total Brønsted acid is determined mainly from the higher coverage samples, the integrations are the main source of experimental uncertainty.

To perform such measurements, it is essential to ensure that the repolarization time (interval between successive NMR scans) is sufficiently long. In a sample with several NMR lines, it is possible that different resonances have different spin–lattice relaxation times (T_1). Too short a repolarization delay will then lead to spectra in which the more quickly relaxing lines appear artifically intensified in comparison with the more slowly relaxing species. In our measurements, care was taken either a) to measure the ^{31}P T_1 values and ensure that the repolarization time was sufficiently long, or b) to verify that peak ratios did not change significantly for a three-fold change in repolarization time. In some cases data were corrected for short repolarization time using the measured values of T_1, in cases where the correction would not exceed 20% in relative intensity. It was found that loosely bound phosphine species typically had significantly shorter T_1 values than protonated or Lewis-bound phosphines, and such precautions are definitely required. As a result of these considerations, repolarization times varied from 0.5 to 5 s on different samples.

RESULTS AND DISCUSSION

Figure 1a shows the spectrum of PMe_3 on SiO_2. We refer to the species involved as "physically adsorbed," although there is undoubtedly some weak interaction with the surface OH groups. Since silica does not have surface acid sites, no other peaks are observed. The position of the single peak varies from −59 ppm at low coverage to −61 ppm at high coverage. This is in agreement with the findings of Maciel and co-workers (2), and is not surprising, given a liquid-phase chemical shift of −62 ppm for PMe_3. In no case have we found a line near −67 ppm as reported by Lunsford and co-workers (1, 3) for PMe_3 in zeolites.

Figure 1b shows the spectrum on Al_2O_3. A substantial peak centered at −48 ppm arises from bonding to Lewis sites (2). The fine structure in this peak is likely due to scalar coupling of P to ^{27}Al, as reported by Lunsford and co-workers (9) for PMe_3 interacting with $AlCl_3$ in zeolite Y. The separation of our sub-peaks is essentially the same as theirs, 300 Hz. As can be seen, we find little or no Brønsted acid on this surface.

Figure 2 shows a series of spectra of PMe_3 at different coverages on commercial SiO_2–Al_2O_3 cracking catalyst. As can be seen, a peak at −4.9 ppm due to PMe_3H^+ appears first, together with peaks due to Lewis-bound PMe_3. The peak at −4.9 ppm was verified by delayed decoupling to arise from phosphorous with a directly bonded proton. These peaks grow with increasing amount of adsorbed phosphine, and a new peak appears when the adsorbed amount exceeds 0.5 μmol/m^2. This peak grows and shifts upfield as coverage increases, and at the highest coverage is indistinguishable from the peak observed on SiO_2.

An attempt to measure total protonated phosphine from the total adsorbed amount, together with the fraction of the total area in the PMe_3H^+ peak, leads to the results shown by the open symbols in Fig. 3. It can be seen that at the higher coverages, the amount of protonated phosphine appears to decrease. A genuine decrease in total protonated phosphine is totally unreasonable, on thermodynamic grounds, thus some protonated phosphine must be resonating elsewhere than in the −4.9-ppm peak. The data can be rationalized by the assumption that physically adsorbed PMe_3 appears above 0.5 μmol/m^2, and that a fraction of the protonated molecules can exchange with this, and are indeed undergoing fast exchange under our experimental conditions. This accounts both for the decrease in the −4.9-ppm peak, and the coverage-dependent shift of the new peak which appears above this coverage. The whole of the PMe_3H^+ population cannot be undergoing exchange, since a substantial unshifted peak remains at −4.9 ppm.

Accepting this view regarding exchange, we can say that the observed shift of the coverage-dependent peak

