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Surface Characterization of Systems with Diphenylphosphinoethylsilane Immobilized on Silica Gel

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Diphenylphosphinoethyltriethoxysilane and alkylsilylating reagents have been reacted with silica gel to produce a surface with anchored ligands within a hydrophobic matrix. The extent of surface coverage has been determined using elemental analysis data. Cross-polarization/magic angle spinning, nuclear magnetic resonance has contributed toward a description of the diphenylphosphinoethylsilyl anchored on the surface. Using high-performance liquid chromatography, the extent of substrate coverage and ligand stability were evaluated. The experimental data provide some insight into the synthetic procedure which is most effective for the preparation of stable diphenylphosphine moieties immobilized on silica gel. Since diphenylphosphinoethylsilyl is often used to immobilize metal complexes, the information should be useful for optimizing systems for use in heterogeneous catalysis.

INTRODUCTION

Transition metal complexes have been bound to a variety of polymeric and oxide supports in an attempt to prepare fixed-bed catalysts (*1, 2*). Some of the advantages in generating such heterogeneous catalysts are that they can be easily separated from the reaction mixture, the support can isolate the reactive site and inhibit the formation of inactive dimers, and the reaction selectivity can be modified by tailoring the local complex environment.

One of the more common approaches used to bind a transition metal complex to an inorganic oxide support involves using a bifunctional molecule that has a ligand function on the end of a spacer chain, and an anchoring function on the opposite end which can react with surface hydroxyl groups (*2, 3*). One of the more commonly employed bifunctional molecules is diphenylphosphinoethyltriethoxysilane. This functionality has been chemically bonded to silica gel (*4, 5*) and then subsequently reacted with rhodium complex precursors (*5, 6*). The immobilized complexes thus produced have exhibited catalytic activity in the hydrogenation of olefins (*5, 6*) and the hydrosilylation of hexene (*7*).

In order to elucidate the underlying principles that promote catalytic activity, some systematic studies have been conducted to assess the system parameters that yield the most effective immobilized diphenylphosphine–rhodium catalysts. Several investigators have studied the effect of the silica support (*2*), the role of chloro and alkoxyl groups attached to the silyl moiety of the bifunctional molecule (*8*), the effects of the length of the spacer (*7*), and the role of the catalyst precursor (*7*).

In order to extend further our knowledge about the nature of the diphenylphosphinoethylsilane (DPP) moiety immobilized

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on silica gel, we have prepared some DPP-silicas, most of which have been imbedded within a hydrophobic matrix employing combinations of octadecyldimethylsilyl (ODS), octadecylsiloxyl (OTS), and trimethylsilyl (3MS) moieties attached to the silica surface. Using ^{29}Si, ^{31}P, and ^{13}C solid-state nuclear magnetic resonance (NMR), we have obtained information about the anchoring of the DPP functionality on the surface and the stability of the diphenylphosphine phosphorus. Using high-performance liquid chromatography (HPLC), we have implemented a novel approach for determining the extent of the surface coverage and the stability of the ligand silica. The experimental data elucidate the nature of the surface and provide some insight into the synthetic procedure that is most effective for the preparation of isolable and stable diphenylphosphine moieties immobilized on silica gel.

METHODS

A. Synthesis of Modified Silicas

The silica gel used to prepare the samples was Shandon Hypersil. (BET surface area, $S_{BET} = 170$ m^2 g^{-1}; particle diameter, dp = 5 μm.) The silica gel was dried for at least 18 h at 150°C prior to use.

Toluene was distilled over sodium and stored over a 5-Å molecular sieve prior to use. Proton Sponge [1,8-*bis*(dimethylamino)-naphthalene] and trichlorosilane reducing agent were purchased from Aldrich. Diphenylphosphinoethyltriethoxysilane, octadecyldimethylchlorosilane, octadecyltriethoxysilane, and trimethylchlorosilane were all purchased from Petrarch.

(*i*) *Synthesis of diphenylphosphinoethyl–octadecyldimethyl–trimethyl–silyl* (*DPP-ODS-3MS*) *silicas* (*Samples 1–3*). A 2.56-g (6.80 mmol) portion of diphenylphosphinoethyltriethoxysilane in 100 ml of toluene was added to 10.0 g of silica gel. The suspension was refluxed under N_2 for 15 h, filtered, and the precipitate washed with successive 40-ml portions of toluene, methanol, water, and acetone. The resulting modified silica gel was heated at 140°C for 1.5 h. A portion was then set aside for characterization (Sample 1). 2.36 g (6.80 mmol) of octadecyldimethylchlorosilane, 3.03 g (14.1 mmol) of Proton Sponge, and 75 ml of toluene were added to ~9 g of the DPP-silica (Sample 1). The suspension was refluxed under N_2 for 4 h, and then a mixture of 5 ml (39.5 mmol) of trimethylchlorosilane, 3.02 g (14.1 mmol) of Proton Sponge, and 15 ml of toluene were added through a septum using a syringe. The reaction mixture remained at room temperature for 20 h, was then filtered, and the precipitate (DPP-ODS-3MS-silica) washed with successive 75-ml portions of toluene, methanol, water, and acetone, and then air dried (Sample 2).

DPP-ODS-3MS silica (Sample 2) ~8 g was reduced by adding to it 25 ml (0.25 moles) of trichlorosilane and 25 ml of toluene. The reaction proceeded at room temperature for 21 h; the trichlorosilane was then removed by vacuum distillation and the precipitate washed with successive 50-ml portions of methanol, water, and acetone (Sample 3, DPP-ODS-3MS silica-R).

