Surfaces and Interfaces

Structures and Unexpected Dynamic Properties of Phosphine Oxides Adsorbed on Silica Surfaces

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Abstract: Solid-state NMR spectroscopy of selected phosphine oxides adsorbed on silica surfaces establishes the surface mobilities, even of phosphine oxides with high melting points. Crystal structures of the adducts Ph₃PO·HOSiPh₃ and Cy₃PO·H₂O indicate that the interactions with silica involve hydrogen bonding of the P=O group to adsorbed water and surface silanol groups.

Phosphine oxides represent an immensely important class of compounds.[1] They are by-products of phosphine chemistry, and are generated as stoichiometric co-products of the Wittig, Appel, and other reactions. They are also indispensable probes for surface acidities of oxides[2] and recently received attention in the decomposition of warfare agents.[3] Another long-standing question in the field of immobilized catalysts[4] is whether adsorbed phosphine oxides mimic the ³¹P MAS (magic angle spinning) NMR signals of phosphine linkers quaternized to form phosphonium salts.[5] Despite their importance, the surface chemistry of phosphine oxides is not well documented. Herein, we prove using solid-state NMR techniques that even phosphine oxides with high melting points possess heretofore unappreciated surface mobilities in the absence of solvents. The silica-adsorption process of phosphine oxides proceeds at ambient temperature by co-grinding the dry components. Crystal structures of model compounds show that interactions with surface silanol groups and adsorbed water mediate the adsorption and mobility, which correlates with leaching data in various solvents.

The ³¹P CP/MAS (cross-polarization with MAS) spectrum of polycrystalline, adduct-free[1] Ph₃PO shows that the chemical shift anisotropy (CSA)[6] is large, and the span (δ₁₁–δ₃₃)[6a] of the wideline signal amounts to δ = 200.6 ppm (Figure 1, bottom). However, when Ph₃PO is adsorbed on SiO₂[7] as a monolayer,[8] the CSA vanishes (Figure 2) and comparatively narrow, unstructured signals result even without sample spinning (Figure 2, bottom). The absence of a CSA of the ³¹P MAS signals compared to the polycrystalline Ph₃PO proves that the crystal lattice is no longer present and that the adsorbed phosphine oxides are very mobile on the surface. The Lorentzian line-shape implies that an isotropic reorientation of the molecules occurs, which indicates a translational mobility of the molecules, spiraling along the walls inside the silica pores. This phenomenon has recently been described for the ¹³C MAS NMR signals of adsorbed metallocenes.[9]

Figure 1. ³¹P MAS NMR spectra of polycrystalline Ph₃PO (bottom) and Ph₃PO·HOSiPh₃ (top). The arrows indicate the isotropic lines.

Figure 2. ³¹P MAS (top) and ³¹P wideline (bottom) NMR spectra of Ph₃PO adsorbed[8] on dry SiO₂.[7]
The residual linewidth is smallest (1.3 kHz) when Ph₃PO is adsorbed on dry SiO₂.[7] (Figure 2). Ph₃PO is more strongly bound on wet SiO₂,[6] leading to slightly reduced mobility and a broader line (1.5 kHz). The sample spinning is not responsible for the removal of the CSA, because even the wideline signal is only 2.4 kHz broad (Figure 2, bottom).

Further proof of the translational mobility of Ph₃PO on SiO₂ is realized by applying it to the surface by co-grinding with the dry SiO₂.[7] Although the melting point of Ph₃PO is high (157 °C),[15] the crystal lattice disintegrates within a few days, and a monolayer of adsorbed phosphine oxide forms. For this process to proceed to completion, the individual molecules have to move away from the contact points of Ph₃PO with SiO₂ in a translational motion to make space for successors.

Further proof for the translational mobility of surface-adsorbed Ph₃PO is provided by variable-temperature ³¹P MAS measurements. At higher temperatures, narrower lines are obtained, whereas at low temperatures, the signals broaden.[16] Within the range of 20 to 50 °C, a linear correlation is found between the linewidth values and the temperatures.[17] Furthermore, the linewidth changes are reversible, which excludes any reaction of the phosphine oxide with the silica.

Besides signal intensity changes resulting from contact time variation,[17] T₁ relaxation times are important indicators for mobilities.[18] In the solid state, the shorter the T₁ times, the more mobile molecules or functional groups are.[16] While crystalline, immobile triaryl phosphine species have ³¹P T₁ relaxation times in the range of minutes,[12] the values obtained by measurements of adsorbed Ph₃PO performed as described earlier are only seconds.[17] For a monolayer of Ph₃PO adsorbed on silica (206 molecules per 100 nm²), a T₁ relaxation time of about 4 s results. A sub-monolayer of Ph₃PO on the surface (27 molecules per 100 nm²) gives a T₁ value of only about 2 s. This proves that the surface-adsorbed phosphine oxide is mobile, and that the mobility increases when there are fewer molecules on the surface that impede this mobility. The T₁ values being a function of the surface coverage again corroborates the translational mobility of the adsorbed phosphine oxides.

