Rhodium amine complexes tethered on silica-supported metal catalysts. Highly active catalysts for the hydrogenation of arenes†

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Rhodium amine complexes, $RhCl(CO)_2[Et_2N(CH_2)_3Si(OCH_3)_3]$ (Rh—NEt_2), $RhCl(CO)_2[H_2N(CH_2)_3Si(OC_2H_5)_3]$ (Rh—NH_2) and $RhCl(COD)[H_2NCH_2CH_2NH(CH_2)_3Si(OCH_3)_3]$ (Rh(COD)(N—N)), were tethered to the silica-supported metal heterogeneous catalysts, M—SiO_2 (M = Pd, Ni, Au), to give the TCSM (tethered complex on supported metal) catalysts, Rh—NEt_2/M—SiO_2 (M = Pd, Ni, Au), Rh—NH_2/Pd—SiO_2 and Rh(COD)(N—N)/Pd—SiO_2. These TCSM catalysts exhibit activities, at 40 °C and 1 atm of H_2 pressure, for the hydrogenation of arenes that are higher than those of the separate homogeneous rhodium amine complexes, the separate silica-supported metal heterogeneous catalysts or the rhodium complex catalysts tethered on just SiO_2. The activities of the TCSM catalysts are strongly affected by both the tethered rhodium amine complex and the SiO_2-supported metal. Among these TCSM catalysts, Rh—NEt_2/Pd—SiO_2 exhibits the highest activity for the hydrogenation of toluene; its maximum TOF is 7.2 mol H_2 (mol Rh min)$^{-1}$ while its TO is 1919 mol H_2 (mol Rh)$^{-1}$ during a 5 h period. IR(DRIFT) spectral studies of the TCSM catalysts before and after being used for the hydrogenation of toluene show that during the hydrogenation, the two CO ligands of Rh—NEt_2/M—SiO_2 (M = Pd, Ni, Au) are lost from the rhodium center. After standing in air for one month, Rh—NEt_2/Pd—SiO_2 becomes more active for the hydrogenation of toluene, but the activity of the air-aged Rh(COD)(N—N)/Pd—SiO_2 is lower than that of the fresh catalyst.

Over the past few decades, intensive research work has been devoted to the development of heterogenized transition metal complex catalysts.[1] This type of catalyst can, in principle, combine the positive aspects of a homogeneous catalyst, that is, high activity, high selectivity and good reproducibility, with those characteristic of a heterogeneous catalyst, that is, long lifetime and ease of separation. The most common method to heterogenize metal complex homogeneous catalysts is to tether them to an insoluble organic or inorganic support, and a large number of catalysts have been made in this manner.[2,3] However, in most cases the tethering process reduces the catalytic activity of the complex, and many factors including the nature of the insoluble support influence the activities of the immobilized complexes. Silica has been widely used as a support since transition metal complexes can be easily tethered on its surface through a ligand in the complex that has alkoxy- or chlorosilane functional groups that react with surface hydroxy groups on the SiO_2.

Silica-supported metal heterogeneous catalysts, such as Pd—SiO_2, Ni—SiO_2 and Au—SiO_2, also have surface hydroxy groups that could be used to tether transition metal complexes. The resulting combined homogeneous-heterogeneous catalyst consisting of a tethered complex on a supported metal (TCSM) catalyst (Fig. 1) could have not only the advantages of conventional silica-tethered complex catalysts, but also function by synergistic action of both catalyst components. We have previously[4] reported that the rhodium complexes, $RhCl[CN(CH_2)_3Si(OC_2H_5)_3]_3$ and $RhCl(CO)[CN(CH_2)_3Si(OC_2H_5)_3]_2$, when tethered to silica-supported palladium (Pd—SiO_2), give TCSM catalysts that exhibit very high activities for the hydrogenation of arenes under the mild conditions of 40 °C and 1 atm. The activities of these combined catalysts are much higher than those of the separate homogeneous rhodium isocyanide complex catalysts, the separate heterogeneous silica-supported palladium metal catalyst or the rhodium isocyanide complex catalysts tethered on just SiO_2. A possible explanation[4] for the high activities of these TCSM catalysts must take into account the roles of both the tethered complex and the supported metal. The Pd metal may be the site where H_2 dissociates and then spills over onto the SiO_2. The tethered homogeneous complex may bind and activate the arene substrate for reaction with the "spillover" hydrogen. While this explanation accounts for the high activities of these TCSM catalysts and is consistent with the known ability of Pd—SiO_2 to produce spillover hydrogen,[5] it is possible that the combined effect of both catalyst components occurs by some other mechanism.

In the present study, we examine the activities of TCSM catalysts prepared from rhodium amine complexes tethered on SiO_2-supported metals with the goal of exploring the effects of different tethered homogeneous catalysts and different supported metals on the activities of TCSM catalysts. The rhodium amine complexes, $RhCl(CO)_2[Et_2N(CH_2)_3Si(OCH_3)_3]$, $RhCl(COD)[H_2NCH_2CH_2NH(CH_2)_3Si(OCH_3)_3]$ (COD = 1,5-cyclooctadiene) and $RhCl(CO)_2[H_2N(CH_2)_3Si(OC_2H_5)_3]$, were tethered on silica-supported metal heterogeneous cata-

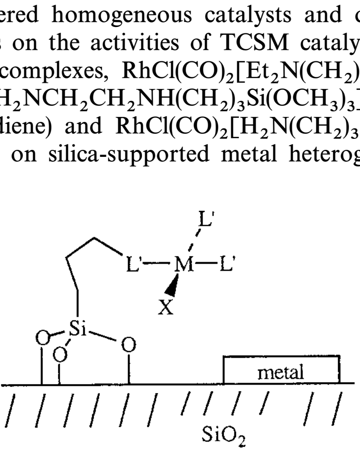

Fig. 1 Conceptual illustration of a TCSM catalyst consisting of a tethered homogeneous complex catalyst on a supported metal heterogeneous catalyst.

