Rhodium–phosphine complex catalysts tethered on silica-supported heterogeneous metal catalysts: arene hydrogenation under atmospheric pressure

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Abstract

The rhodium–phosphine complex, $RhCl(CO)[Ph_2P(CH_2)_3Si(OC_2H_5)_3]_2$ (Rh–P), was tethered to silica-supported metal heterogeneous catalysts, $Pd–SiO_2$, $Ni–SiO_2$ and $Au–SiO_2$, to give the tethered complex catalysts $Rh–P/Pd–SiO_2$, $Rh–P/Ni–SiO_2$ and $Rh–P/Au–SiO_2$. An IR (DRIFTS) study shows that the structure of the tethered rhodium–phosphine complex (Rh–P) in all of these combination catalysts is the same as that of the free Rh–P complex. These heterogenized complex catalysts consisting of a tethered complex on a supported metal (TCSM) were used to catalyze the hydrogenation of arenes under the mild conditions of 40°C and 1 atm of H_2. The most active TCSM catalyst $Rh–P/Pd–SiO_2$ is not only much more active than the homogeneous Rh–P complex and $Pd–SiO_2$ but also much more active than the rhodium–phosphine complex tethered on just SiO_2 ($Rh–P/SiO_2$). The $Rh–P/Pd–SiO_2$ catalyst gives a maximum turnover frequency (TOF, mol H_2/mol Rh min) of 2.9 and a turnover (TO, mol H_2/mol Rh) of 1940 during a 23 h period in the hydrogenation of toluene. When the tethered rhodium–phosphine complex catalyst stands in air for 2 months or longer, the phosphine ligand is oxidized to the phosphine oxide. This air-aged $Rh–P/Pd–SiO_2$ is much more active than the fresh catalyst for the hydrogenation of toluene, but the air-aged $Rh–P/SiO_2$ becomes inactive for this reaction. These two air-aged catalysts were characterized by solid state ^{31}P NMR and DRIFTS using CO as a probe. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Rhodium–phosphine complex; Supported metal catalysts; TCSM; Tethered complex catalysts; Silica; Palladium; Nickel; Gold

1. Introduction

Immobilized homogeneous transition metal complex catalysts offer the advantage over their homogeneous counterparts of easy separation from the reactant and product solutions. Consid-erable work has been devoted to tethering homo-geneous metal complex catalysts to either or-ganic or inorganic supports [1–11]. In most of the work reported to date, silica has generally been used as the support since transition metal complexes can easily be tethered by reacting the surface hydroxyl groups of silica with alkoxyl- or chlorosilane functional groups of ligands in the complexes [12–21]. Silica-supported hetero-geneous metal catalysts, such as $Pd–SiO_2$, Ni–

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SiO_2 and $Au–SiO_2$, also have surface hydroxyl groups that could be used to tether homogeneous transition metal complex catalysts. This type of combined catalyst consisting of a tethered complex on a supported metal (TCSM) catalyst (Fig. 1) could function by synergistic action of both catalyst components and potentially have high activity and/or selectivity. One possible mode by which such a TCSM catalyst could function in hydrogenation reactions involves initial adsorption of H_2 on the supported metal followed by spillover of hydrogen [22–24] onto the silica where it is transferred to an unsaturated hydrocarbon that is activated by coordination to the metal in the tethered complex. Recently, we reported [25] the first example of such a combined catalyst, one consisting of a rhodium–isocyanide complex, e.g., $RhCl[CN(CH_2)_3Si(OC_2H_5)_3]_3$ ($Rh–CNR_3$) tethered to silica-supported palladium. This $Rh–CNR_3/Pd–SiO_2$ catalyst exhibits high activity for the hydrogenation of arenes under the mild conditions of 1 atm of H_2 and 40°C. Its activity (TOF = 5.5 and TO = 2420 for 8.5 h) for toluene hydrogenation is substantially higher than that of the separate homogeneous $RhCl[CN(CH_2)Si(OC_2H_5)_3]_3$ catalyst, the separate heterogeneous $Pd–SiO_2$ catalyst, or the rhodium–isocyanide complex catalyst tethered on just silica. In the present study, we describe new TCSM catalysts that are composed of the rhodium–phosphine complex, $RhCl(CO)[Ph_2P(CH_2)_3Si(OC_2H_5)_3]_2$, tethered on the silica-supported metal catalysts $M–SiO_2$ (M = Pd, Ni and Au). The catalytic activities of the resulting

TCSM catalysts in the hydrogenation of arenes, their characterization by DRIFT spectroscopy, and their long-term stabilities toward air are reported.

2. Experimental

2.1. Materials and analyses

$Rh_2Cl_2(CO)_4$, $PdCl_2$, $HAuCl_4 \cdot xH_2O$ (Au, 49%) and $Ni(NO_3)_2 \cdot 6H_2O$ were purchased from Strem. Silica gel 100 (B.E.T. surface area, 400 $m^2 g^{-1}$) was obtained from Fluka. $Ph_2P(CH_2)_3Si(OC_2H_5)_3$ was prepared according to the literature method [26]. Toluene and pentane solvents were dried by distillation over CaH_2 under nitrogen prior to use. The arene substrates were used directly as obtained from commercial sources without further purification.