(*ii*) *Synthesis of diphenylphosphinoethyl–octadecyltriethoxy–trimethylsilyl* (*DPP-OTS-3MS*) *silica* (*Samples 4–6*). Diphenylphosphinoethyltriethoxysilane, 2.61 g (6.93 mmol), 2.81 g (6.74 mmol) of octadecyltriethoxysilane, and 75 ml of toluene were added to 10.0 g of silica gel. The suspension was refluxed under N_2 for 21 h; the mixture was filtered and the precipitate washed with successive 40-ml portions of toluene, methanol, water, and acetone. The DPP-ODS-silica was heated at 115°C for 2 h (Sample 4). Trimethylchlorosilane, 7.0 ml (55.3 mmol), 3.03 g (14.1 mmol) of Proton Sponge, and 40 ml of toluene were added to the DPP-OTS-silica (Sample 4). The resulting suspension was refluxed under N_2 for 4 h, and then the reaction proceeded for an additional 18 h at room temperature. The mixture was filtered and the precipitate (DPP-OTS-3MS-silica) was washed with successive 40-ml portions of toluene, methanol, water, and acetone (Sample 5). About 9 g of the modified silica (Sample 5) was reduced by adding it to 20 ml (0.1981 moles) of trichlorosilane and 20 ml of toluene. The reaction was allowed to proceed at room temperature for 18 h; then the trichlorosilane was removed by vacuum distillation and the precipitate washed with 100 ml of methanol, 50 ml of water, and 50 ml of acetone (Sample 6, DPP-OTS-3MS-silica-R).

(iii) Synthesis of trichlorosilane–silica (Sample 7). Trichlorosilane, 9.0 ml (.0891 moles), 3.01 g (14.1 mmol) of Proton Sponge, and 80 ml of toluene were added to 10.0 g of silica gel. The reaction proceeded under N_2 for 21 h at room temperature; then the unreacted trichlorosilane was vacuum distilled and the precipitate washed with 40 ml of toluene, 80 ml of methanol, 40 of water, and 40 ml of acetone.

(iv) Synthesis of diphenylphosphineoxide–trimethylsilyl (DPPO-3MS) silica (Sample 8). Diphenylphosphinoethyltriethoxysilane [5.12 g (13.6 mmol)] and 50 ml of toluene were added to 10.0 g of silica gel. The suspension was refluxed under N_2 for 25 h, and then cooled to room temperature and exposed to air for 42 h. The mixture was filtered and the precipitate washed with successive 50-ml portions of methanol, water, and acetone. The DPPO silica was heated at 115°C for 1.5 h. Trimethylchlorosilane [8 ml (63.2 mmol)] 2.99 g (14.0 mmol) of 1,8-*bis*(dimethylamino)-naphthalene, and 50 ml of toluene were added to the DPPO-silica. The reaction proceeded under N_2 for 19 h at room temperature; then the mixture was filtered and the precipitate (DPPO-3MS-silica) washed with 100 ml of methanol, 30 ml of water, and 30 ml of acetone.

B. Elemental Analyses

Carbon and hydrogen analyses were performed either in-house using a Perkin-Elmer Model 240B elemental analyzer or by MicAnal Organic Microanalysis, Tucson, Arizona. Phosphorus analyses were performed by Industrial Testing Laboratories, Inc., St. Louis, Missouri. The silica gel samples for phosphorus analysis were digested with $HClO_4:HNO_3$, then precipitated with Quimociac reagent. The method is based on the gravimetric determination of $(C_9H_7N)_3 \cdot H_3PO_4 \cdot 12\ MoO_3 \cdot H_2O$.

C. Nuclear Magnetic Resonance

The solid-state ^{29}Si NMR spectra were obtained at 39.75 MHz on a modified Nicolet NT-200 spectrometer. The solid-state ^{13}C and ^{31}P NMR spectra were obtained at 37.74 MHz and at 60.75 MHz, respectively, on a modified Nicolet NT-150 spectrometer. Magic angle spinning was carried out at 3.5–4.0 kHz using Kel-F or Delrin rotors modified from the design of Wind *et al.* (*9*). The coupler field was approximately 50 kHz in each case. A cross-polarization contact time of 2 msec and a pulse repetition time of 1 or 2 sec were found to be adequate for all three nuclides. Approximately 0.3–0.5 cm^3 of sample were used. The ^{29}Si and ^{31}P NMR chemical shifts were reported relative to the external standard, 85% H_3PO_4. The ^{13}C NMR chemical shift is reported relative to external tetramethylsilane.

D. Physical Evaluation of the Fixed Bed Reactor

To evaluate the reactor, a chromatographic system incorporating a Model 951 HPLC pump (Tracor, Austin, Tex.), a Model 7125 automatic syringe-loading sample injector (Rheodyne, Berkeley, Calif.), a Model 970A variable wavelength detector (Tracor), and a Model 3390A reporting integrator (Hewlett-Packard, Avondale, Pa.) was used. The DPP-ODS-3MS-silica-R (Sample 3), the DPP-OTS-3MS-silica-R (Sample 6), and trichlorosilane-silica (Sample 7) were slurry packed into 150 mm × 3 mm glass-lined columns (Scientific Glass Engineering, Austin, Tex.) (*10*).

All probes were prepared as concentrated solutions and then diluted to the desired mobile phase composition. Water was distilled and then aspirated through a 0.5-μm cellulose acetate filter. Chromatographic grade acetonitrile (MCB Manufacturing) was used as received. The detector wavelength was set at 254 nm for all probes injected. The flow rate was set at 1.0 ml · min^{-1}.

RESULTS AND DISCUSSION

A. Elemental Analysis

The reaction schemes used to prepare the DPP-ODS-3MS-silica-R, the DPP-OTS-3MS-silica-R and the DPPO-3MS-silica are outlined in Fig. 1. Table 1 lists the results of elemental analyses for Samples 1–6 and 8. The surface coverage of bonded groups (determined from elemental analyses) is expressed in micromoles of diphenylphosphinoethylethoxysilane per square meter of surface area. The calculations are based on the method of Unger *et al.* (*11*) as modified by Feibush *et al.* (*12*).