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† *Non-SI unit employed*: 1 atm ≈ 101 kPa.

lysts, Pd—SiO_2, Ni—SiO_2 or Au—SiO_2. In addition to studies of their catalytic activities in the hydrogenation of arenes, their durabilities, sensitivities to air, and infrared spectra were investigated.

Experimental

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}), 3-aminopropyltriethoxysilane [$H_2N(CH_2)_3Si(OC_2H_5)_3$], 3-diethylaminopropyltrimethoxysilane [$Et_2N(CH_2)_3Si(OCH_3)_3$], and 3-(2-aminoethylamino)propyltrimethoxysilane [$H_2NCH_2CH_2$ NH $(CH_2)_3$-$Si(OCH_3)_3$] were obtained from Fluka. Toluene and CH_2Cl_2 solvents were dried by refluxing over CaH_2 under nitrogen prior to use. The arene substrates were obtained from Aldrich and used without further purification.

FTIR and DRIFT (diffuse reflectance infrared Fourier transform) 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 salt plates. The DRIFT spectra were recorded with the 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 using a 25 m HP-1 capillary column with a FID detector.

For the determination of the rhodium content of the TCSM catalysts using atomic emission spectroscopy, the samples were prepared by treating the catalyst (50 mg) successively with 5 mL of aqua regia (5–10 min) and 5 mL of aqueous HF (5%) (5–10 min) at 90 °C, and then diluting the resulting solution with water to 25 mL.

Preparation of the silica-supported heterogeneous metal catalysts (M—SiO_2, M = Pd, Ni, Au)

Pd—SiO_2. This SiO_2-supported palladium was prepared by a procedure similar to that described in the literature.[6] 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 using a rotary evaporator at 80 °C. The resulting 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 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 the black Pd—SiO_2 (Pd, 10 wt%) powder.

Ni—SiO_2.[7] 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 in a tube furnace at 120 °C under flowing air overnight. The solid was reduced under a H_2 flow at 450 °C for 6 h and then cooled in a N_2 atmosphere. The black silica-supported nickel catalyst, Ni—SiO_2, has a Ni content of 10 wt%.

Au—SiO_2.[8] 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 solution (0.2 M) was stirred at room temperature overnight. After the water was removed with a rotary evaporator at ~80 °C, the 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%).

Rh/Pd—SiO_2. The mixed metal (Rh and Pd) SiO_2-supported catalyst Rh/Pd—SiO_2 was prepared as follows: An aqueous solution of $RhCl_3 \cdot 3H_2O$ (prepared by dissolving 2.38 g of $RhCl_3 \cdot 3H_2O$ in 24 mL of H_2O) was added to a beaker containing 3.00 g of Pd—SiO_2 (10 wt% Pd). After the mixture was stirred at room temperature for 1 h, the water solvent was evaporated by stirring the mixture on a hot plate. The resulting solid material was dried in an oven at 110 °C overnight and then transferred to a glass tube and heated in a furnace at 200 °C under a flow of N_2 for 2 h to desorb most of the water. The sample was finally reduced with a H_2 flow at 200 °C for 3 h and at 250 °C for 5 h to give the black Rh/Pd—SiO_2 (Rh, 2.55 wt%) powder.

Preparation of the homogeneous complexes

$RhCl(CO)_2[Et_2N(CH_2)_3Si(OCH_3)_3]$ (Rh—NEt_2). A mixture of $[Rh(CO)_2Cl]_2$ (79 mg, 0.20 mmol) and $Et_2N(CH_2)_3Si(OCH_3)_3$ (94 mg, 0.40 mmol) in 20 mL of toluene was stirred at room temperature for 30 min. After filtration, the solvent was evaporated under vacuum at room temperature. The oily residue was washed with hexanes (2 mL) and dried in vacuum to give the rhodium complex Rh—NEt_2 as a yellow-gray, air- and moisture-sensitive oil. IR (toluene) ν(CO): 2078(s), 2000(s) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 3.58 (s, 9H, OCH_3), 3.08 (m, 4H, CH_3CH_2N), 2.97 (m, 2H, NCH_2CH_2), 1.90 (m, 2H, $CH_2CH_2CH_2$), 1.30 (t, 6H, NCH_2CH_3), 0.62 (m, 2H, CH_2Si).

$RhCl(CO)_2[H_2N(CH_2)_3Si(OC_2H_5)_3]$ (Rh—NH_2). This air- and moisture-sensitive complex was prepared from $[RhCl(CO)_2]_2$ (79 mg, 0.20 mmol) and $H_2N(CH_2)_3Si$-$(OCH_2CH_3)_3$ (88 mg, 0.40 mmol) according to the procedure described above for the preparation of Rh—NEt_2. IR (toluene) ν(CO): 2085(s), 2025(s) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 3.82 (q, 6H, CH_3CH_2O), 3.11 (br, 2H, NH_2), 2.94 (m, 2H, $H_2NCH_2CH_2$), 1.75 (m, 2H, $CH_2CH_2CH_2$), 1.23 (t, 9H, OCH_2CH_3), 0.65 (m, 2H, CH_2Si). Anal. calcd for $C_{11}H_{23}O_5NSiClRh$: C, 30.17; H, 5.79; N, 3.54. Found: C, 31.78; H, 5.58; N, 3.37.