FTIR and DRIFT spectra were recorded on a Nicolet 560 spectrophotometer equipped with a TGS detector in the main compartment and a MCT detector in the auxiliary experiment module (AEM). The AEM housed a Harrick diffuse reflectance accessory. The solution IR spectra were measured in the main compartment using a solution cell with NaCl plates. The DRIFT spectra were recorded on samples in the Harrick microsampling cup. A Varian 3400 GC interfaced to a Finnigan TSG 700 high-resolution magnetic sector mass spectrometer with electron ionization (70 eV) was used for all GC-MS measurements. Gas chromatographic analyses were performed with a Varian 3400 GC with a FID detector using 25 m HP-1 capillary column. Solution ^1H and $^{31}P\{H\}$ NMR spectra were measured on Brucker AC 200-MHz and Nicolet NT 300-MHz spectrometers. All ^{31}P solid-state NMR spectra were recorded on a Bruker MSL 300 spectrometer. These spectra were measured at room temperature and referenced with respect to 80% H_3PO_4 (aq) by setting the ^{31}P NMR peak of solid $NH_4H_2PO_4$ to +0.8 ppm. The Hartmann–Hahn match was set by using solid
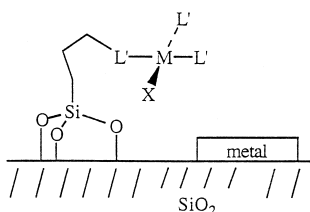

Fig. 1. Conceptual illustration of a TCSM catalyst consisting of a tethered homogeneous complex catalyst on a supported metal heterogeneous catalyst.

$NH_4H_2PO_4$, and a typical 90° pulse width was 4 μs.

The rhodium content of the TCSM catalysts was determined by atomic emission spectroscopy. The samples were prepared for analysis by treating the catalyst (50 mg) successively with 5 ml of aqua regia and 5 ml of aqueous HF (5%) at 90°C, and then diluting the resulting solution with water to 25 ml.

2.2. Preparation of the catalysts

2.2.1. Preparation of the silica-supported heterogeneous metal catalysts (M–SiO$_2$, M = Pd, Ni, Au)

Pd–SiO$_2$: Pd–SiO$_2$ was prepared by a procedure similar to that described in the literature [27]. An aqueous solution of H_2PdCl_4 (prepared by dissolving 1.2 g of $PdCl_2$ in 80 ml of aqueous HCl (0.2 M)) was added to a flask containing 7.0 g of SiO$_2$. After the mixture was stirred at room temperature overnight, the water was removed by slow evaporation in a rotary evaporator at 80°C. The resulting solid sample was dried in an oven at 110°C for 5 h and then calcined in a tube furnace at 500°C in an air flow for 4 h. The calcined sample was subsequently reduced in the tube furnace in a H$_2$ flow for 4 h at 380°C and then passivated under a flow of air at room temperature for 1 h to give black Pd–SiO$_2$ (Pd, 10 wt.%) powder.

Ni–SiO$_2$ [28]: A solution of $Ni(NO_3)_2 \cdot 6H_2O$ (2.4 g) in 40 ml of water was added dropwise to a flask containing 5.0 g of SiO$_2$; then about 30 ml of water was added dropwise. The resulting slurry was stirred vigorously on a hot plate until all excess liquid was evaporated; the resulting solid was dried overnight in a tube furnace at 120°C under flowing air. The solid was reduced under a H$_2$ flow at 450°C for 6 h and then cooled in a flowing N$_2$ atmosphere. The black silica-supported nickel catalyst, Ni–SiO$_2$, has a Ni content of 10 wt.%.

Au–SiO$_2$ [29]: A mixture of 5.0 g of SiO$_2$ and 1.0 g of $HAuCl_4 \cdot xH_2O$ (Au, 49%) in 30 ml of aqueous HCl (0.2 M) was stirred at room temperature overnight. After the water was removed in a rotary evaporator at 80°C, the resulting solid was dried in an oven at 110°C for 5 h. Then, the solid was reduced by a flow of H$_2$ at 250°C for 4 h to give a red-brown powder of Au–SiO$_2$ (Au, 10 wt.%).

2.2.2. Preparation of RhCl(CO)[Ph$_2$P(CH$_2$)$_3$-Si(OC$_2$H$_5$)$_3$]$_2$ (Rh–P)

Following the procedure [30] for the synthesis of other RhCl(CO)(PR$_3$)$_2$ complexes, a mixture of 0.43 g (1.1 mmol) of [RhCl(CO)$_2$]$_2$ and 1.71 g (4.4 mmol) of $(C_2H_5O)_3Si(CH_2)_3PPh_2$ in 40 ml of toluene was stirred at room temperature for 2 h. The solution was evaporated under vacuum to a small volume, and pentane was added to give a yellow precipitate of RhCl(CO)[Ph$_2$P(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$]$_2$ (Rh–P). IR (ν_{CO}, toluene): 1967 cm^{-1}. Anal. calc. for C$_{43}$H$_{62}$O$_7$Si$_2$P$_2$ClRh: C, 54.51; H, 6.59. Found: C, 55.03; H, 6.14. ^{31}P{^{1}H} NMR (CDCl$_3$, 200 MHz): δ 21.92 (d, J_{Rh-P} = 122 Hz).

2.2.3. Preparation of the tethered rhodium–phosphine complex catalysts

A mixture of 0.50 g of M–SiO$_2$ (M = Pd, Ni, Au) and 0.10 g of Rh–P in 20 ml of toluene was refluxed under an N$_2$ atmosphere for 12 h. After filtration, the solid was washed with toluene (6 × 15 ml) and pentane (15 ml) and dried in vacuum to give the tethered rhodium–phosphine complex catalysts Rh–P/Pd–SiO$_2$ (0.65 wt.% Rh), Rh–P/Ni–SiO$_2$ (0.60 wt.% Rh) and Rh–P/Au–SiO$_2$ (0.60 wt.% Rh). IR (DRIFT, ν_{CO} for the three catalysts): 1980 cm^{-1}.