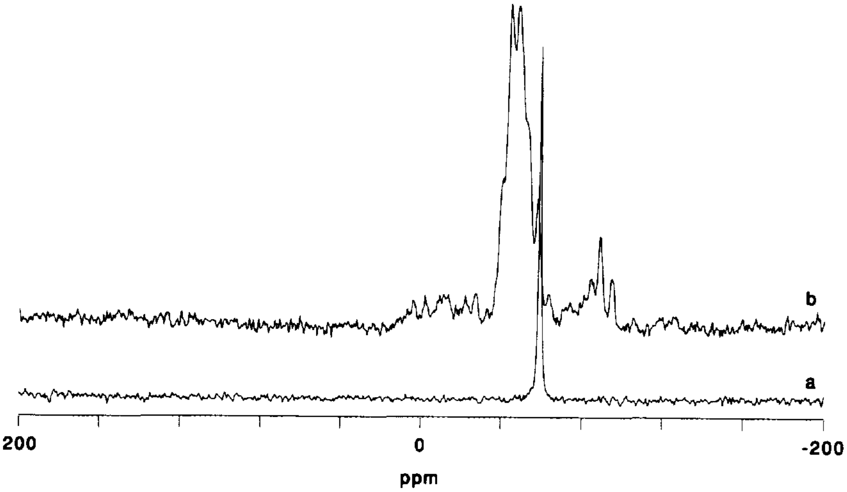

FIG. 1. ^{31}P spectra of PMe_3 adsorbed on (a) silica gel and (b) alumina. The small features in (b) near −5 and −80 ppm are spinning sidebands.

is a mole-fraction-weighted average of the −4.9-ppm shift associated with PMe_3H^+ and −62 ppm of physisorbed species. From the observed position of the line, one can then calculate the mole fraction of protonated phosphine in the line:

$$\text{fraction protonated} = \frac{\text{observed ppm} - (-62\ \text{ppm})}{-4.9\ \text{ppm} - (-62\ \text{ppm})}$$

From this fraction and the area of the peak we find the amount of exchanging PMe_3H^+. This is added to the PMe_3H^+ in the −4.9-ppm peak to give the total amount, leading to the filled symbols in Fig. 3. (It will be appreciated that the calculated amount of H^+ at the highest coverages is very sensitive to the shift assumed for the physisorbed species, since the numerator of the above fraction becomes small. We are always able to obtain consistent results with an assumed value in the range of −62 ppm (liquid) to −61 ppm (adsorbed on SiO_2). The total calculated acid at 0.5 to 0.8 $\mu mol/m^2$ adsorbed PMe_3 is insensitive to the choice of values in this range, and an uncertainty estimate of 5% for the total Brønsted site concentration is appropriate, based on uncertainties of integration.)

The above procedure gives a maximum concentration of 0.21 $\mu mol/m^2$ of protonated phosphine, which is a lower limit to the amount of Brønsted acid available on the surface. From Fig. 2a we can obtain a lower limit of 0.08 $\mu mol/m^2$ for Lewis acid on this surface. Thus we obtain at least 0.29 $\mu mol/m^2$ of total acid. This may be compared with our previous measurement of 0.5 $\mu mol/m^2$ obtained (6) for this catalyst using NH_3 and 4-ethylpyridine adsorp-

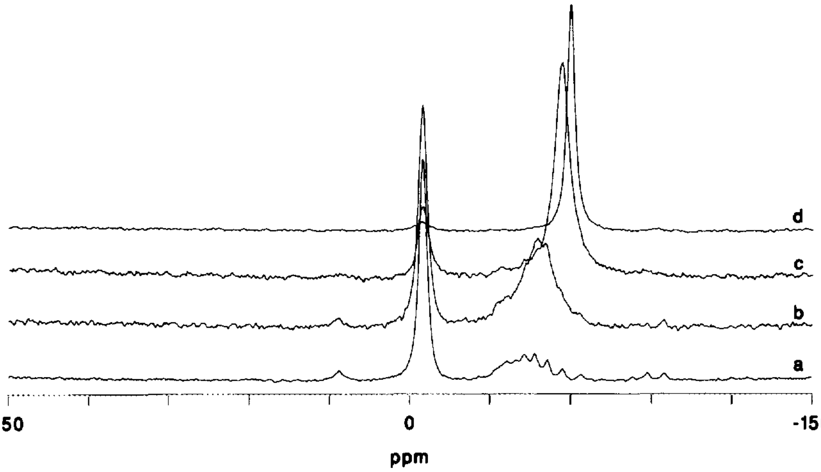

FIG. 2. ^{31}P spectra of PMe_3 on commercial SiO_2–Al_2O_3 cracking catalyst at various coverages: (a) 0.23, (b) 0.42, (c) 0.82, and (d) 2.02 $\mu mol/m^2$.