$RhCl(COD)[H_2NCH_2CH_2NH(CH_2)_3Si(OCH_3)_3]$ (Rh-(COD)(N—N)). A mixture of $[Rh(COD)Cl]_2$[9] (90 mg, 0.25 mmol) and $H_2NCH_2CH_2NH(CH_2)_3Si(OCH_3)_3$ (0.12 mL, 0.50 mmol) in 10 mL of CH_2Cl_2 was stirred at room temperature for 1 h. After the solvent was removed under vacuum at room temperature, the solid was washed with hexanes (3 mL) and dried under vacuum to give a yellow powder of Rh(COD)(N—N). ^1H NMR ($CDCl_3$) δ: 4.99 (br, 1H, CH_2NHCH_2), 4.41 (br, 2H, H_2NCH_2), 4.22 (s br, 4H, $CH{=}CH$), 3.56 (s, 9H, OCH_3), 2.98 (m, 2H, $H_2NCH_2CH_2$), 2.73 (m, 2H, $H_2NCH_2CH_2NH$), 2.51 (m, 2H, $CH_2NHCH_2CH_2$), 2.35 (m, 4H, $CH_2CH{=}CH$), 1.76–1.81 (m, 6H, CH_2CH_2Si and $CH_2CH{=}CH$), 0.57 (m, 2H, CH_2Si). Anal. calcd for $C_{16}H_{34}O_3N_2SiClRh$: C, 40.53; H, 7.02; N, 6.03. Found: C, 40.98; H, 7.31; N, 5.97.

Preparation of the tethered rhodium complex catalysts

Rh—NEt_2/Pd—SiO_2. A mixture of 1.0 g of Pd—SiO_2 and 0.16 g of Rh—NEt_2, prepared as described above, in 10 mL of toluene was refluxed for 4 h. After filtration, the solid was washed with toluene (3 × 10 mL) to give, after being dried under vacuum, the tethered rhodium amine complex catalyst (Rh—NEt_2/Pd—SiO_2) with a rhodium content of 1.25 wt%.

IR(DRIFT) ν(CO): 2085(s), 2005(s) cm^{-1}.

Rh—NEt$_2$/Ni—SiO$_2$, Rh—NEt$_2$/Au—SiO$_2$ and Rh—NEt$_2$/SiO$_2$. These catalysts were prepared in the same manner as Rh—NEt$_2$/Pd—SiO$_2$ by using 0.16 g of Rh—NEt$_2$ and 1.0 g of Ni—SiO$_2$, Au—SiO$_2$ or SiO$_2$, respectively. The rhodium content was 3.64 wt% for Rh—NEt$_2$/Ni—SiO$_2$, 0.85 wt% for Rh—NEt$_2$/Au—SiO$_2$ and 2.80 wt% for Rh—NEt$_2$/SiO$_2$. IR(DRIFT) ν(CO): 2085(s), 2005(s) cm^{-1} for Rh—NEt$_2$/Ni—SiO$_2$; 2083(s), 2004(s) cm^{-1} for Rh—NEt$_2$/Au—SiO$_2$; and 2080(s), 2005(s) cm^{-1} for Rh—NEt$_2$/SiO$_2$.

Rh—NH$_2$/Pd—SiO$_2$. This catalyst was prepared by the same procedure described above for the preparation of Rh—NEt$_2$/Pd—SiO$_2$ by using 1.0 g of Pd—SiO$_2$ and 0.10 g of Rh—NH$_2$ instead of Rh—NEt$_2$. The rhodium content of the catalyst was 2.20 wt%. IR(DRIFT) ν(CO): 2090(s), 2030(s) cm^{-1}.

Rh(COD)(N—N)/Pd—SiO$_2$. A mixture of 1.0 g of Pd—SiO$_2$ and 0.20 g of Rh(COD)(N—N) in 15 mL of CH_2Cl_2 was refluxed for 4 h. After filtration, the solid was washed with CH_2Cl_2 (3 × 10 mL) and then dried in vacuum to give the tethered rhodium diamine complex catalyst (Rh(COD)(N—N)/Pd—SiO$_2$) with a rhodium content of 2.94 wt%.

Rh(COD)(N—N)/SiO$_2$. This catalyst with a rhodium content of 3.40 wt% was prepared as described for Rh(COD)(N—N)/Pd—SiO$_2$ by using 0.20 g of Rh(COD)(N—N) and 1.0 g of SiO$_2$ instead of Pd—SiO$_2$.

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 adsorbed catalyst (Rh—Cl/Pd—SiO$_2$) was 1.45 wt%. IR(DRIFT) ν(CO): 2095(s), 2028(s) cm^{-1}.

Rh—NHPr$^i_2$/Pd—SiO$_2$ and Rh—NHPr$^i_2$/SiO$_2$. A mixture of 0.60 g of Pd—SiO$_2$ (or SiO$_2$) and 43 mg of $RhCl(CO)_2(NHPr^i_2)$ (Rh—NHPr$^i_2$) [ν(CO): 2083(s), 2001(s) cm^{-1}, 0.045 g), which was prepared according to the literature method,[10] was refluxed in toluene for 4 h. After filtration, the solid was washed with toluene (3 × 10 mL) and dried in vacuum to give the adsorbed rhodium catalysts Rh—NHPr$^i_2$/Pd—SiO$_2$ [Rh, 1.90 wt%; IR(DRIFT) ν(CO): 2085(s), 2010(s) cm^{-1}] and Rh—NHPr$^i_2$/SiO$_2$ [Rh, 1.05 wt%; IR(DRIFT) ν(CO): 2084(s), 2015(s) cm^{-1}].