The rhodium–phosphine complex catalyst tethered on SiO$_2$, Rh–P/SiO$_2$, (0.60 wt.% Rh), was prepared by the same procedure as that used for the preparation of Rh–P/M–SiO$_2$ by using 0.5 g of SiO$_2$ instead of M–SiO$_2$. IR (DRIFT, ν_{CO}): 1980 cm^{-1}.

2.2.4. Preparation of the adsorbed [RhCl(CO)$_2$]$_2$ catalyst (Rh–Cl / Pd–SiO$_2$)

A mixture of [RhCl(CO)$_2$]$_2$ (30 mg, 0.077 mmol) and 0.50 g of Pd–SiO$_2$ in 10 ml of

toluene was refluxed for 4 h. After filtration, the solid was washed with toluene (2×15 ml) and then dried in vacuum at room temperature. The rhodium content of the resulting anchored catalyst was 1.45 wt.%. IR (DRIFTS, ν_{CO}): 2095(s), 2028(s) cm^{-1}.

2.3. Catalytic hydrogenation studies

The hydrogenation reactions were carried out in a three-necked, jacketed vessel containing a stirring bar and closed with a self-sealing silicon rubber cap; the vessel was connected to a vacuum/hydrogen line and to a constant pressure gas buret. The temperature of the ethylene glycol that circulated through the jacket was maintained with a constant temperature bath. The reaction temperature and H_2 pressure were 40°C and 1 atm, respectively. After the catalyst was added and the atmosphere in the vessel was replaced with hydrogen, the arene substrate was added and the hydrogen uptake was followed with the constant-pressure gas buret.

3. Results

3.1. Synthesis of the TCSM catalysts

Since most transition metals form stable complexes with phosphines, $Ph_2P(CH_2)_3$-$Si(OC_2H_5)_3$ is often used as the linker to tether homogeneous transition metal complex catalysts to silica. Either the preformed complex containing the $Ph_2P(CH_2)_3Si(OC_2H_5)_3$ ligand(s) can

be tethered to the SiO_2 or the silica can be functionalized with $Ph_2P(CH_2)_3Si(OC_2H_5)_3$ first and then reacted with a metal complex precursor. For the synthesis of TCSM catalysts, the first approach not only offers control over the metal–ligand ratio in the complex but also avoids adsorption or coordination of the phosphine end of $(C_2H_5O)_3Si(CH_2)_3PPh_2$ on the silica-supported metal. Therefore, this method was used for the preparation of the TCSM catalysts described herein. The three TCSM catalysts, Rh–P/Pd–SiO$_2$, Rh–P/Ni–SiO$_2$ and Rh–P/Au–SiO$_2$, were prepared by reaction of $Rh_2Cl_2(CO)_4$ with $(C_2H_5O)_3Si(CH_2)_3PPh_2$ in a mole ratio of 1:4 to form RhCl(CO)-$[Ph_2P(CH_2)_3Si(OC_2H_5)_3]_2$, which was reacted with hydroxyl groups on the surface of the silica-supported metal catalysts, Pd–SiO$_2$, Ni–SiO$_2$ and Au–SiO$_2$ (Scheme 1). DRIFT spectra of all the TCSM catalysts show a strong CO band at 1980 cm^{-1}, which is very similar to those of the analogous *trans*-RhCl(CO)(PPh$_3$)$_2$ (1980 cm^{-1}) [30], RhCl(CO)[Ph$_2$P(CH$_2$)$_3$-Si(OC$_2$H$_5$)$_3$]$_2$ (1967 cm^{-1}), and Rh–P/SiO$_2$ (1980 cm^{-1}), which suggests that the *trans*, square-planar geometry of RhCl(CO)(PPh$_3$)$_2$ is also present in the tethered complex catalysts.

3.2. Catalytic activities of the TCSM catalysts for the hydrogenation of toluene

The rates of hydrogenation (Table 1) of toluene to methylcyclohexane at 40°C and under 1 atm of H_2 in the presence of the TCSM catalysts (Rh–P/Pd–SiO$_2$, Rh–P/Ni–SiO$_2$ and
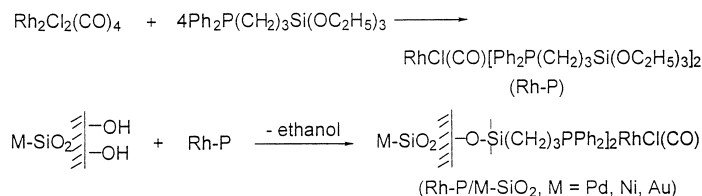
Scheme 1.

Table 1
Hydrogenation of toluene to methylcyclohexane[a]

Catalyst	Maximum TOF[b] (mol H_2/mol Rh min)	TO[c] (mol H_2/mol Rh)	H_2 uptake[c] (mmol)
Ni–SiO$_2$	–	–	0(23)
Au–SiO$_2$	–	–	0(23)
Pd–SiO$_2$	–	–	1.05(23)
P/Pd–SiO$_2$[d]	–	–	0.45(23)
Rh–P[e]	0.07	45(24)	0.66(24)
RhCl(CO)(PPh$_3$)$_2$[f] + Pd–SiO$_2$	0.03	33(26)	0.67(26)
Rh–P/SiO$_2$	0.29	361(23)	1.05(23)
Rh–P/Ni–SiO$_2$	0.25	273(23)	0.79(23)
Rh–P/Au–SiO$_2$	1.10	665(20)	1.74(20)
Rh–P/Pd–SiO$_2$	2.90	1940(23)	6.13(23)

[a] Reaction conditions: catalyst 50 mg; 5 ml of toluene; 40°C, 1 atm.
[b] TOF is defined as moles of H_2 uptake per mole rhodium per min.
[c] Turnover (TO) and H_2 uptake correspond to the reaction time in parentheses (in h).
[d] P/Pd–SiO$_2$ is $Ph_2P(CH_2)_3Si(OC_2H_5)_3$ tethered on Pd–SiO$_2$.
[e] 14.5 μmol of Rh–P.
[f] 20 μmol of RhCl(CO)(PPh$_3$)$_2$.