To obtain additional quantitative information about the surface mobility of phosphine oxides, ²H MAS NMR of adsorbed ([D₃]Ph)Ph₃PO was utilized. The polycrystalline material gives a Pake pattern with a quadrupolar coupling constant Q₀ of 175.2 kHz.[15] The Pake pattern collapses upon adsorption and an unstructured signal with a halfwidth of 5.4 kHz results (Figure 3). This phenomenon has been described for deuterated polycrystalline and adsorbed ferrocene,[9] and was also found for mobile components in polymer networks.[15]

For averaging out a Pake pattern completely, an isotropic reorientation is needed. For example, ²H MAS gives a Pake pattern for solid poly[(D₅)methyl methacrylate] (PMMA).[16] although the CD groups rotate rapidly around a C₅ axis,[18] similarly, solid ([D₃]C₅)Fe gives a Pake pattern[9] despite fast Cp ring rotation,[18] and also confined, but rotating benzene.[17] The gradual collapse of Pake patterns and their resulting shapes have been visualized for angle-dependent movements.[18] Comparing the ²H MAS signal of adsorbed ([D₃]Ph)Ph₃PO with the calculated Pake pattern shapes[18] leads to the conclusion that there has to be isotropic mobility with a reorientation time of the molecules close to 300 ns. This means that the adsorbed ([D₃]Ph)Ph₃PO migrates over surface silanol groups and reorients isotropically by spiraling in a translational motion across the inner walls of the pores.[19]

Additional proof for isotropic translational mobility comes from variable-temperature ²H MAS measurements. As for ³¹P, the residual linewidths of the ²H MAS signals show a linear correlation with the temperature.[17] For example, at 77 °C the linewidth is only 1.1 kHz, whereas at 17 °C, it is 6.7 kHz. The linewidth changes are reversible, indicating a dynamic scenario and excluding any reaction of ([D₃]Ph)Ph₃PO with the surface.

Regarding how phosphine oxides attach to the SiO₂ surface, the P-O groups could either bind covalently, or interact with the protons of surface silanol groups.[12,3] The mobility of the adsorbed phosphine oxides on the surface excludes a covalent bond, but we have demonstrated recently that phosphine oxides form rather stable hydrogen-bonded adducts with H₂O.[1] The downfield shift of the ³¹P signal when transitioning from the polycrystalline to the adsorbed Ph₃PO (δ = 26.3 to 36.4 ppm) suggests the formation of hydrogen bridges. There is also a δ difference of 1.4 ppm between the signals of Ph₃PO adsorbed on wet and dry SiO₂ (36.4 and 35.0 ppm). Therefore, hydrogen bonding to different surface species is likely, presumably to H₂O, being abundant on the surface of wet SiO₂, and to surface silanol groups, which represent the dominant functional groups on dry SiO₂ apart from surface siloxane groups.[20]

Indeed, when H₂O was added to Cy₃PO in a stoichiometric amount, crystals of a 1:1 hydrogen-bonded adduct were obtained (Figure 4).[21] The H₂O molecule is bound to the P=O group through a single hydrogen atom. The strength of the interaction is reflected in the lengthening of the P=O bond from 1.490 Å in pure Cy₃PO[22] to 1.501/1.499 Å (two independent molecules) in the H₂O adduct.

Next, we sought to mimic the SiO₂ surface by using a silanol as molecular model. When Ph₃SiOH was added to phosphine oxides in stoichiometric amounts, large single crystals of 1:1 hydrogen-bonded adducts were formed, for example, Ph₃PO·HOSiPh₃ (Figure 5).[23] The strength of the interaction of the P-O group with the hydrogen atom is indicated by the lengthening of the P=O bond from 1.479 Å in pure Ph₃PO[24] to 1.503 Å (1.493 Å in the second molecule) in the silanol adduct.
The melting point of the silanol adduct (123 °C) is high enough for recording the 31P MAS spectrum (Figure 1, top). The $\delta^{(31)P}$ of the isotropic line of Ph$_3$PO·HOSiPh$_3$ decreased to 25.6 ppm compared to 26.3 ppm for Ph$_3$PO (Figure 1, bottom). The CSA of Ph$_3$PO·HOSiPh$_3$ was reduced by about 20 ppm to 180.3 ppm ($\delta_{11} = 91.0$, $\delta_{22} = 74.9$, $\delta_{33} = -89.3$ ppm) compared to 200.6 ppm for Ph$_3$PO ($\delta_{11} = 98.0$, $\delta_{22} = 83.4$, $\delta_{33} = -102.5$ ppm). Therefore, we conclude that the 31P signals of adsorbed phosphine oxides lack a CSA mainly because of their surface mobility, and only a small CSA reduction is due to hydrogen bonding to silanol groups.