TABLE 1

Modified Silicas

Silica gel modification	Sample number	%P	%C	DPP coverage based on %P (μmol/m^2)
DPP	1	0.62	—	1.3
DPP-ODS-3MS	2	0.56	6.35	1.2
DPP-ODS-3MS-R	3	0.54	5.99	1.1
DPP-OTS	4	—	8.47	2.2[a]
DPP-OTS-3MS	5	—	8.47	2.2[a]
DPP-OTS-3MS-R	6	0.96	8.26	2.1
Trichlorosilane	7	—	—	—
DPPO-3MS	8	0.75	5.25	1.6

[a] %P assumed to be 1.00% based on the data in Sample 6 and the previously reported insensitivity of %P to subsequent reaction with $(CH_3)_3SiCl$ and $HSiCl_3$.

The DPP coverage for Sample 1, was 1.3 μmol · m^{-2} (see Table 1). After reaction with octadecyldimethylchlorosilane and trimethylchlorosilane, the DPP coverage was

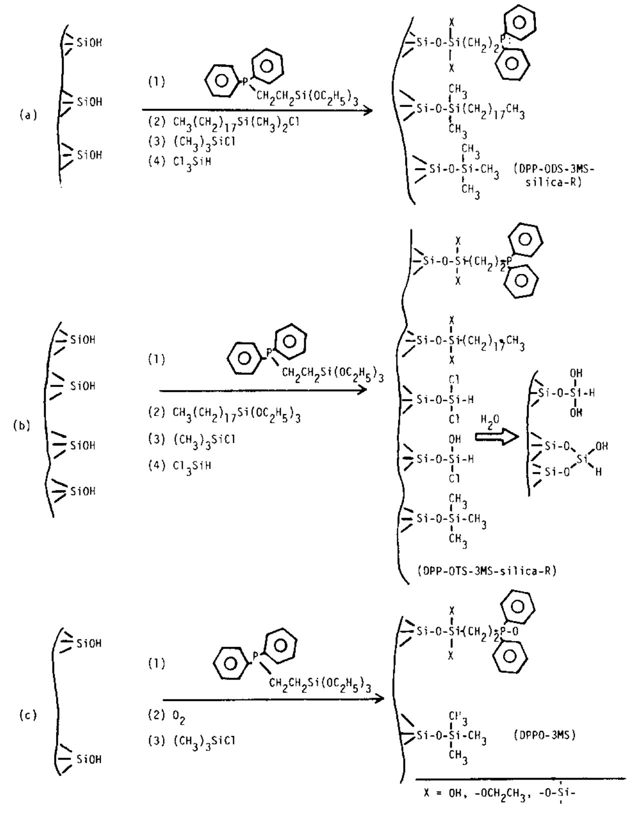

FIG. 1. Reaction schemes used to prepare (a) DPP-ODS-3MS-silica-R, (b) DPP-OTS-3MS-silica-R, and (c) DPPO-3MS-silica.

1.2 μmol · m^{-2}, and after reduction with trichlorosilane, the DPP coverage was 1.1 μmol · m^{-2}. The results indicate that DPP silica is very stable since subsequent silylations do not significantly reduce the surface coverage. One possible explanation is that since diphenylphosphinoethyltriethoxysilane is a trisilylating reagent which can in principle form up to three bonds to the silica substrate, heat-curing promotes additional bond formation, thus making DPP silica more impervious to acid hydrolysis (*13*). The subsequent addition of monochlorosilylating reagents does not significantly affect the DPP-surface coverage.

Since space-filling models indicate that a diphenylphosphine group occupies 0.5 nm^2 of silica surface (*2*), saturation coverage of the Shandon Hypersil would require 3.3 μmol · m^{-2} of surface coverage or 0.57 mmol of DPP/g of silica. The results on Sample 1 indicate a coverage of 1.3 μmol · m^{-2} representing approximately 38% coverage. This value compares favorably with that obtained by Boucher *et al.*, who found that immobilizing DPP results in 28% coverage (*8*).

The DPP coverage for DPP-OTS-silica (Sample 4) is 2.2 μmol · m^{-1}. It is unlikely that all of the diphenylphosphinoethyltriethoxysilane that is consumed in the preparation of the sample has reacted with surface hydroxyls forming a monolayer of DPP (*2*). It is more probable that some multilayer formation has occurred at the surface. Two DPP molecules might react to form a bisphosphine product and thus extend the coverage by more than a monolayer; however, the bisphosphine species has been reported to be too sterically constrained to react with the silica surface (*2*). More likely is the possibility that diphenylphosphinoethyltriethoxysilane in the presence of $(C_3H_5O)_3Si(CH_2)_{17}CH_3$ forms a copolymer that has access to the surface. Octadecylsilylating reagents with three anchoring functionalities are known to form polymeric layers on silica gel (*14*). The actual surface organization of DPP and OTS should have a profound effect on the catalytic properties of an immobilized complex. A polymeric network can inhibit transport of the substrate to the catalytic site, or it might more efficiently cover any unreacted surface silanols. A third promising aspect in forming a polymeric hydrophobic surface is the creation of an environment that has a high affinity for nonpolar functionalities—this can influence the selectivity of the catalyst and favor the hydrogenation and hydrosilylation of nonpolar substrates.

The DPP-surface coverage for DPPO-3MS-silica (Sample 8) is 1.6 μmol · m^{-2}. The coverage is higher than that of DPP in DPP-silica. One possible explanation is that 1.36 mmol · g^{-1} of diphenylphosphinoethyltriethoxysilane was used in the synthesis of DPPO-3MS-silica, whereas only 0.68 mmol · g^{-1} was used to synthesize DPP-silica. Although it has been reported that excess reactant and extended reaction time do not enhance the surface coverage (*2*), other investigators have demonstrated a pronounced correlation between reaction time and temperature and extent of surface coverage (*16*).