Hydrogenation reactions

The hydrogenation reactions were carried out in a three-necked, jacketed vessel closed with a self-sealing silicon rubber cap and stirring bar; the vessel was connected to a vacuum/hydrogen line and a constant pressure gas buret. The temperature of the ethylene glycol that was 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. When the catalyst was used in several successive toluene hydrogenations, the reaction mixture after the first cycle was filtered and the solid catalyst was washed with toluene, dried under vacuum, and used for the hydrogenation of a new batch of toluene by following the same procedure as that in the first cycle. After the second cycle, the catalyst was treated as after the first cycle; the isolated catalyst was used for the third cycle; the procedures were the same for the fourth and fifth cycles. For the many runs that were repeated two or more times, the rates were reproducible within ±5%.

Results

Hydrogenation of arenes with the tethered rhodium catalysts

The TCSM catalysts Rh—NEt$_2$/M—SiO$_2$ (M = Pd, Ni, Au), Rh—NH$_2$/Pd—SiO$_2$ and Rh(COD)(N—N)/Pd—SiO$_2$ were used to catalyze the hydrogenation of toluene to methylcyclohexane under the conditions of 40 °C and 1 atm. Table 1 gives the hydrogenation activities of the TCSM catalysts, the homogeneous rhodium complex catalysts, and the silica-supported metal heterogeneous catalysts. From the data in Table 1, it can be seen that the TCSM catalysts are much more active than either the homogeneous rhodium complex catalysts or the SiO$_2$-supported metal heterogeneous catalysts. The activities [as measured by the maximum turnover frequency (TOF), turnover number (TO), or H_2 uptake] of Rh—NEt$_2$/Pd—SiO$_2$ and Rh—NH$_2$/Pd—SiO$_2$ catalysts are at least 45 or 35 times greater, respectively, than the activities of the homogeneous Rh—NEt$_2$ or Rh—NH$_2$ catalysts or the heterogeneous Pd—SiO$_2$ catalyst. Similarly, the Rh(COD)(N—N)/Pd—SiO$_2$ catalyst is at least 20 times more active than Rh(COD)(N—N) or Pd—SiO$_2$. Although the silica-supported metal catalysts Au—SiO$_2$ and Ni—SiO$_2$ are inactive for the hydrogenation of toluene under these mild conditions, the combined TCSM catalysts

Table 1 Catalytic hydrogenation of toluene to methylcyclohexane[a]

Catalyst	Maximum TOF[b]/mol H_2 (mol Rh min)$^{-1}$	TO[c]/mol H_2 (mol Rh)$^{-1}$	H_2 uptake[c]/mmol
Au—SiO$_2$	—	—	0 (12)
Ni—SiO$_2$	—	—	0 (12)
Pd—SiO$_2$	—	—	1.05 (23)
Rh—NEt$_2$	0.017	19.0 (18)	0.38 (18)
Rh—NH$_2$	0.028	33.5 (22)	0.67 (22)
Rh/Pd—SiO$_2$	1.4	235 (5)	2.90 (5.0)
Rh—NEt$_2$/Au—SiO$_2$	0.66	200 (5.5)	0.82 (5.5)
Rh—NEt$_2$/Ni—SiO$_2$	1.2	422 (6.5)	7.46 (6.5)
Rh—NEt$_2$/Pd—SiO$_2$	7.2	1919 (5.0)	11.65 (5.0)
Rh—NH$_2$/Pd—SiO$_2$	6.0	1043 (9.5)	21.70 (9.5)
Rh—NEt$_2$/SiO$_2$	0.80	244 (6.0)	3.32 (6.0)
Rh(COD)(N—N)	0.06	23 (13.5)	0.45 (13.5)
Rh(COD)(N—N)/Pd—SiO$_2$	3.0	383 (6.5)	5.47 (6.5)
Rh(COD)(N—N)/SiO$_2$	0.06	23 (9.0)	0.38 (9.0)

[a] Reaction conditions: 50 mg catalyst (20 μmol for the homogeneous catalysts Rh—NEt$_2$, Rh—NH$_2$ or Rh(COD)(N—N), 5 mL toluene, 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 values correspond to the reaction times (in h) given in parentheses.

Rh—NEt$_2$/Au—SiO$_2$ and Rh—NEt$_2$/Ni—SiO$_2$ are active for the hydrogenation and exhibit activities that are at least 20 times (for Rh—NEt$_2$/Ni—SiO$_2$) or 10 times (for Rh—NEt$_2$/Au—SiO$_2$) higher than that of the homogeneous Rh—NEt$_2$. It can also be seen that except for Rh—NEt$_2$/Au—SiO$_2$ (which has about the same activity as Rh—NEt$_2$/SiO$_2$), the other three TCSM catalysts, Rh—NEt$_2$/Pd—SiO$_2$, Rh—NEt$_2$/Ni—SiO$_2$ and Rh(COD)(N—N)/Pd—SiO$_2$ are more active than the rhodium amine complexes Rh—NEt$_2$ or Rh(COD)(N—N) tethered on SiO$_2$ [Rh—NEt$_2$/SiO$_2$ and Rh(COD)(N—N)/SiO$_2$]. Moreover, the TCSM catalysts, Rh—NEt$_2$/Pd—SiO$_2$ and Rh(COD)(N—N)/Pd—SiO$_2$ are more active than the mixed Rh/Pd—SiO$_2$ heterogeneous supported metal catalyst, which has a Rh content (2.55 wt%) that is similar to that of the TCSM catalysts.

The activities of the TCSM catalysts are strongly affected by both the nature of the tethered rhodium complex and the SiO$_2$-supported metal. The three TCSM catalysts with the same Rh—NEt$_2$ complex show activities that decrease in the order: Rh—NEt$_2$/Pd—SiO$_2$ > Rh—NEt$_2$/Ni—SiO$_2$ > Rh—NEt$_2$/Au—SiO$_2$. The percent conversions of toluene after 6.5 h decrease in the same order: 24.8% > 15.9% > 1.7%. When tethered on the same Pd—SiO$_2$ support, the rhodium monoamine complex catalysts (Rh—NEt$_2$/Pd—SiO$_2$ and Rh—NH$_2$/Pd—SiO$_2$) are more active than the tethered rhodium diamine complex catalyst [Rh(COD)(N—N)/Pd—SiO$_2$].