Rh–P/Ni–SiO$_2$), the soluble homogeneous complex (Rh–P) catalyst and the heterogeneous catalysts (Pd–SiO$_2$, Ni–SiO$_2$ and Au–SiO$_2$) were determined by following the rate of H_2 uptake. Fig. 2 shows plots of turnover frequency (TOF) vs. time for the hydrogenation of toluene over the catalysts, Rh–P/Pd–SiO$_2$, Rh–P/Ni–SiO$_2$, Rh–P/Au–SiO$_2$ and Rh–P/SiO$_2$. Except for Rh–P/Ni–SiO$_2$, which shows an induction period of about 1 h after which its activity increases slowly, all the other catalysts are active from the beginning. The TOF values of the four tethered catalysts, Rh–P/M–SiO$_2$ (M = Pd, Ni, Au) and Rh–P/SiO$_2$, increase initially, and then after reaching a maximum, they slowly decrease with time. From the data in Table 1, it is evident that the activity (as measured by the maximum TOF, TO or H_2 uptake) of the TCSM catalyst with Pd as the supported metal is much greater than those with Ni or Au. The activity of Rh–P/Pd–SiO$_2$ is about 40 times higher than that of the homogeneous catalyst (Rh–P), six times higher than the heterogeneous silica-supported palladium (Pd–SiO$_2$), and about six times higher than that of the complex Rh–P tethered to just SiO$_2$ (Rh–P/SiO$_2$). Rh–P/Ni–SiO$_2$ and Rh–P/Au–SiO$_2$

are also more active than the homogeneous catalyst Rh–P and the heterogeneous supported metal catalysts Ni–SiO$_2$ and Au–SiO$_2$. The activity (TO) of Rh–P/Au–SiO$_2$ is about two times higher than that of Rh–P/SiO$_2$, but Rh–P/Ni–SiO$_2$ is about the same as Rh–P/SiO$_2$.

It can also be seen that the activity of the non-rhodium-containing catalyst P/Pd–SiO$_2$, which was prepared by tethering $Ph_2P(CH_2)_3$-
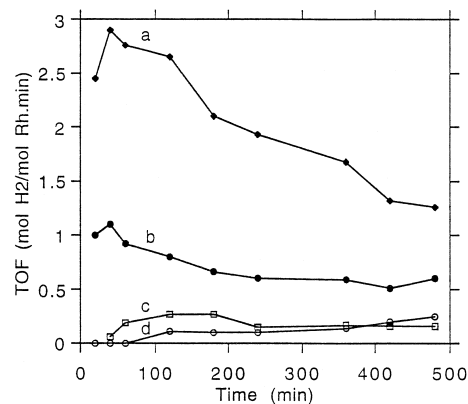

Fig. 2. Plots of the rates (TOF) of hydrogenation of toluene over (a) Rh–P/Pd–SiO$_2$, (b) Rh–P/Au–SiO$_2$, (c) Rh–P/SiO$_2$ and (d) Rh–P/Ni–SiO$_2$. Reaction conditions are the same as those in Table 1.

$Si(OC_2H_5)_3$ to $Pd–SiO_2$ under the same conditions as those used for making the tethered complex catalyst ($Rh–P/Pd–SiO_2$), is much lower than that of $Rh–P/Pd–SiO_2$ and even lower than that of $Pd–SiO_2$, which suggests that the tethering conditions are not, in some manner, activating the $Pd–SiO_2$. Furthermore, the activity (TO) of the soluble, non-tethered rhodium–phosphine complex $RhCl(CO)(PPh_3)_2$ in combination with $Pd–SiO_2$ is only about 2% of that of the tethered catalyst $Rh–P/Pd–SiO_2$, which indicates that tethering the complex to the surface is important for the TCSM catalyst activity. Although the activity of the $Rh–P/Pd–SiO_2$ TCSM catalyst is lower than that of the rhodium–isocyanide complexes ($RhCl(CO)[CN(CH_2)_3Si(OC_2H_5)_3]_2$, and $RhCl[CN(CH_2)_3Si(OC_2H_5)_3]_3$) tethered on $Pd–SiO_2$ as reported in our previous paper [25], it is, to the best of our knowledge, higher than that of any other homogeneous complex or immobilized complex catalysts reported in the literature for the hydrogenation of toluene under these mild conditions. Under similar conditions, Blum et al. [31] used $RhCl_3$-Aliquat-336 to catalyze the hydrogenation of toluene in a medium of $H_2O–CH_2Cl_2$. After 5 h, only ca. 3 mol of toluene were converted to methylcyclohexane per mole of rhodium. The TO value for the immobilized complex catalyst prepared from $[RhCl(nbd)]_2$ (nbd = norbornadiene) and phosphinated silica is 200 at 80 atm of H_2 and 30°C for 1.5 h [32]. Recently, Corma et al. [33] reported that the rhodium complex $[Rh(COD)(N–N)]PF_6$ (COD = 1,5–cyclooctadiene, N–N = 2-(3-triethoxysilypropyl-aminocarbonyl)pyrrolidine) anchored on zeolites catalyzes the hydrogenation of arenes under 6 atm of H_2 and at 80°C. Hydrogenation of arenes in the presence of homogeneous catalysts is generally performed under high (≥ 15 atm) H_2 pressure [34–41]. Only a few homogeneous catalysts are active using 1 atm of H_2, but their activities are low [42–45].