B. Nuclear Magnetic Resonance

The synthetic route adopted for immobilizing diphenylphosphinoethylsilane results in some oxidation of the phosphine moiety, producing a heterogeneous DPP-silica (*17*). Both the phosphine and the phosphine oxide are produced when preparing DPP-ODS- and DPPO-3MS-silicas (*3*).

The ^{31}P CP/MAS NMR spectrum of DPPO-3MS-silica (Sample 8) is given in Fig. 2a. The NMR spectrum reveals the presence of the following two structural moieties, which have been identified on the basis of previously reported ^{31}P NMR chemical shifts (*17*); (A) phosphine (−8 ppm) and (B) phosphine oxide (+40 ppm). The NMR spectrum shows that both the phosphine and the phosphine oxide moieties are present, and that the peak ratio of phosphine oxide to phosphine is about 6 to 1. The appearance of the large amount of

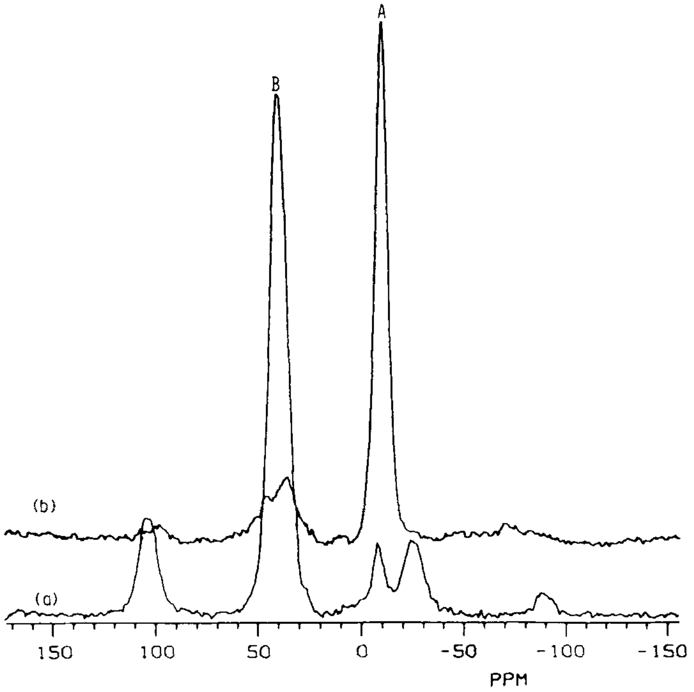

FIG. 2. ^{31}P CP/MAS NMR of (a) DPPO-3MS-silica and (b) DPP-OTS-3MS-silica-R, (Samples 8 and 6, respectively).

phosphine oxide indicates that the deliberate air oxidation of the phosphine moiety has been successful. The peaks at +105, −25, and −90 ppm are spinning sidebands.

Figure 2b illustrates the ^{31}P CP/MAS NMR spectrum of DPP-OTS-3MS-silica-R (Sample 6). The results indicate that the reduction with trichlorosilane is effective since the peak ratio of phosphine to phosphine oxide is about 9 to 1 rather than the much smaller ratio obtained before. Similar results were obtained for DPP-ODS-3MS-silica-R. These data verify that the nature of the diphenylphosphine can be radically altered depending upon the reaction conditions. If air enters the reaction flask, the phosphine oxide will preponderate, whereas if the DPP-silica is reduced with trichlorosilane then the phosphine moiety will predominate on the surface (*17*).

Since the reducing agent, trichlorosilane, can also modify the silica substrate, a series of ^{29}Si CP/MAS NMR spectra were obtained on trichlorosilane as well as other samples listed in Table 1. Figure 3 illustrates all the possible types of silicon present on silica gel after silanization and washing. The corresponding ^{29}Si NMR chemical shift (relative to tetramethylsilane) is given next to the chemical structure; the chemical shift correlations are based on literature data (*18–21*).

The ^{29}Si CP/MAS NMR spectrum of DPPO-3MS-silica (Sample 8) is illustrated in Fig. 4. The spectrum is similar to a ^{29}Si CP/MAS NMR spectrum of diphenylphosphinoethylsilane silica gel modified with trimethylchlorosilane (*22*). Chemical shifts of −107 ppm (Peak A) and −99 ppm (Peak B) can be attributed to silicon atoms on the surface of silica gel with 0 and 1 attached OH groups, respectively. The relative intensity of Peak A to Peak B increases after the derivitization of silica gel by diphenylphosphinoethyltriethoxysilane. This indicates that surface hydroxyls have reacted to form siloxane linkages with the DPP. Additional peaks appear at −49, −55, and −65 ppm; these are due to DPP immobilized on the surface. The peak at −49

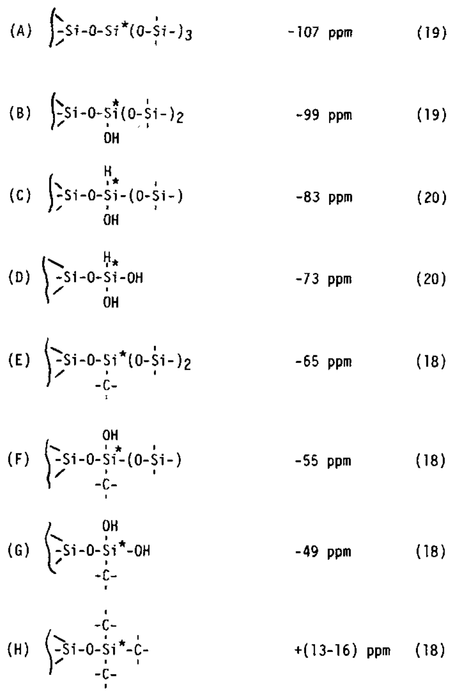

FIG. 3. Silicon functionalities at the surface of modified silica gel.

ppm (Peak G) is due to the reaction of one Si-ethoxy group with the surface; the second peak at −55 ppm (Peak F) is consistent with the reaction of two Si-ethoxy groups either with surface hydroxyl or with another SiOH moiety associated with the silylating reagent. The peak at −65 ppm (Peak E) is associated with DPP silicon that has a tridentate linkage to other silicons. There is no peak at −65 ppm until after trimethylchlorosilane has been added. This indicates that DPP does not form a tridentate linkage with the surface, and that trimethylchlorosilane reacts with hydroyzed DPP to form linkages similar to those shown in Fig. 5. Peak H has been attributed to 3MS silica (*18*).

