The Preparation and Catalytic Properties of the Silica-supported Rhodium Complex

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Synopsis. The $RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$ complex is attached to the phosphinated silica prepared from a new linking agent, $Ph_2PCH_2CH_2CH_2Si(OCH_3)_3$. The supported complex is an active catalyst for the hydrogenation of methyl cinnamate with CO and H_2O, and it can be used repeatedly with little loss of activity, whereas the polystyrene-supported one is not recoverable because of the insufficient complexation of the rhodium.

Recently, much attention has been focused on the chemistry of polymer-supported complex catalysts[1] because of their potential advantages. Functionalized polystyrenes have widely been studied as support, but few reports on silica have appeared. In contrast with polystyrene, silica is rigid and hydrophilic, and it is superior in thermal stability. Making good use of these characteristics, we have tried utilizing the silica-supported rhodium catalyst in the hydrogenation, using H_2O and CO as reducing agents.

The phosphinated silica[2] was synthesized by the following reactions.

$$ClCH_2CH_2CH_2Si(OCH_3)_3 \xrightarrow{Ph_2PH,\ NaH} Ph_2PCH_2CH_2CH_2Si(OCH_3)_3$$

$$\xrightarrow[HCl\ aq]{silica} Ph_2PCH_2CH_2CH_2Si\text{–}O\text{–}SiO_2$$

The linking agent, $Ph_2PCH_2CH_2CH_2Si(OCH_3)_3$, was prepared by the reaction of 3-chloropropyltrimethoxysilane with diphenylphosphine in the presence of sodium hydride. This reaction is a convenient alternative to the general synthetic method, which is based on the slow photochemical addition of diphenylphosphine to vinylsilanes.[3] The phosphination of silica was achieved by the hydrolysis of the linking agent in the presence of hydrochloric acid. The IR spectrum of the phosphinated silica thus prepared showed strong absorptions (3600—3200, 1200—1000, 960, 800 cm^{-1}) attributed to silica and weak absorptions (2930, 2870, 1420, 720, 685 cm^{-1}) attributed to the organofunctional group. The elemental analysis for phosphorus showed the content of the phosphine group to be 0.56 mmol/g. The hydrogen content observed was higher than the value calculated on the basis of the phosphorous content. This may be attributed to ≡Si–OH groups and/or adsorbed water on the silica surface. Since the surface area of the parent silica is 362 m^2/g, the average distance between the phosphino groups is estimated to be about 10 Å (1.8×10^{-6} mol/m^2).[4] Possessing some flexibility attributed to the trimethylene chain, the adjacent phosphines may act as a bidentate ligand with regard to the coordination to metals.

We have previously reported that halide-free rhodium phosphine complexes, such as $RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$ and $RhH(CO)(PPh_3)_3$, are efficient catalysts for the homogeneous hydrogenation of olefins with CO and H_2O.[5] The catalytic properties of the silica-supported catalyst were examined in hydorgenation of methyl cinnamate with CO in aqueous THF, in comparison with a polystyrene-supported one. The polystyrene support, which contains a diphenylphosphinomethyl group (7.9×10^{-4} mol/g, 1.7×10^{-6} mol/m^2), was prepared from a highly cross-linking polystyrene (divinylbenzene content, >30%; surface area, 590 m^2/g). The results are shown in Fig. 1. In the first run (R-0), a mixture of the silica or polystyrene support and $RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$ was used as a catalyst without any prior isolation of the supported complex. The catalysts were recovered by filtration and then reused in the succeeding runs. It seems that the homogeneous

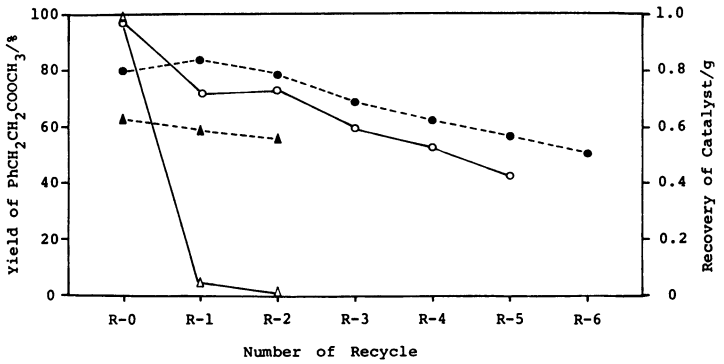

Fig. 1. Recycling of silica- and polystyrene-supported rhodium catalysts.
——: Yield, ------: recovery, ○, ●: silica-supported complex, △, ▲: polystyrene-supported complex. The weight of catalyst in R-0 is represented by the sum of the weight of support and $RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$.