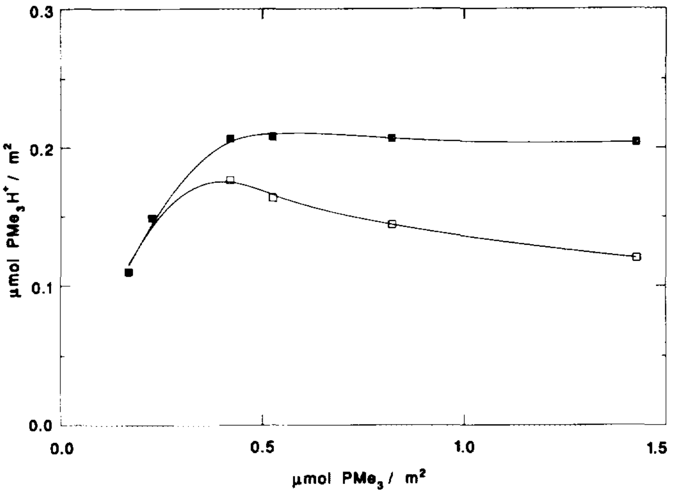

FIG. 3. Concentration of PMe$_3$H$^+$ on commercial SiO$_2$–Al$_2$O$_3$ cracking catalyst as a function of adsorbed PMe$_3$ coverage. Open symbols: calculated from area of − 4.9 ppm peak only. Closed symbols: calculated using exchange model described in text.

TABLE 2

Acid Concentration as Function of SiO$_2$ Content in Monolayer Catalysts

SiO$_2$/nm^2	H$^+$ (µmol/m^2)	Lewis (µmol/m^2)
0.0	0.0	1.3
1.3	0.17	0.9
4.2	0.27	0.4
8.2	0.30	0.18
12.3	0.21	0.12
17.5	0.13	0.08

tion. Our total Brønsted concentration is somewhat lower than the value of 0.47 µmol/m^2 found by Maciel and coworkers (2) on a catalyst from a different source. This, together with the rather different exchange behavior indicates that nominally similar catalysts from different suppliers can have rather different surface properties. The discrepancy in total acid compared to (6) may be due to the presence of Lewis sites which are accessible to nitrogen bases but not to phosphines. However the measured total acid values in (6) range from 0.3 to 0.6 µmol/m^2, and with such a scatter it is not easy to draw firm conclusions.

Figure 4 shows a similar series of spectra for a SiO$_2$ on Al$_2$O$_3$ monolayer catalyst containing 8.2 SiO$_2$ per nm^2. It can be seen that the same type of exchange phenomenon is operating here. If the maximum PMe$_3$H$^+$ concentrations are evaluated as described above, we obtain the results given in Table 2 for catalysts of varying SiO$_2$ levels. The amount of Brønsted acid has an uncertainty of 10% for the 1.3 SiO$_2$/nm^2 catalyst, and 5% for the higher silica contents, as noted above. The amounts of Lewis acid quoted are lower limits, based on the size of the Lewis peak at low coverages, where no exchanging peak is seen. Once the latter appears, it prevents the observation of any further bonding of PMe$_3$ to Lewis sites at higher coverages.

If all surface H$^+$ is accessible to PMe$_3$, the figures in Table 2 should give the total amount of surface Brønsted acid. If steric considerations make some H$^+$ inaccessible, the table values are lower limits. Maciel and co-workers (2) found lower apparent H$^+$ concentrations on commercial SiO$_2$–Al$_2$O$_3$ catalysts using triethyl- or tributylphosphines. This may well be a steric effect arising from the larger probe molecules. Lunsford *et al.* (3) also found steric effects in zeolites containing high levels of H$^+$,

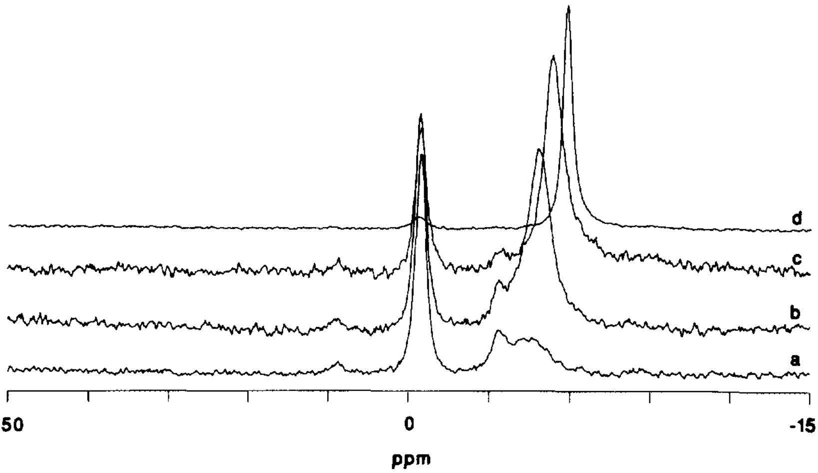

FIG. 4. ^{31}P spectra of PMe$_3$ on SiO$_2$ on Al$_2$O$_3$ monolayer catalyst with 8.2 SiO$_2$ per nm^2. PMe$_3$ coverages are (a) 0.20, (b) 0.63, (c) 0.91, and (d) 2.74 µmol/m^2.

because enough PMe_3 molecules could not be accommodated in a cage to react with all of the H^+ present. In the present work, any steric effects must arise either from H^+ confined in narrow pores which PMe_3 cannot enter, or from very close aggregations of H^+; the observed amount of H^+ is always small compared to the maximum amount of PMe_3 adsorbed, which in turn is always less than a statistical monolayer, based on the liquid density.