After the TCSM, $Rh–P/M–SiO_2$, catalysts were used for the hydrogenation of toluene, IR spectra (DRIFTS) of the used catalysts showed one $v(CO)$ band very near 1980 cm^{-1}, which is the same as the fresh catalyst. This suggests that the tethered rhodium complex is stable under the hydrogenation conditions.

3.3. Effect of air on the hydrogenation activity

After the TCSM catalysts and $Rh–P/SiO_2$ were exposed to air by allowing them to stand in screw-capped vials in air for about 2 months, their activities in the hydrogenation of toluene were different (Table 2) from those of the fresh catalysts. The air-aged $Rh–P/Pd–SiO_2$ is much more active than the fresh one. Its maximum TOF increases from 2.90 to 5.4 and the TO increases from 1940 during a 23 h time period to 2464 during a 9 h period. However, the activities of the other two TCSM catalysts, $Rh–P/Ni–SiO_2$ and $Rh–P/Au–SiO_2$ are about the same as those of the fresh catalysts. The catalyst tethered on just SiO_2, $Rh–P/SiO_2$, becomes inactive for the hydrogenation of toluene after it stands in air for about 2 months. The IR spectra (DRIFTS) of all the air-aged TCSM catalysts and $Rh–P/SiO_2$ show that the intensity of the CO absorption at 1980 cm^{-1} is markedly reduced compared to that of the fresh catalysts. After standing in air for about 4 months, the v_{CO} band of $Rh–P/Pd–SiO_2$ at 1980 cm^{-1} disappeared (Fig. 3c). It was also observed that

Table 2
Hydrogenation of toluene to methylcyclohexane over air-aged tethered rhodium catalysts[a]

Catalyst[b]	Maximum TOF[b] (mol H_2/mol Rh min)	TO[c] (mol H_2/mol Rh)
$Rh–P/SiO_2$	0	0(15)
$Rh–P/Ni–SiO_2$	0.3	250(23)
$Rh–P/Au–SiO_2$	1.5	481(15)
$Rh–P/Pd–SiO_2$	5.4	2464(9)

[a]Reaction conditions are the same as those in Table 1.
[b]Air-aged for 2 months.
[c]TOF is defined as moles of H_2 uptake per mole rhodium per min.
[d]TO and H_2 uptake correspond to the reaction time in parentheses (in h).
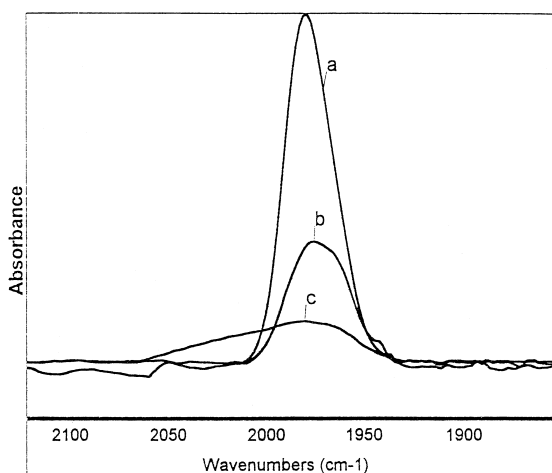
Fig. 3. IR spectra of (a) fresh Rh–P/Pd–SiO$_2$, (b) after Rh–P/Pd–SiO$_2$ was exposed to a mixture of gaseous N$_2$ and H$_2$O for 3 weeks, (c) air-aged Rh–P/Pd–SiO$_2$ after 4 months.

after the Rh–P/Pd–SiO$_2$ catalyst was exposed to a mixture of gaseous H$_2$O and N$_2$ for 3 weeks, the ν_{CO} absorption at 1980 cm^{-1} also decreased (Fig. 3b). This suggests that the decrease in the ν_{CO} intensity of the air-aged catalysts is due to the water in the air, which may mean that water displaces the CO ligand from the tethered rhodium complex. A similar effect of water on IR spectra of catalysts prepared by the immobilization of [RhCl(CO)$_2$]$_2$ on phosphinated silica was reported by Bartholin et al. [45].

The air-aged Rh–P/Pd–SiO$_2$ catalyst is also very active for the hydrogenation of other arenes under the same mild conditions (Table 3). The higher rate of anisole hydrogenation as compared with that of methyl benzoate suggests that electron donating substituents in the arene accelerate the rate. A comparison of the hydrogenation rate (maximum TOF and TO) of benzene with those of toluene and anisole indicates that steric effects are relatively unimportant.

3.4. Characterization of Air-aged Rh–P / Pd–SiO$_2$ and Rh–P / SiO$_2$

In order to understand the basis for the effect of air on the hydrogenation activity of Rh–

Table 3
Hydrogenation of arenes over air-aged Rh–P/Pd–SiO$_2$[a]

Substrate	Maximum TOF[b] (mol H$_2$ /mol Rh min)	TO[c] (mol H$_2$ /mol Rh)
Toluene	4.5	1780(8)
Anisole	4.7	2060(8)
Benzene	5.0	1582(8)
Methyl benzoate	1.5	600(10)

[a]Reaction conditions: 25 mg of catalyst (air-aged for 2 months); 5 ml of heptane solvent; 0.5 ml of substrate, 40°C, 1 atm.
[b]TOF is defined as moles of H$_2$ uptake per mole rhodium per min.
[c]TO and H$_2$ uptake correspond to the reaction time in parentheses (in h).