The ^{29}Si CP/MAS NMR spectrum of trichlorosilane-silica (Sample 7) is given in Fig. 6. In addition to peaks normally observed for silica gel samples (A, B), peaks appear at −83 and −73 ppm (Peaks C and D); these are assigned to trichlorosilane derivitized silica gel. Based on the reaction of trichlorosilane with silica gel (*20*), and on the assumption of hydrolysis of the silicon–chlorine bond when exposed to moisture (*23*), and on the fact that substitution of an ethoxy group for a hydroxy group leads to an 8-ppm shift to lower shielding (*21*), the two peaks at −83 and −73 ppm are assigned to hydroxyhydridosiloxyl (Peak C) and dihydroxyhydridosilyl (Peak D) (*20, 21*). (See Fig. 3 for the structural representations.)

The ^{29}Si CP/MAS NMR spectra for DPP-ODS-3MS-silica (a) before and (b) after reduction (Samples 2 and 3) with trichlorosilane are illustrated in Fig. 7. The spectrum of Sample 3 (Fig. 7b) includes a new peak (Peak D) at −73 ppm, which indicates that trichlorosilane has reacted with the surface. In addition, both Peaks B and F diminish because of the substitution of a siloxane for a silanol bond.

Figure 8 illustrates the ^{29}Si CP/MAS NMR spectrum of DPP-OTS-3MS-silica-R (Sample 6). The spectrum includes two peaks at −71 ppm (Peak D) and −83 ppm (Peak C), in addition to the peaks expected

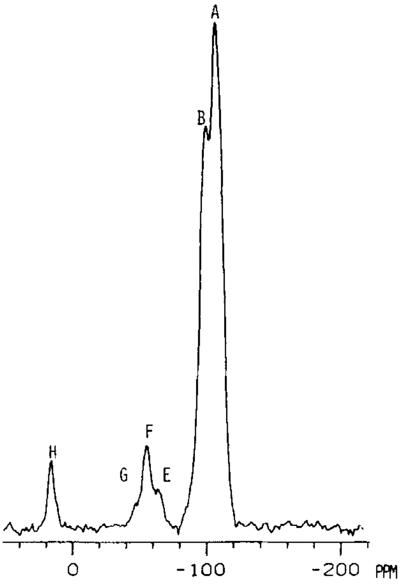

FIG. 4. ^{29}Si CP/MAS NMR of DPPO-3MS-silica (Sample 8).

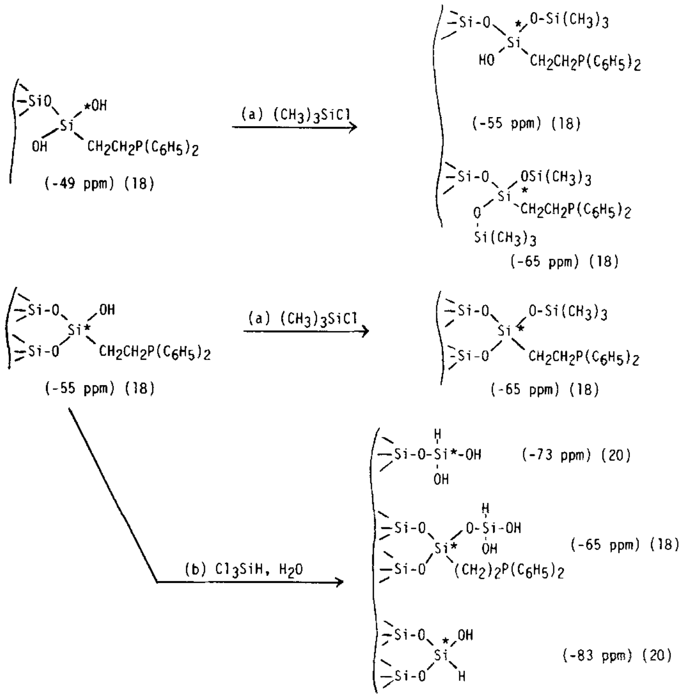

FIG. 5. Reactions between DPP-silica and (a) $(CH_3)_3SiCl$ and (b) $Cl_3)SiH$.

of a modified silica gel. These peaks are very intense, and indicate substantial reaction of the trichlorosilane with silica gel or with the DPP or OTS moieties on the surface. This spectrum contrasts vividly with that of DPP-ODS-3MS-silica-R (Fig. 7b) which has been influenced only slightly by the reaction with trichlorosilane. Compare the relative intensities of the peak at −83 ppm (position C) in Figs. 7b and 8. Trich-

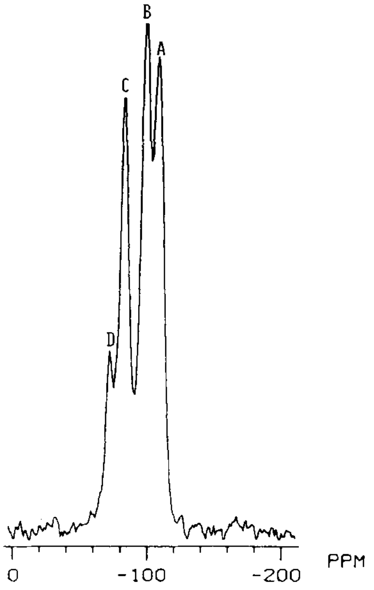

FIG. 6. ^{29}Si CP/MAS NMR of trichlorosilane-silica (Sample 7).