Fig. 2 shows the activity (TOF) of the five TCSM catalysts as a function of reaction time. All five catalysts are active from the outset. As the reactions proceed, the TOF values for Rh—NEt$_2$/Pd—SiO$_2$ and Rh—NEt$_2$/Au—SiO$_2$ decrease only slightly, but for Rh(COD)(N—N)/Pd—SiO$_2$ and Rh—NH$_2$/Pd—SiO$_2$ the TOF values decrease sharply. However, the TOF of the Rh—NEt$_2$/Ni—SiO$_2$ catalyst increases to a maximum value after about 1.5 h and then decreases slightly.

The TCSM catalysts, Rh—NEt$_2$/Pd—SiO$_2$ and Rh(COD)(N—N)/Pd—SiO$_2$ were also used to catalyze the hydrogenation of other arenes under the mild conditions of 40 °C and 1 atm (Table 2). The data in Table 2 show that for both catalysts the hydrogenation rate is greater for arenes with electron-donating substituents than for arenes with electron-withdrawing substituents.

Durability of TCSM catalysts in the hydrogenation

The durabilities of the Rh—NEt$_2$/Pd—SiO$_2$ and Rh(COD)(N—N)/Pd—SiO$_2$ catalysts were tested by using them for several successive hydrogenations of toluene (Table 3). Both catalysts are more active in the second cycle than in the first. The activities of both catalysts decrease after several cycles but Rh(COD)(N—N)/Pd—SiO$_2$ shows better durability than Rh—NEt$_2$/Pd—SiO$_2$. The decrease in activity of Rh(COD)(N—N)/Pd—SiO$_2$ in the 4th and 5th cycles may result from fracturing of the catalyst particles over long stirring periods with a stirring bar.

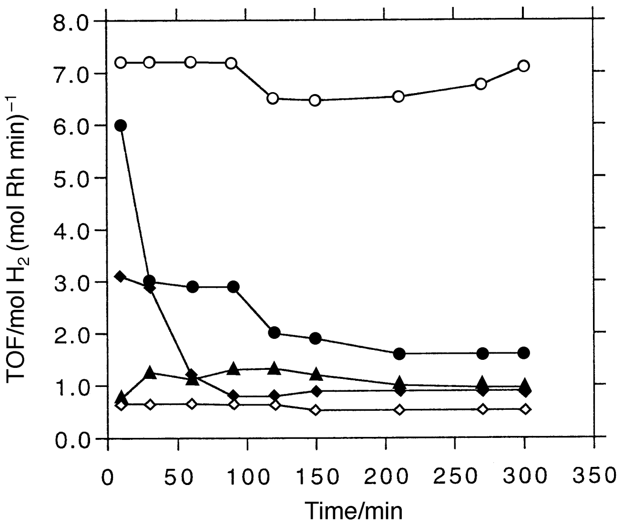

Fig. 2 Toluene hydrogenation activities of TCSM catalysts as a function of reaction time: (◆) Rh(COD)(N—N)/Pd—SiO$_2$, (▲) Rh—NEt$_2$/Ni—SiO$_2$, (●) Rh—NH$_2$/Pd—SiO$_2$, (○) Rh—NEt$_2$/Pd— SiO$_2$, (◇) Rh—NEt$_2$/Au—SiO$_2$. Reaction conditions are the same as those given in Table 1.

Influence of the amine ligand

In order to determine whether tethering of the rhodium amine complex on the surface was essential to the high activities of the TCSM catalysts, non-tethered RhCl(CO)$_2$(HNPr$^{i}_{2}$) and Rh$_2$Cl$_2$(CO)$_4$ were adsorbed on Pd—SiO$_2$ to give the heterogenized rhodium complex catalysts Rh—NHPr$^{i}_{2}$/Pd—SiO$_2$ and Rh—Cl/Pd—SiO$_2$ (see Experimental), which were used to catalyze the hydrogenation of toluene. From the data in Table 4, it is evident that the TCSM catalyst Rh—NEt$_2$/Pd—SiO$_2$ is about 3 times more active than the adsorbed Rh—Cl/Pd—SiO$_2$ catalyst. Although the maximum TOF [6.0 mol H$_2$ (mol Rh min)$^{-1}$] of the Rh—NHPr$^{i}_{2}$/Pd—SiO$_2$ catalyst is only a little lower than that [7.2 mol H$_2$ (mol Rh min)$^{-1}$] of Rh—NEt$_2$/Pd—SiO$_2$, the activity of Rh—NEt$_2$/Pd—SiO$_2$ is much more stable than that of Rh—NHPr$^{i}_{2}$/Pd—SiO$_2$ (Fig. 3). As for the Rh—NEt$_2$ complex tethered on Pd—SiO$_2$ and SiO$_2$, the activity of Rh—NHPr$^{i}_{2}$ adsorbed on SiO$_2$ is much lower (about 15 times) than that of Rh—NHPr$^{i}_{2}$ adsorbed on Pd—SiO$_2$.