P/SiO$_2$ and the TCSM catalysts, the air-aged catalysts of Rh–P/Pd–SiO$_2$ and Rh–P/SiO$_2$ were further characterized by the solid state ^{31}P NMR and DRIFTS using CO as a probe. Table 4 gives solid state ^{31}P NMR chemical shifts of the air-aged catalysts, Rh–P/Pd–SiO$_2$ and Rh–P/SiO$_2$, and related samples. The data in Table 4 show that the ^{31}P chemical shifts of the air-aged Rh–P/Pd–SiO$_2$ and Rh–P/SiO$_2$ are about the same as that of the oxidized phosphine–siloxane, Ph$_2$P(O)(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$ tethered on SiO$_2$ (P=O/SiO$_2$), which suggests that in the air-aged catalysts, the phosphine–siloxane tether has been oxidized to Ph$_2$P-(O)(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$. When air-aged Rh–P/Pd–SiO$_2$ and Rh–P/SiO$_2$ were stirred in toluene under a CO atmosphere overnight, both samples exhibited two ν_{CO} adsorptions at 2093

Table 4
^{31}P chemical shifts from ^{31}P MAS NMR studies of the tethered rhodium–phosphine catalysts and related compounds

Sample	Fresh or air-aged[a]	$\delta(^{31}$P)
P/SiO$_2$[b]	fresh	−17.6
P=O/SiO$_2$[c]	–	39.5
Rh–P	fresh	23.2
Rh–P/Pd–SiO$_2$	fresh	23.0
Rh–P/Pd–SiO$_2$	air–aged	38.6
Rh–P/SiO$_2$	air–aged	39.0

[a]Air-aged for 4 months.
[b]P/SiO$_2$ is Ph$_2$P(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$ tethered on SiO$_2$.
[c]P=O/SiO$_2$ is Ph$_2$P(O)(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$ tethered on SiO$_2$. See Ref. [12].
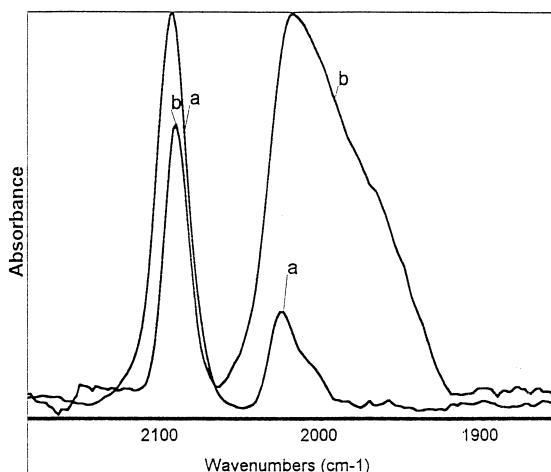
Fig. 4. IR spectra of (a) air-aged Rh–P/Pd–SiO$_2$ after treatment with CO, (b) air-aged Rh–P/SiO$_2$ after treatment with CO.

and 2023 cm^{-1}. No ν_{CO} band was observed at 1980 cm^{-1}. However, the relative intensities of the two ν_{CO} absorptions were different for the two catalysts (Fig. 4). For Rh–P/SiO$_2$, the intensities of the two bands were about the same, but for Rh–P/Pd–SiO$_2$, the intensity of the band at 2093 cm^{-1} was much stronger than that of the band at 2023 cm^{-1}.

Further experiments (Scheme 2) showed that after the air-aged Rh–P/Pd–SiO$_2$ (A) was treated with CO in toluene at room temperature overnight, the resulting sample B exhibits a

TOF of 6.7 and a TO of 3145 during 9 h for the hydrogenation of toluene, which is higher than that of the untreated catalyst A. No CO band was observed in the DRIFT spectrum of the used catalyst C. Yet when C was treated with CO, the resulting sample D gives two CO bands at 2093(s) and 2023(w) cm^{-1} again. Moreover, after the air-aged Rh–P/Pd–SiO$_2$ (A) was used for the hydrogenation of toluene followed by treatment with CO, the resulting sample (F) also gives two CO adsorptions at 2093(s) and 2023(w) cm^{-1}. Although the IR spectra of A, B and F are very similar, F is more active than A or B in the hydrogenation of toluene. Its maximum TOF is 10.4 and TO is 3908 during a period of 8 h. However, the air-aged Rh–P/SiO$_2$, even after treatment with CO, is still inactive for the hydrogenation of toluene.

4. Discussion

4.1. TCSM catalysts

The simple tethering of RhCl(CO)[Ph$_2$P-(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$]$_2$ to the silica surface of SiO$_2$-supported metal catalysts M–SiO$_2$ (M = Pd, Ni. Au) gives TCSM catalysts Rh–P/M–SiO$_2$, in which the Rh complex retains its *trans-*, square planar geometry as indicated by DRIFT
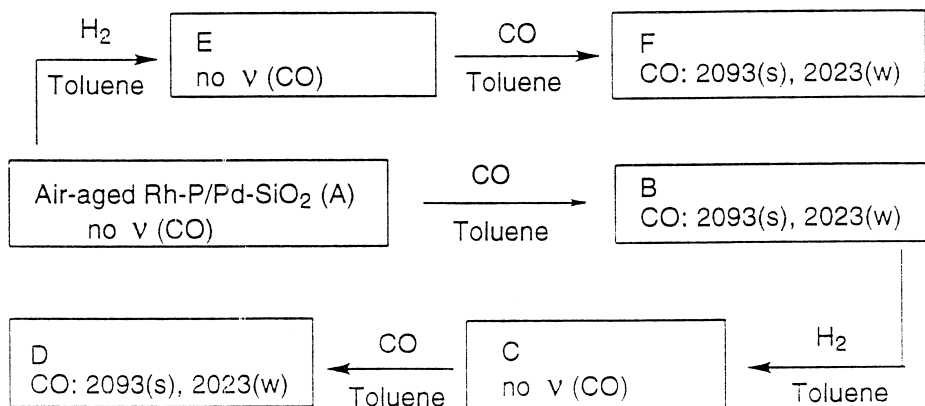
Scheme 2.