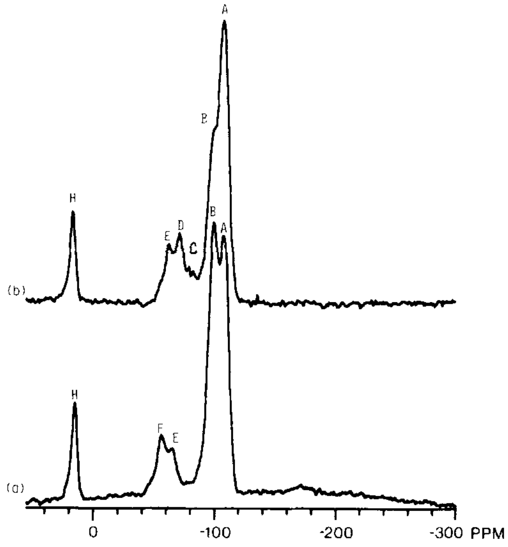

FIG. 7. ^{29}Si CP/MAS NMR of DPP-ODS-3MS-silica (a) before and (b) after reduction (Samples 2 and 3).

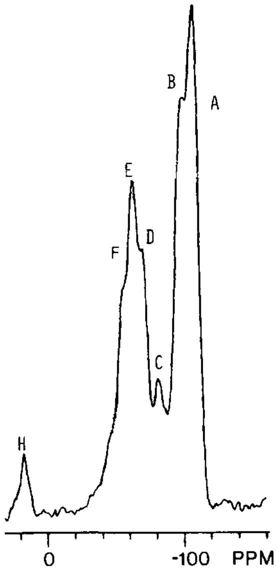

FIG. 8. ^{29}Si CP/MAS NMR of DPP-OTS-3MS-silica-R (Sample 6).

lorosilane when it reacts with silica gel exhibits two new peaks which can be assigned to the hydroxyhydridosiloxyl (−83 ppm) and the dihydroxyhydridosilyl (−73 ppm) moieties.

Figure 9 lists the ^{13}C CP/MAS NMR assignments for systems immobilized on silica gel. The ^{13}C NMR chemical shift (relative to external tetramethylsilane) is given adjacent to the corresponding carbon atom. All assignments are based on literature data for analogous compounds (*18*, *24*, *25*).

Figure 10 gives the ^{13}C CP/MAS NMR spectra for (a) DPP-ODS-3MS-silica and (b) DPP-ODS-3MS-silica-R Samples 2 and 3. This figure indicates that the concurrent immobilization of moieties derived from diphenylphosphinoethyltriethoxysilane and octadecyldimethylchlorosilane produces a modified silica for which the carbons belonging to different moieties are readily distinguishable by ^{13}C CP/MAS NMR. The methylene carbons in a long chain (+31 ppm) can only be attributed to ODS, whereas the phenyl carbons (128–141 ppm)

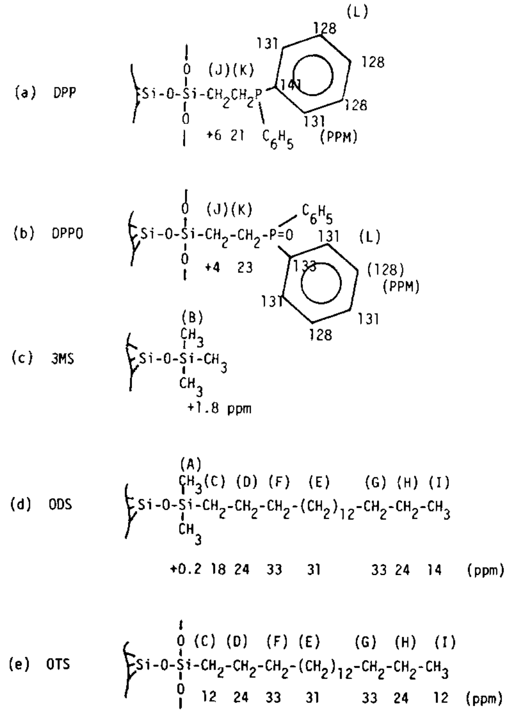

FIG. 9. ^{13}C CP/MAS NMR assignments for carbons immobilized on silica gel.

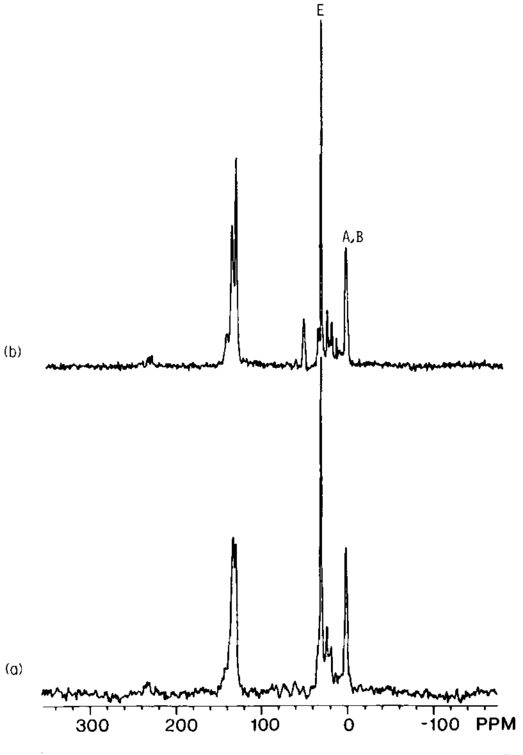

FIG. 10. ^{13}C CP/MAS NMR of (a) DPP-ODS-3MS-silica and (b) DPP-ODS-3MS-silica-R (Samples 2 and 3).

are assigned to DPP. The data also indicate that the methyl carbons associated with 3MS and the two methyl carbons attached to silicon in ODS are not resolved.