Effect of air on TCSM catalytic activity

After the tethered rhodium monoamine complex catalysts, Rh—NEt$_2$/M—SiO$_2$ (M = Pd, Ni, Au) and Rh—NEt$_2$/SiO$_2$, were allowed to stand in air in a screw-capped vial, the activities of the air-aged catalysts for the hydrogenation of toluene were different from those of the fresh catalysts. Although the

Table 2 Catalytic hydrogenation of arenes over Rh—NEt$_2$/Pd—SiO$_2$ and Rh(COD)(N—N)/Pd—SiO$_2$

Substrate	Maximum TOF/mol H$_2$ (mol Rh min)$^{-1}$	TO[a]/mol H$_2$ (mol Rh)$^{-1}$	Product
Rh—NEt$_2$/Pd—SiO$_2$ catalyst[b]			
Anisole	7.6	2169 (6.5)	$C_7H_{14}O$
Naphthalene	4.7	1413 (9.0)	$C_{10}H_{14}$
Toluene	3.3	1214 (7.0)	C_7H_{14}
Benzene	3.0	749 (6.5)	C_6H_{12}
Dimethyl terephthalate	1.2	330 (6.5)	$C_{10}H_{16}O_4$
Rh(COD)(N—N)/Pd—SiO$_2$ catalyst[c]			
Anisole	1.3	470 (9.5)	$C_7H_{14}O$
Toluene	1.5	576 (10.5)	C_7H_{14}
Methyl benzoate	0.2	92 (8.0)	$C_8H_{14}O_2$

[a] TO values correspond to the reaction times (in h) given in parentheses. [b] Reaction conditions: 50 mg catalyst, 1 mL substrate, 5 mL ethanol solvent, 40 °C, 1 atm. [c] Reaction conditions: 25 mg catalyst, 4 mmol substrate, 5 mL heptane solvent, 40 °C, 1 atm.

Table 3 Durability of Rh—NEt_2/Pd—SiO_2 and Rh(COD)(N—N)/Pd—SiO_2 in the hydrogenation of toluene[a]

Reaction cycle	Maximum TOF/mol H_2 (mol Rh min)$^{-1}$	TO[b]/mol H_2 (mol Rh)$^{-1}$
Rh—NEt_2/Pd—SiO_2 catalyst		
1st	7.2	1963 (5.0)
2nd	13.0	2167 (4.5)
3rd	8.5	1362 (4.0)
Rh(COD)(N—N)/Pd—SiO_2 catalyst		
1st	3.0	675 (11)
2nd	4.1	2171 (11)
3rd	4.5	2236 (11)
4th	3.7	1468 (11)
5th	2.1	938 (11)

[a] Reaction conditions are given in footnote *a* of Table 1. [b] TO values correspond to the reaction times (in h) given in parentheses.

activity of Rh—NEt_2/Pd—SiO_2 for toluene hydrogenation does not change if it is stored in a N_2 atmosphere for one week, when the catalyst is stored in a screw-capped vial in air for one week, the TOF and TO values of this catalyst increase from 7.2 and 1919 (in 5 h) to 9.0 and 2624 (in 5 h). Also, the activity of Rh—NEt_2/Pd—SiO_2 increases with increasing contact time with air. However, its hydrogenation activity does not increase further beyond about one month in air.

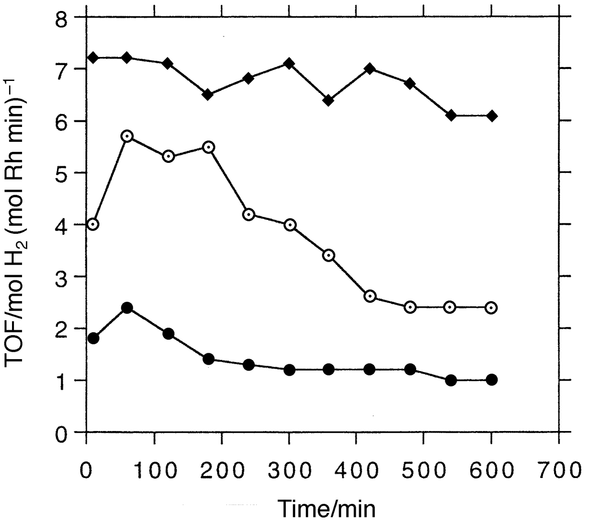

Fig. 3 Toluene hydrogenation activities of (◆) Rh—NEt_2/Pd—SiO_2, (○) Rh—$NHPr^i_2$/Pd—SiO_2 and (●) Rh—Cl/Pd—SiO_2 as a function of the reaction time. Reaction conditions are the same as those in Table 1.

Table 5 shows the activities of the rhodium mono- and diamine tethered complexes after standing in air for about one month. Comparing the data in Tables 1 and 5, it is evident that the effect of air on the catalyst activity is different for each catalyst. The maximum TOF and TO values of the air-aged Rh—NEt_2/Pd—SiO_2 increase to 13.7 mol H_2 (mol Rh · min)$^{-1}$ and 3670 mol H_2 (mol Rh)$^{-1}$ (in 5 h) respectively, which are about 2 times greater than those of the fresh catalyst. The air-aged Rh—NEt_2/Au—SiO_2 is about 5 times more active than the fresh catalyst. However, the activity of the air-aged Rh—NEt_2/Ni—SiO_2 is about the same as that of fresh Rh—NEt_2/Ni—SiO_2. For Rh—NEt_2/SiO_2, the maximum TOF and TO values of the air-aged catalyst are about 7 times and 3 times, respectively, greater than those of the fresh catalyst. The activity of the air-aged Rh(COD)(N—N)/Pd—SiO_2 is lower (3 times) than the fresh catalyst, and the air-aged Rh(COD)(N—N)/SiO_2 becomes inactive for the hydrogenation of toluene under these mild reaction conditions. Fig. 4 shows the TOF of the air-aged catalysts, Rh—NEt_2/M—SiO_2 (M = Pd, Ni, Au) and Rh—NEt_2/SiO_2, as a function of reaction time. It can be seen that as the hydrogenation proceeds, the activities (TOF) of the air-aged Rh—NEt_2/Pd—SiO_2, Rh—NEt_2/Ni—SiO_2 and Rh—NEt_2/Au—SiO_2 catalysts decrease slightly, but the activity of the air-aged Rh—NEt_2/SiO_2 decreases markedly.