spectra of the catalysts in the ν_{CO} region. Since the ν_{CO} value is the same for the Rh–P/M–SiO_2 catalysts and Rh–P/SiO_2, there appears to be no direct interaction between the Rh complex and the supported metal M.

Of the TCSM catalysts, Rh–P/Pd–SiO_2 is the most active (Table 1). Its activity is greater than that of the homogeneous Rh–P complex, the heterogeneous supported palladium catalyst (Pd–SiO_2) or Rh–P tethered on just SiO_2. Thus, both the tethered complex (Rh–P) and supported metal (Pd–SiO_2) components are necessary for the high catalytic activity of TCSM catalysts. The function of the supported metal (Pd–SiO_2) may be to generate spillover hydrogen onto the SiO_2 surface. It is well known [22–24] that inorganic oxide supported heterogeneous metal catalysts, such as Pd–SiO_2, Pt–SiO_2, Pd–Al_2O_3, etc., can dissociatively adsorb hydrogen which spills over onto the oxide surface. This behavior of Pd–SiO_2 suggests that the Rh–P/Pd–SiO_2 catalyst functions by activating H_2 on the Pd–SiO_2. The resulting spillover hydrogen on the silica surface is then in the vicinity of the tethered Rh–P complex which coordinates and activates toluene for reaction with the spillover hydrogen. While this spillover mechanism logically explains the high activity of the TCSM catalysts, it does not exclude the possibility that a mechanism requiring the close proximity of the tethered complex and supported metal is involved. In such a mechanism, the tethered Rh may coordinate to toluene via only two of the toluene carbons. Then, the remaining four carbons are hydrogenated on the supported Pd if the tethered complex is near a Pd island. Supporting this type of mechanism is the known [46] hydrogenation of $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}$ to the cyclohexene complex $[Os(NH_3)_5(\eta^2\text{-}C_6H_{10})]^{2+}$ in the presence of Pd/C under 1 atm of H_2 and 30°C. Under the same conditions, Pd/C is inactive for the hydrogenation of benzene.

The lower activity of Rh–P/Au–SiO_2 as compared with Rh–P/Pd–SiO_2 may be related to the fact that gold is a very poor metal for the

adsorption and activation of H_2 [47]. The induction period and lower activity (Fig. 2d) of Rh–P/Ni–SiO_2, as compared to Rh–P/Pd–SiO_2 may be due to a slow and incomplete reduction of the oxided Ni under the reaction conditions. In addition, nickel metal is a poorer hydrogen spillover initiator compared to palladium metal because the strength of the Ni–H bond is greater than that of the Pd–H bond [48].

The activity of Rh–P/Pd–SiO_2 is also much higher than that of P/Pd–SiO_2 or the combination of $RhCl(CO)(PPh_3)_2$ with Pd–SiO_2. The first result excludes the possibility that the high activity of Rh–P/Pd–SiO_2 results from an alteration of the supported palladium particles during the tethering process. The second result shows that tethering of the rhodium complex to the surface is required for the high activity of Rh–P/Pd–SiO_2.

4.2. Effect of air-aging on Rh–P / Pd–SiO_2 and Rh–P / SiO_2

Samples of Rh–P/Pd–SiO_2 that are allowed to stand in air for 2 months are more active than the fresh catalyst for the hydrogenation of toluene. However, air-aged Rh–P/SiO_2 is inactive for this hydrogenation. Solid state ^{31}P NMR and DRIFTS analyses show that the original rhodium–phosphine complex (Rh–P) in the air-aged catalysts has been transformed into a new species that does not contain a CO ligand. However, upon treatment of the air-aged Rh–P/Pd–SiO_2 and Rh–P/SiO_2 with CO, these samples exhibit DRIFT spectra with ν_{CO} bands at 2093(s), 2023(w) cm^{-1} for Rh–P/Pd–SiO_2 and 2093(s), 2023(s) cm^{-1} for Rh–P/SiO_2. These adsorptions are very similar to those (2095(s), 2027(s) cm^{-1}) for $Rh^I(CO)_2$ on SiO_2 [49,50]. The positions and relative intensities of the ν_{CO} bands for CO-treated, air-aged Rh–P/SiO_2 suggest that $Rh^I(CO)_2$ is indeed formed on this catalyst. This formation of $Rh^I(CO)_2$ from the tethered complex is accompanied by the generation of tethered phosphine oxide $Ph_2P(O)(CH_2)_3Si(OC_2H_5)_3$, which suggests