The results for H^+ concentrations in Table 2 can be understood on the basis of a simple model. Since neither SiO_2 nor Al_2O_3 has a significant amount of Brønsted acid, the acid on the monolayer catalysts must be produced by the interaction of the two oxides. As SiO_2 is progressively added to an initially bare Al_2O_3 surface, the number of sites of interaction will first rise linearly with SiO_2 coverage. Eventually, however, Al_2O_3 surface becomes increasingly unavailable, due to coverage by SiO_2, and acid sites which were formed initially may also be covered by SiO_2, leading to an eventual decline in the amount of Brønsted acid as SiO_2 coverage increases.

We attempt a simple quantitative model as follows: writing Θ_S for the fraction of Al_2O_3 surface covered by SiO_2, and n for the total amount of SiO_2 deposited, we assume that SiO_2 covers bare Al_2O_3 or previously deposited SiO_2 randomly, and hence write

$$\frac{d\Theta_S}{dn} = k(1 - \Theta_S), \qquad [1]$$

which yields

$$\Theta_S = 1 - e^{-kn}. \qquad [2]$$

Writing Θ_H for the fraction of surface covered with Brønsted sites, we further assume that formation of such a site requires that SiO_2 be deposited on bare Al_2O_3, that there be an adjacent bare site for acid formation, and that an existing acid site could be covered with equal probability. This gives

$$\frac{d\Theta_H}{dn} = k'[(1 - \Theta_S)^2 - \Theta_H]; \qquad [3]$$

substituting (2) for Θ_S and solving gives

$$\Theta_H = \frac{k'}{k' - 2k}[e^{-2kn} - e^{-k'n}]. \qquad [4]$$

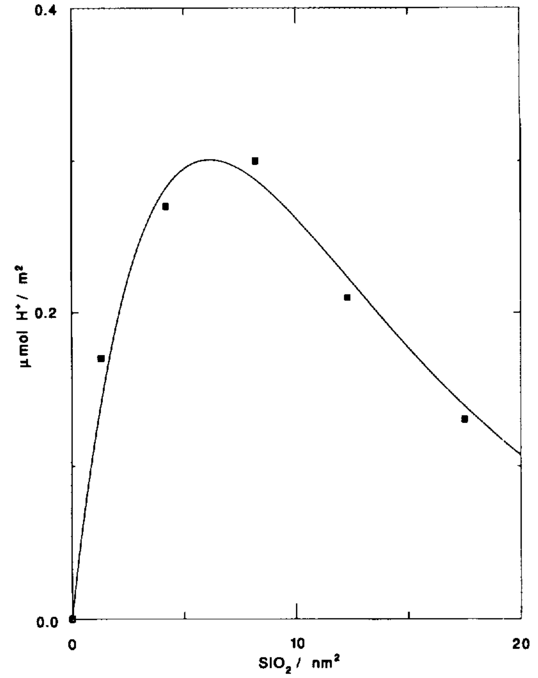

FIG. 5. Plot of data from Table 2 (points) together with graph of Eq. [4] (line).

Figure 5 shows a plot of this equation for values of k = 0.10 nm^2 and k′ = 0.13 nm^2, with the ordinate scaled to match the data as well as possible. It can readily be seen that the above simple model gives a good account of the development of Brønsted acidity on the monolayer catalysts.

Niwa *et al.* (4) and Sato *et al.* (5) have studied the acid-catalyzed cumene cracking reaction on similar catalysts. They find maxima in the rate for deposition of about 11 and 9 SiO_2 per nm^2, respectively. Thus the assumption of these authors that the rate of reaction is proportional to the concentration of Brønsted sites is supported by our results. Our maximum in Brønsted acidity occurs at 8 SiO_2 per nm^2, and the small difference may result from different preparation methods, or from a population of weak sites which are detected by phosphine adsorption, but are not strong enough to crack cumene.

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