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MICROENVIRONMENT OF PHOSPHINE GROUP ON A PHOSPHINATED SILICA SURFACE AS PROBED BY SOLID-STATE HIGH-RESOLUTION ^{31}P NMR SPECTROSCOPY

Sumio SHINODA, Kenichi NAKAMURA, and Yasukazu SAITO*
Institute of Industrial Science, The University of Tokyo,
22-1, Roppongi 7 Chome, Minato-ku, Tokyo 106

Two types of microenvironments were discriminated for the $Ph_2P(CH_2)_8Si\equiv$ group fixed on a silica gel by use of solid-state high-resolution ^{31}P NMR spectroscopy. While one is also detectable with conventional (solution) NMR in a suspended state, another shows more solid-like mobility.

In the last few years, there has been a growing interest in silica surfaces modified by chemical bonding of organosilanes to the surface. The technique is widely used in such diverse and important areas of chemistry as chromatography, catalysis, composite materials, pigments, etc. To characterize the modified surfaces, NMR is recognized as a powerful tool because it may give information on not only the structure but also the motion1-3) of the adsorbates.

We have found that with a suitable solvent to suspend the modified silica gel (H_2O, MeOH for aminated silica; toluene for phosphinated silica)4-6) the conventional FT-NMR method provides satisfactory spectral resolution to elucidate motional characteristics1) and complexing properties with heavy metals.6,7) For dry powdered samples, effectiveness of cross polarization (CP)/magic angle spinning

Table 1. Preparation of phosphinated silica gels

	Evacuation temperature of silica (°C)	Amount of added silane (mmol g^{-1}silica)	Fixed amount of phosphine$^{c)}$ (mmol g^{-1})	Average surface density (groups nm^{-2})
P-SIL-1	280	0.090$^{a)}$	0.087	0.26
P-SIL-2	25	1.00$^{b)}$	0.60	1.8

a) Silica 10 g, toluene 200 cm^3. b) Silica 4 g, toluene 200 cm^3.
c) Determined from the elemental analysis for P.

(MAS) technique[8,9] was demonstrated very recently with various magnetic nuclei including ^{31}P.[10] We attempted here to clarify the microenvironment of the phosphine group on a phosphinated silica surface with the joint use of both methods.

Two kinds of phosphinated silica gels were prepared with different amount of fixed phosphine (Table 1).[6] Silica gel (Spherosil XOA 200 (type B), 100-200 mesh, S_{BET} = 203 m^2 g^{-1}; Rhône-Poulenc, Paris) was dried by evacuation at different temperatures (0.13 Pa, 4 h); evacuation at 280 °C is expected to remove physically-adsorbed water completely. Surface silylation reaction with $Ph_2P(CH_2)_8SiCl_3$[11] in anhydrous toluene (dried over Na) was performed for 3 d at room temperature. The crude product was filtered, dried in vacuo, washed with toluene (150 cm^3), and then dried under vacuum. All the operations were carried out under inert atmosphere.

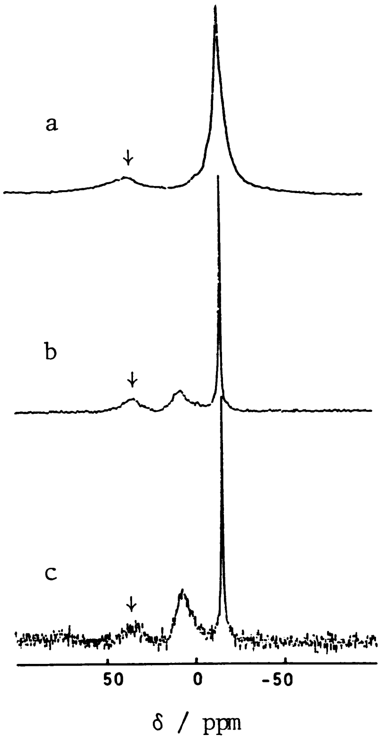

Fig. 1. ^{31}P NMR spectra of $Ph_2P(CH_2)_8Si\equiv$ group fixed on a silica gel (P-SIL-2).
a) $^{31}P\{^1H\}$ (90° pulse, 40,000 scans, pulse interval 0.5 s)
b) Gated/MAS (90° pulse, 800 scans, pulse interval 60 s)
c) CP/MAS (90° pulse, 500 scans, pulse interval 30 s, mixing time 2 ms)
Arrows indicate the resonance of $Ph_2P(=O)(CH_2)_8Si\equiv$.

^{31}P NMR spectrum for the toluene-suspended sample was measured with noise-modulated proton decoupling on a Fourier transform pulsed NMR spectrometer (Jeol JNM-FX60Q), operating at 24.2 MHz. A coaxial capillary tube containing D_2O was used to obtain lock. The pulse intervals were so taken as to exceed $5T_1$.[12] Before the measurement, the suspended sample was sedimented in an NMR sample tube (10 mmϕ) on standing overnight, and fixed with a Teflon plug. Solid-state NMR spectra for the dry samples were obtained on a Jeol JNM-FX200 spectrometer (80.8 MHz) with an external lock. The chemical shifts are reported in ppm downfield from 85% H_3PO_4.