IR spectroscopic studies

IR(DRIFT) spectra of the three fresh TCSM catalysts Rh—NEt_2/M—SiO_2 (M = Pd, Ni, Au) and Rh—NEt_2/SiO_2 show two ν(CO) bands in the ranges 2080–2085 and 2004–2005 cm^{-1}, which are very similar to those (2078 and 2000

Table 4 Hydrogenation of toluene to methylcyclohexane over tethered and adsorbed rhodium amine complex catalysts[a]

Catalyst	Maximum TOF/mol H_2 (mol Rh min)$^{-1}$	TO[b]/mol H_2 (mol Rh)$^{-1}$
Rh—NEt_2/Pd—SiO_2	7.2	1919 (5)
Rh—NEt_2/SiO_2	0.8	211 (5)
Rh—$NHPr^i_2$/Pd—SiO_2	6.0	2058 (9)
Rh—Cl/Pd—SiO_2	2.4	562 (6)
Rh—$NHPr^i_2$/SiO_2	0.4	72 (9)

[a] Reaction conditions are given in footnote *a* of Table 1. [b] TO values correspond to the reaction times (in h) given in parentheses.

Table 5 Influence of air on the catalytic activities of tethered rhodium amine complex catalysts in the hydrogenation of toluene[a]

Catalyst[b]	Maximum TOF/mol H_2 (mol Rh min)$^{-1}$	TO[c]/mol H_2 (mol Rh)$^{-1}$
Rh—NEt_2/Pd—SiO_2	13.7	3670 (5.0)
Rh—NEt_2/Au—SiO_2	3.7	856 (5.5)
Rh—NEt_2/Ni—SiO_2	1.6	542 (6.5)
Rh—NEt_2/SiO_2	5.3	781 (5.0)
Rh(COD)(N—N)/Pd—SiO_2	1.3	320 (7.0)
Rh(COD)(N—N)/SiO_2	0	0 (7.0)

[a] Reaction conditions are given in footnote *a* of Table 1. [b] After standing in air for one month. [c] TO values correspond to the reaction times (in h) given in parentheses.

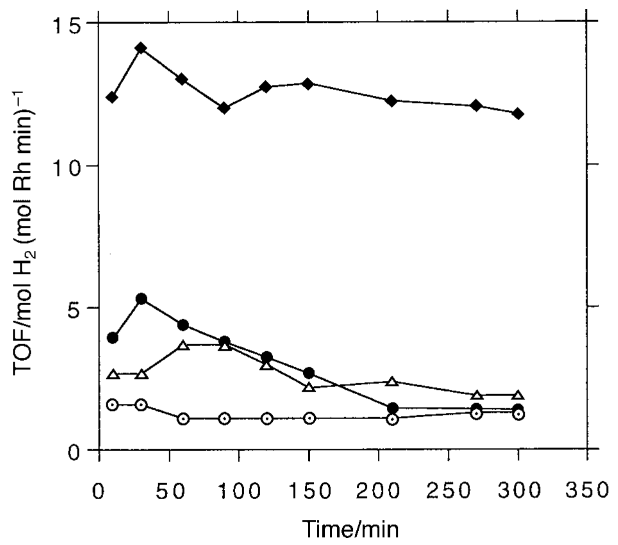

Fig. 4 Toluene hydrogenation activities of air-aged tethered rhodium complex catalysts as a function of reaction time: (◆) Rh—NEt$_2$/Pd—SiO$_2$, (●) Rh—NEt$_2$/SiO$_2$, (○) Rh—NEt$_2$/Au—SiO$_2$, (△) Rh—NEt$_2$/Ni—SiO$_2$.

cm^{-1} in toluene) of the free Rh—NEt$_2$ complex. After the catalysts were used for the hydrogenation of toluene for 12 h, IR analysis showed that the two ν(CO) bands had almost disappeared. However, after the used catalysts were stirred in toluene under a CO atmosphere at room temperature overnight, the two ν(CO) bands at 2080–2085 and 2004–2005 cm^{-1} were restored, and no other ν(CO) bands were observed. While these results are consistent with the amine ligand remaining coordinated to the rhodium center during the hydrogenation reaction, it should be noted that CO adsorbed on silica-supported rhodium gives very similar ν(CO) bands [2095(s), 2027(s) cm^{-1}] that are attributed to Rh$^{\mathrm{I}}$(CO)$_2$.[11–13] Thus, the ν(CO) spectra of the CO-treated TCSM catalysts do not exclude the possibility that the Rh is actually adsorbed on the silica surface.

The adsorbed catalysts, Rh—NHPr$^{\mathrm{i}}_2$/Pd—SiO$_2$ and Rh—Cl/Pd—SiO$_2$, have two ν(CO) bands at 2085(s) and 2010(s) cm^{-1}, and 2095(s) and 2028(s) cm^{-1}, respectively. After they were used for the hydrogenation of toluene for 10 h, these ν(CO) bands almost completely disappeared. But when the used catalysts were stirred in toluene under a CO atmosphere at room temperature overnight, the ν(CO) bands for both of the catalysts were restored. When the mixed metal (Rh and Pd) SiO$_2$-supported catalyst Rh/Pd—SiO$_2$ was treated with CO by the same procedure, the DRIFT spectrum of the resulting sample showed two ν(CO) bands at 2091(s) and 2030(s) cm^{-1}, which are very similar to those of the adsorbed catalyst Rh—Cl/Pd—SiO$_2$ and to those of Rh$^{\mathrm{I}}$(CO)$_2$ formed by CO treatment of Rh (2.0 wt%) on SiO$_2$ and Rh (2.2 wt%) on Al$_2$O$_3$, as previously reported by Yang and Garland[13a] and by Yates and coworkers,[13b] respectively. Thus, it appears that Rh$^{\mathrm{I}}$(CO)$_2$ is formed on Rh—Cl/Pd—SiO$_2$ and CO-treated Rh/Pd—SiO$_2$, and it is also possible that Rh$^{\mathrm{I}}$(CO)$_2$ is formed on the CO-treated Rh—NHPr$^{\mathrm{i}}_2$/Pd—SiO$_2$ catalyst.