A comparison between the ^{13}C CP/MAS NMR spectra of the DPP-ODS-3MS-silica, before and after reduction, shows that after reduction the height of the peak at 128 ppm increases relative to the height of the peak at 131 ppm. Based on the information summarized in Fig. 9, DPPO contributes three carbon positions to the intensity at about 131 ppm, while two carbon positions contribute to the peak at about 128 ppm. Upon reduction, only two carbon positions appear at about 131 ppm, while three appear at 128 ppm. Hence it is reasonable that, upon reduction, the intensity of the peak should increase relative to the peak at 131 ppm as observed. After several months of storage in dry air, another ^{13}C CP/MAS NMR spectrum was run on the DPP-ODS-3MS-silica-R; no oxidation of the phosphine on the surface was apparent in the spectrum of the stored sample.

The ^{13}C CP/MAS NMR spectra of DPPO-3MS-silica (Sample 8) and DPP-OTS-3MS-silica-R (Sample 6) are given in Figs. 11a and b, respectively. One obvious difference between the two spectra lies in the range between 30 and 35 ppm. The ^{13}C spectrum of DPP-OTS-3MS-silica-R (Fig. 11b) has a peak at 31 ppm (Peak E) which has been assigned to the methylene carbons in the long alkyl chain of OTS (*18*). This peak does not appear in the spectrum of DPPO-3MS-silica. A second more subtle difference between the two spectra lies in the range between 128 and 131 ppm. DPPO-3MS-silica does not have a discernible peak at 128 ppm. This is in agreement with the ^{31}P-NMR data, which indicate that most of the diphenylphosphine moiety has been oxidized. The peak at 128 ppm decreases in intensity upon oxidation.

A comparison of the ^{13}C CP/MAS NMR spectra of DPP-ODS-3MS-silica-R (Fig. 10b) and DPP-OTS-3MS-silica-R (Fig. 11b) indicates that the two modified silicas are very similar. In both cases peaks are observed at -55 ppm which implies the generation of $-Si-O-CH_3$ during the methanol wash. A ^{13}C CP/MAS NMR spectrum of DPP-OTS-silica taken after several months in dry air indicates that the diphenylphosphine is relatively stable in the absence of water.

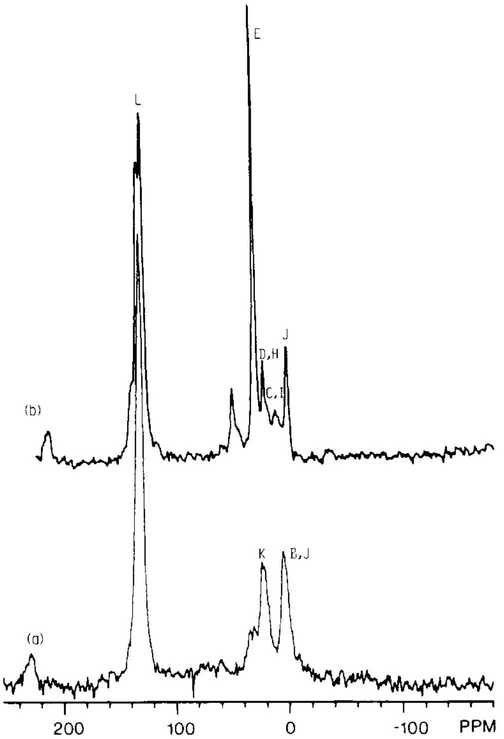

FIG. 11. ^{13}C CP/MAS NMR of (a) DPPO-3MS-silica and (b) DPP-OTS-3MS-silica-R (Samples 8 and 6, respectively).

C. Assessment of the Stability of Fixed-Bed Reactors

Much of the current methodology applied to the evaluation of chromatographic columns may also be applied to the evaluation of fixed-bed reactors used for heterogeneous catalysis. Although the catalytic activity of the bed can only be evaluated by using reactive compounds, nonreactive species can be used in order to assess some of the physical characteristics of the bed. In particular, by using a fixed-bed reactor as a chromatographic column, a great deal of information can be generated about the extent of surface coverage, the presence of reactive silanols (*26*), the uniformity of the packed bed (*9*), and the chemical or physical stability of the bed. Many experimental methods used to evaluate high-performance liquid chromatography (HPLC) columns can be directly applied, with little or no modification, to the evaluation of fixed-bed reactors. In our systems, for instance, alkyl groups were concurrently immobilized with DPP, and many investigators have developed approaches for elucidating the effects of alkyl chain length (*27–29*) and endcapping (*30, 31*).

Samples of the DPP-ODS-3MS-silica-R, DPP-OTS-3MS-silica-R, and trichlorosilane silica (Samples 3, 6, and 7, respectively) were all evaluated after packing into a fixed bed. Using a number of probe molecules, the efficiency of packing (N) and the capacity factor (k') were determined and the information used to evaluate the physical character of the bed. Efficiency of packing (N) can be evaluated by using

$$N = 5.54\left(\frac{t_R}{w_{1/2}}\right)^2$$

where t_R is the retention time of the probe and $w_{1/2}$ is the width of the eluting peak at one-half maximum peak height (*32*). Efficiency is a measure of peak broadening and can be used to estimate whether a modified silica has been well packed or is deteriorating with use. Capacity factor (k') can be defined as: $k' = (t_R - t_0)t_0^{-1}$, where t_R is retention time and t_0 is the time of elution for an unretained probe. Capacity factors are constant unless the packing material begins to decompose, at which time the value of k' begins to decrease. Capacity factors and efficiencies can thus be used to evaluate the stability of a packed reactor.