that the air-aging process involves oxidation of the phosphine and formation of Rh^I/SiO_2. To further confirm the assignment of $Rh^I(CO)_2/SiO_2$ to the equal intensity bands (2093(s), 2023(s) cm^{-1}) of the CO-treated, air-aged Rh–P/SiO$_2$, we prepared a sample of $Rh_2Cl_2(CO)_4$ adsorbed on Pd–SiO$_2$ under the same conditions used for preparing the tethered catalysts. The DRIFT spectrum of this catalyst gives two CO bands at 2095 and 2020 cm^{-1} with about the same intensities (Fig. 5a). Although the lower energy band is broad, suggesting the presence of other species, the positions and intensities of these bands indicate that $Rh^I(CO)_2$ is also formed on the Rh–Cl/Pd–SiO$_2$ catalyst. The activity of Rh–Cl/Pd–SiO$_2$ for the hydrogenation of toluene (maximum TOF = 2.4 and TO = 521 during 6 h) is also lower than that of the air-aged Rh–P/Pd–SiO$_2$. After Rh–Cl/Pd–SiO$_2$ stands in air for about 2 months, its two v(CO) bands disappear in the DRIFT spectrum (Fig. 5b). However, its activity (maximum TOF = 2.6 and TO = 628 during 6 h) for the hydrogenation of toluene is about the same as that of the fresh sample. Thus, although Rh–Cl/Pd–SiO$_2$ and the CO-treated, air-aged samples of Rh–P/SiO$_2$ have similar IR spectra, the catalytic inactivity of Rh–P/SiO$_2$ and sig-

nificant activity of Rh–Cl/Pd–SiO$_2$ suggests that there are additional species on the Rh–Cl/Pd–SiO$_2$ that give rise to its activity.

Of the air-aged catalysts (Rh–P/SiO$_2$, Rh–P/Pd–SiO$_2$, Rh–Cl/Pd–SiO$_2$), Rh–P/Pd–SiO$_2$ is the most active for the hydrogenation of toluene. Its IR spectrum, after being treated with CO, shows two bands of unequal intensity (2093(s), 2023(w) cm^{-1}) that are clearly different from that (1980 cm^{-1}) of the fresh catalyst. The spectrum also indicates that a species different from those in CO-treated, air-aged Rh–P/SiO$_2$ and Rh–Cl/Pd–SiO$_2$ is present. The ^{31}P NMR spectrum of air-aged Rh–P/Pd–SiO$_2$ shows that the phosphine ligand is converted to the oxidized phosphine $(Ph_2P(O)(CH_2)_3Si-(OC_2H_5)_3)$, which may or may not be coordinated to the Rh. Whatever Rh species is produced in air-aged Rh–P/Pd–SiO$_2$, this catalyst is much more active than air-aged Rh–P/SiO$_2$, Rh–Cl/Pd–SiO$_2$, Rh–P/Ni–SiO$_2$ or Rh–P/Au–SiO$_2$. Moreover, the air-aged Rh–P/Pd–SiO$_2$ (maximum TOF = 5.4 mol H$_2$/mol Rh min and TO = 2464 mol H$_2$/mol Rh in 9 h) is much more active for the hydrogenation of toluene than the fresh Rh–P/Pd–SiO$_2$ (maximum TOF = 2.9 mol H$_2$/mol Rh min and TO = 1940 mol H$_2$/mol Rh in 23 h).
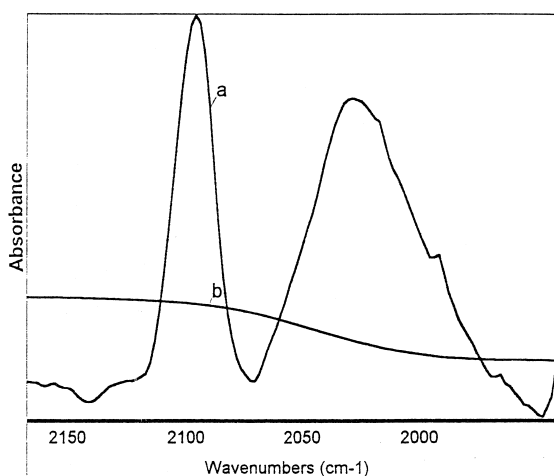

Fig. 5. IR spectra of (a) fresh Rh–Cl/Pd–SiO$_2$, (b) air-aged Rh–Cl/Pd–SiO$_2$.

5. Conclusions

The high arene hydrogenation activity of the fresh Rh–P/Pd–SiO$_2$ TCSM catalyst requires the presence of both components, the tethered rhodium complex (Rh–P) and the supported metal (Pd) on the SiO$_2$ surface. As compared with our previously reported TCSM catalysts [25], Rh–CNR$_3$/Pd–SiO$_2$ (maximum TOF = 5.5 mol H$_2$/mol Rh min and TO = 2420 mol H$_2$/mol Rh in 8.5 h) and Rh–CNR$_2$/Pd–SiO$_2$ (maximum TOF = 1.8 mol H$_2$/mol Rh min and TO = 1750 mol H$_2$/mol Rh in 8.5 h), prepared by tethering RhCl[CN(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$]$_3$ and RhCl(CO)[CN(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$]$_2$ to Pd–

SiO_2, Rh–P/Pd–SiO_2, is somewhat less active (maximum TOF = 2.9 mol H_2/mol Rh min, TO = 1940 mol H_2/mol Rh in 23 h) for the hydrogenation of toluene under the mild conditions of 40°C and 1 atm of H_2. However, when the Rh–P/Pd–SiO_2 is allowed to stand in air for 2 months, its activity (maximum TOF = 5.4 mol H_2/mol Rh min, TO = 2464 mol H_2/mol Rh in 9 h) is greater than that of Rh–CNR_2/Pd–SiO_2 and about the same as that of Rh–CNR_3/Pd–SiO_2. Although the mechanism of action of these TCSM catalysts is not clear, it is evident that combinations of tethered complexes and supported metals offer opportunities for the creation of highly active catalysts.

Acknowledgements

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