In Fig. 1, ^{31}P NMR spectra of the phosphinated silica gel (P-SIL-2) are compared, which were taken with the conventional method as a suspension (a), and with Gated/MAS (b) or CP/MAS (c) technique as a dry powder; P-SIL-2 fixed a more abundant amount of phosphine

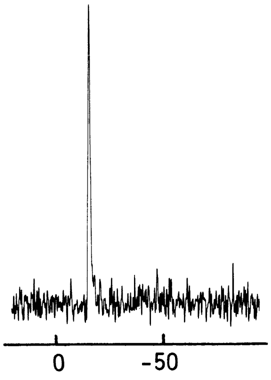

Fig. 2. CP/MAS ^{31}P NMR spectrum of $Ph_2P(CH_2)_8Si\equiv$ group fixed on a silica gel (P-SIL-1); 90° pulse, 160 scans, pulse interval 30 s, mixing time 2 ms.

group than P-SIL-1 (Table 1). The "gate" process here limits the supply of high-power ^1H decoupling to the period of FID storing, with the conventional ^1H irradiation applied during other periods. In the spectra (a)-(c), two peaks commonly appear at δ -15 and 33 ppm. The latter corresponds to $Ph_2P(=O)(CH_2)_8Si\equiv$ formed by air oxidation. This oxide peak had not been observed for the fresh sample,6) although Bemi et al. noted that the fixing treatment of $Ph_2P(CH_2)_2Si(OEt)_3$ on silica gel resulted in substantial oxidation of the tertiary phosphine.10)

It is obvious in Fig. 1 that an extra peak appeared at δ 9 ppm in (b) and (c), namely only when the high-power ^1H decoupling/MAS technique was applied. This means the extra peak relates to a less mobile (more solid-like) state of the phosphine group in comparison with the state characteristic of the peak at δ -15 ppm. Further, the intensity ratio of the 9 ppm peak to the -15 ppm peak is larger in the CP/MAS spectrum (c) than in the Gated/MAS spectrum (b). Since the intensity enhancement with CP is more effective for rigid C-H orientation,8,9) this fact provides another evidence for the solid-like nature of the extra peak.

An interesting feature is that such an extra peak was not observed for the phosphinated silica gel with less abundant amount of fixed phosphine (P-SIL-1) (Fig. 2). The characteristic appearance of the extra peak for P-SIL-2 may be due to its higher loading of phosphine, which would bring about a crowded portion in part. In view of the bulkiness of the phenyl substituent, the value of average surface density for P-SIL-2 (1.8 groups nm^{-2}; Table 1) indicates a steric interaction taking place among the surface phosphine groups; actually the value is very close to the saturation coverage of $Ph_2P(CH_2)_2Si\equiv$ group, which was estimated as ≈2 groups nm^{-2}.11) Consequently, surface topography

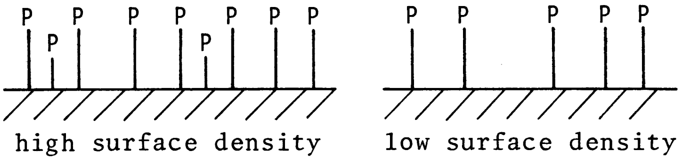

Fig. 3. Proposed model of phosphinated silica surfaces with different amounts of fixation.

P| : mobile surface phosphine (also observable with conventional NMR in suspended state).

P| : surface phosphine restricted in mobility.

may impose restricted motion on some of the fixed phosphine groups. Another possibility is that in the silylation step of P-SIL-2 the presence of physically-adsorbed water may cause the formation of oligomeric patches through self-condensation of $RSi(OH)_3$.[14] The main peak at δ -15 ppm is detectable with the conventional method, and is observed solely in the case of P-SIL-1. Therefore, this peak may correspond to a distribution of the surface groups, in which they are somewhat isolated with each other and hence obtain greater internal mobility. In Fig. 3, two types of microenvironments for the surface phosphine group are depicted as a model.

The structure and catalytic activity of the metal complex catalyst immobilized on the chemically-modified surface are sensitive to the average concentration of the surface ligand.[6,15] However, in order to design the catalyst on a molecular level, the most important is its microscopic environment. Thus, as presented here, NMR characterization seems to provide a promising clue for that purpose.

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12) T_1 for the observed peak (δ -15 ppm) was determined as 0.10 s, which is significantly smaller than dissolved phosphines (PEt_3 10.4, $PPr^n{}_3$ 15.4, PPh_3 30.3 s),[13] and reflects motional constraint due to the fixation on the surface.
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