Table 2 lists the capacity factors for five aromatic compounds injected on three different modified silicas. The eluting solvent was a mixture of isooctane–ethanol–water (84 : 14.5 : 0.5). All other conditions were as described in the experimental section.

Comparing DPP-ODS-3MS-silica-R with DPP-OTS-3MS-silica-R, the capacity factors for toluene and nitrobenzene are lower for DPP-OTS-3MS-silica-R than for DPP-ODS-3MS-silica-R. A general criterion for assessing the availability of reactive silanols is the elution behavior of benzene and nitrobenzene in hexane. If the capacity factors do not exceed 0.1 for benzene and 0.5 for nitrobenzene, than it is concluded that there are no available unreacted silanols (*35*). In general, the lower the capacity factor for these two solutes, the better the surface coverage (*15, 33, 34*). DPP-OTS-3MS-silica-R consistently shows a low affinity for nitroaromatic compounds, indicating that very few if any accessible silanols are present on the surface.

The chemical stability of each reactor was tested under dynamic conditions. An acetonitrile–water (35 : 65) mixture was washed through each reactor, and the efficiency and peak tailing were evaluated after

TABLE 2

Capacity Factors of Aromatic Compounds on Different Modified Silicas

Probe	Modified silicas		
	Trichlorosilane	DPP-ODS-3MS-R	DPP-OTS-3MS-R
Toluene	0.17	0.68	0.21
Nitrobenzene	0.77	1.02	0.43
o-Nitroaniline	1.89	1.50	0.54
m-Nitroaniline	2.86	1.90	0.61
p-Nitroaniline	4.32	2.30	0.79

cycling the mixture at a flow rate of 1 ml · min^{-1} for a period of 16 h. Figure 12 illustrates the "chromatograms" obtained on the DPP-ODS-3MS-silica-R (a) at 0 h and (b) after 16 h. Figure 12b shows peaks with increased peak broadening, as well as increased peak tailing. The efficiency of packing (*N*) has diminished, dropping from 970 to 710 theoretical plates.

In order to see if the loss of reactor efficiency was reversible, 100 ml of 100% acetonitrile were washed through the system. The reactor could be regenerated, producing a "chromatogram" similar to that of Fig. 12a. Repeated use and regeneration of the reactor over a period of 340 h resulted in no permanent loss of packing efficiency. The results indicate that reactive silanols affect the adsorption properties of DPP-ODS-3MS-silica-R. After an induction period of about 4 h, tailing begins to appear and becomes very pronounced after 16 h. Modification of the surface by washing with pure acetonitrile apparently reduces the effect of the reactive silanols.

Figure 13 illustrates the "chromatograms" obtained on DPP-OTS-3MS-silica-R (a) at 0 h and (b) after 16 h. The peaks in Fig. 13b show no perceptible tailing, but the number of theoretical plates has decreased by approximately 13%.

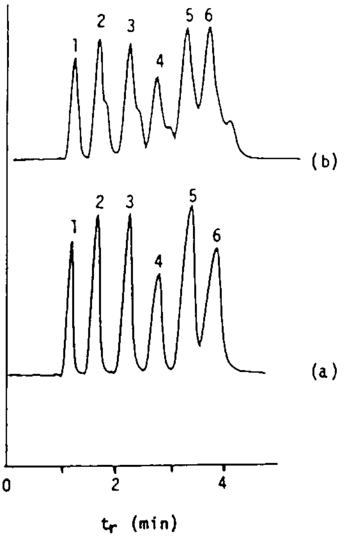

FIG. 12. Separation of phenols on DPP-ODS-3MS-silica-R (Sample 3) after (a) 0 and (b) 16 h of washing with acetonitrile-water (35 : 65). Peaks: (1) resorcinol, (2) phenol, (3) *m*-nitrophenol, (4) *p*-ethylphenol, (5) 2-naphthol, and (6) 1-naphthol.

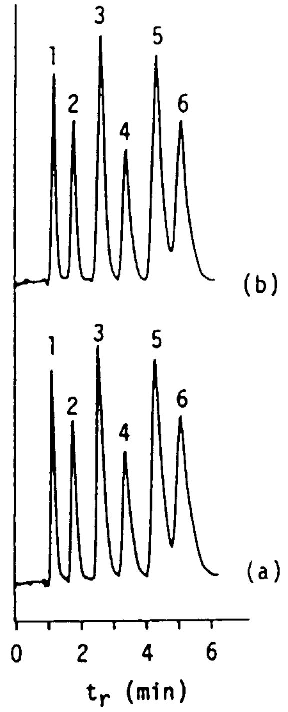

FIG. 13. Separation of phenols on DPP-OTS-silica (Sample 6) after (a) 0 and (b) 16 h of washing with acetonitrile-water (35 : 65). Peaks: are as in Fig. 12.

The results indicate that the silica substrate in DPP-OTS-3MS-silica-R is more fully covered than in DPP-ODS-3MS-silica-R since peaks generated on this modified silica retain their symmetry (Gaussian shape) and do not show any loss in retentive capacity. The DPP-OTS-3MS-silica-R can be regarded as more fully silylated with a surface having more cross-linking and multilayer formation. This surface is then more adept at covering the underlying reactive silanol groups, and maintaining its integrity with continual use. As a direct consequence, the formation of multilayers on a surface of a support has advantages for preparing immobilized homogeneous catalysts. The underlying support is less accessible to the catalyst substrate, more ligand molecules (and therefore more metal complex) can be immobilized, and finally, the immobilizing ligand is now more stable.

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