catalyst is anchored on the supports during the first reaction (R-0), and that the anchoring complex, which is able to exist stably under these reaction conditions, remains on the supports. The high activities of both fresh catalysts (R-0) may be attributed to the presence of some rhodium species uncomplexed on the supports. The polystyrene-based catalyst recovered after the first run was no longer active. In fact, the filtrate of the first run using the silica support was slightly pale yellow, while that using the polystyrene support was deeply colored. The leach of the rhodium from the pre-supported catalyst, which had been prepared by immersing the phosphinated polystyrene in a toluene solution of $RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$ at room temperature for 20 h, was not repressed by the use of double the amount of the support. Therefore, the complexation of the rhodium complex on the polystyrene support was insufficient. On the other hand, the loss of activity in the silica-supported catalyst was still gradual for several repeated uses. The amount of the supported catalyst recovered was also gradually decreased due to the loss in manipulation, except for the first recovery, where the weight was increased by the adsorption of water. Consequently, the corrected activities (R-0, 11.9; R-1, 7.8; R-2, 8.8; R-3, 8.5; R-4, 8.4; R-5, 7.4 mol of product/g of catalyst) of R-2, R-3, and R-4 suggest that the true activity was scarcely affected by the repeated uses. Additionally, the silica-supported catalyst was stable in air for a short time. The catalyst for the last use (R-5) was handled in air, but the loss of activity was small.

The supported complex prepared by immersing the phosphinated silica in a toluene solution of $RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$ at room temperature for 20 h did not show any observable IR absorptions attributed to the anchoring complex. On exposure to carbon monoxide (1 atm), three weak bands (2020, 1975, 1945 cm^{-1}) appeared. Therefore, the active species on the support may be mononuclear because these IR bands are in the region of the stretching vibrations of terminal metal carbonyls and metal hydrides containing phosphine ligands.

Experimental

Unless otherwise noted, all reactions and manipulations were carried out under an atmosphere of nitrogen. Literature methods were employed for the preparations of diphenylphosphine, $PHPh_2$,[6] and bis(triisopropylphosphine)dihydrido(hydrogencarbonato)rhodium(III), $RhH_2(O_2COH)[P(i\text{-}Pr)_3]Pr)_3]_2$.[7] The IR spectra were recorded on a JASCO IRA-1 spectrometer.

Preparation of $Ph_2PCH_2CH_2CH_2Si(OCH_3)_3$. A suspension of NaH (1.7 g, 71 mmol) in diphenylphosphine (12 g, 64 mmol) and Dimethyl Carbitol (30 ml) was heated at 120 °C for 1 h. The resulting red solution was cooled, and then $ClCH_2CH_2CH_2Si(OCH_3)_3$ (10.8 g, 54 mmol) was added. The mixture was heated at 130 °C for 1 h and subsequently, distilled under reduced pressure to give a viscous liquid (14 g, 150—180 °C/1 mmHg, 1 mmHg≈133.322 Pa). The crude product was redistilled to give the pure linking agent (10 g, 157—160 °C/0.5 mmHg) in a 53% yield.

Phosphination of Silica. Silica gel (Wakogel C-300, for column chromatography) was used without further purification. To a suspension of the silica (25 g) in toluene (150 ml) and concd hydrochloric acid (5 ml), we added $Ph_2PCH_2CH_2CH_2Si(OCH_3)_3$ (26 g, 75 mmol). The mixture was then slowly stirred with refluxing for 20 h. After cooling, the silica was collected by filtration, washed successively with water, methanol, benzene, methanol, water, methanol, benzene, and hexane, and then dried in a vacuum oven at 50 °C for 20 h to give white powder of phosphinated silica (28 g). Found: C, 11.70; H, 1.78; P, 1.72%.

Preparation of Phosphinated Polystyrene. Cross-linking polystyrene (Mitsubishi Chemical Ind., Ltd., Dia-ion HP-50: was purified by previously reported methods.[8] Chloromethylation was achieved according to literature methods[9] under the following condition: polystyrene (10 g), CH_3OCH_2Cl (9 ml), $SnCl_4$ (1.1 ml), in CH_2Cl_2 (50 ml), at 25 °C, for 1 h. The resulting chloromethylated polystyrene, which contained 4.41% of chlorine, was phosphinated by previously reported methods[10] with a large excess of $LiPPh_2$ ($LiPPh_2/-CH_2Cl$= 50 mol/mol) in THF at room temperature for 60 h.

Hydrogenation of Methyl Cinnamate. A stainless steel autoclave (65 ml in capacity)was charged with phosphinated silica (724 mg, $-PPh_2$; 0.4 mmol), $PhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$ (97 mg, 0.2 mmol) methyl cinnamate (1.62 g, 10 mmol), H_2O (0.9 g, 50 mmol), and THF (15 ml). The reactor was pressurized with CO (15 atm) and then heated at 130 °C for 20 h. After cooling, the suspension was filtered, and the silica-supported catalyst was washed with benzene. The filtrate was analyzed by GC, using naphthalene as the internal standard The silica was dried at room temperature under reduced presure and then weighed. The silica was used as the catalyst for the next run.

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