The silanol adduct exhibits four Ph$_3$PO·HOSiPh$_3$ assemblies per unit cell (Figure 6). Therefore, theoretically there could be four lines in each 31P NMR spectrum of a single crystal (Figure 7)\[6b,25\]. However, only two orientations of the P=O groups differ significantly from each other (Figure 6), and only two lines are distinguishable in the 31P single crystal NMR spectra.

The adsorption phenomena are also reflected in the IR data of Ph$_3$PO·HOSiPh$_3$. The ν(OH) band of neat Ph$_3$SiOH at 3244 cm$^{-1}$ becomes narrower upon adduct formation. The weakened O–H bond manifests itself in a decreased ν(OH) value in neat Ph$_3$PO·HOSiPh$_3$ (3224 cm$^{-1}$). Analogously, ν(P=O) decreases from 1188 cm$^{-1}$ for neat Ph$_3$PO\[1\] to 1179 cm$^{-1}$ for neat Ph$_3$PO·HOSiPh$_3$. The ν(P=O) IR band of the adduct is very narrow, indicating the well-defined nature of the hydrogen bond.

Next, attention was turned to practical issues. Thus, the maximal monolayer surface coverages\[8\] after the standard immobilization procedure\[8\] and leaching\[26\] with different solvents have been studied (Figure 8). Because there are more H$_2$O molecules and silanol groups available for hydrogen bonding on wet SiO$_2$\[20\] for each phosphine oxide the surface coverages are in general higher than on dry SiO$_2$\[8\] Comparing different phosphine oxides, increasing steric bulk correlates to a decrease of the monolayer surface coverage\[8\].

Figure 8 shows that protic and highly polar solvents detach adsorbed phosphine oxides from the support. Nonpolar and non-protic solvents, such as pentane and toluene, promote only modest leaching. This speaks again for the strong hydrogen bonding of the phosphine oxides with the SiO$_2$ surface.
The leaching characteristic can be used to remove phosphine oxides from reaction mixtures or to purify them by adsorption (Figure 8).

In conclusion, it has been demonstrated that the predominant interaction of phosphine oxides with SiO2 surfaces is hydrogen bonding with silanol groups and adsorbed water. These interactions involve a single hydrogen bond, which mediates dynamic processes and can be transferred to solvents for rapid purification procedures.

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[7] Merck silica (average pore diameter 40 Å, particle size 0.06–0.20 mm, specific surface area 750 m² g⁻¹), dried 4 d in vacuo at 300 °C (dry SiO2), or used as received (wet SiO2).
[8] Typically, 4.0 g of SiO2 is suspended in 120 mL of toluene in a Schlenk flask. After adding an excess of phosphine oxide (ca. 0.5 g), dissolved in 80 mL of toluene, the mixture is stirred at 90 °C overnight. Then the silica is allowed to settle at RT. The supernatant is decanted, and the silica is washed with toluene. After removing the solvent from the combined supernatant and wash phase, the residue is weighed. The amount of adsorbed phosphine oxide is determined from the difference between the recovered phosphine oxide and the original amount. Maximal surface coverages of phosphine oxides on wet/dry SiO2 (molecules per 100 nm²): Me3PO (65/53), Bu3PO (43/29), nBu3PO (29/25), Cy3PO (45/37), Ph3PO (33/26). Alternatively, after drying of the pure phosphine oxides with silica, the adsorption proceeds while the mixture is allowed to stand for a few days.
[10] 31P MAS NMR signal linewidths [kHz] of Ph3PO adsorbed on dry silica: T [°C]: 3.0 (19), 2.6 (27), 2.1 (37), 1.4 kHz (47).
[19] 2H MAS NMR signal linewidths [kHz] of (D3)Ph2PH3 adsorbed on dry silica: T [°C]: 6.7 (17), 6.5 (27), 5.3 (37), 4.0 (47), 1.8 (67), 1.1 kHz (77).
[21] CCDC-920754 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. This material is based upon work supported by The Welch Foundation (A-1706), the National Science Foundation under CHE-0911207, CHE-1300208, CHE-1153085, and CHE-0840464, and the APPEAL Consortium. The leaching characteristic can be used to remove phosphine oxides from reaction mixtures or to purify them by adsorption (Figure 8).

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