The DRIFT spectra of air-aged Rh—NEt$_2$/SiO$_2$ and Rh—NEt$_2$/M—SiO$_2$ (M = Pd, Ni, Au) show that the intensities of the ν(CO) bands at 2080–2085 and 2004–2005 cm^{-1} decrease with the length of the time that the catalysts are exposed to air. After standing in air for more than one month, the two ν(CO) bands nearly disappear. But after the air-aged catalysts were stirred in toluene under a CO atmosphere, the two CO bands are restored. Further experiments show that if Rh—NEt$_2$/Pd—SiO$_2$ is allowed to stand in a mixture of H$_2$O and N$_2$ at room temperature for two weeks, the intensities of the ν(CO) bands at 2085 and 2005 cm^{-1} also decrease markedly, but the ν(CO) bands can also be recovered by stirring the catalyst in toluene under a CO atmosphere. The activity [TOF = 11.5 mol H$_2$ (mol Rh min)$^{-1}$] of the H$_2$O/N$_2$-aged catalyst for the hydrogenation of toluene increased as well.

When fresh Rh(COD)(N—N)/Pd—SiO$_2$ was stirred in toluene under a CO atmosphere at room temperature overnight, the resulting catalyst gave an IR(DRIFT) spectrum that exhibits ν(CO) bands at 2092(s) and 2020(s) cm^{-1}, which are very similar to those [2093(s) and 2023(s) cm^{-1} in toluene] of the rhodium complex Rh(CO)$_2$(N—N) formed from the reaction of Rh(COD)(N—N) and CO in toluene under the same conditions. After the Rh(COD)(N—N)/Pd—SiO$_2$ catalyst was used for the hydrogenation of toluene for four cycles and isolated from the reaction solution, it was treated with CO as for the fresh catalyst. The DRIFT spectrum of the resulting sample exhibited the two characteristic CO bands at 2092(s) and 2023(s) cm^{-1}, and no other CO band was observed, which is consistent with the formation of the tethered Rh(CO)$_2$(N—N) complex, but these bands are also very similar to those attributed to Rh$^{\mathrm{I}}$(CO)$_2$ on silica-supported Rh (see above).

It was observed that when the air-aged Rh(COD)(N—N)/Pd—SiO$_2$ catalyst was stirred with CO in toluene at room temperature overnight, the resulting sample exhibited three CO bands at 2092(s), 2058(m) and 2023(s) cm^{-1}, which are different from those [2092(s) and 2023(s) cm^{-1}] of the fresh catalyst treated with CO. This observation suggests that the structure of the rhodium complex in the air-aged Rh(COD)(N—N)/Pd—SiO$_2$ catalyst is different from that of the fresh catalyst.

Discussion

Despite the immense success that has been achieved in the homogeneous transition metal complex catalyzed hydrogenation of olefins, homogeneous catalysis of arene hydrogenation is much less developed.[14] In the present study, homogeneous catalysts have been tethered to SiO$_2$ that also supports a metal; the resulting catalysts are very active for arene hydrogenation. The TCSM catalysts, Rh—NEt$_2$/M—SiO$_2$ (M = Pd, Ni, Au), Rh—NH$_2$/Pd—SiO$_2$ and Rh(COD)(N—N)/Pd—SiO$_2$, were prepared by tethering the rhodium amine complexes on heterogeneous silica-supported metal catalysts. These new catalysts are very active for the hydrogenation of arenes under the mild conditions of 40 °C and 1 atm of H$_2$. Among these TCSM catalysts, Rh—NEt$_2$/Pd—SiO$_2$ gives the highest activity (TOF = 7.2 and TO = 1919 in a 5 h period) for the hydrogenation of toluene. Its activity is also higher than that (TOF = 5.5 and TO = 2420 in a 9.5 h period) of the TCSM catalyst consisting of RhCl[CN(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$]$_3$ tethered on Pd—SiO$_2$, which we reported previously.[4] To our knowledge, Rh—NEt$_2$/Pd—SiO$_2$ is also more active than any other homogeneous metal complex or immobilized metal complex catalyst reported in the literature for the hydrogenation of arenes under the mild conditions of 40 °C and 1 atm. Under similar conditions, Blum and coworkers[15] used RhCl$_3$–Aliquat-336 to catalyze the hydrogenation of toluene in H$_2$O–CH$_2$Cl$_2$. However, after 5 h, only *ca.* 3 moles of toluene were converted to methylcyclohexane per mole of rhodium. The TO value for the immobilized complex prepared from [RhCl(nbd)]$_2$ (nbd = norbornadiene) and phosphinated silica is 200 at 80 atm of H$_2$ and 30 °C during 1.5 h.[16] Recently, Corma *et al.*[17] reported that the rhodium complex [Rh(COD)(N—N)]PF$_6$ [N—N = 2-(3-triethoxysilylpropylaminocarbonyl)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 H$_2$ pressure ($\geqslant$10 atm).[18] Only a few homogeneous catalysts are active using 1 atm of H$_2$, but their activities are low.[15,19]

The high activities of TCSM catalysts may be attributed to a combination of roles played by both the supported metal and the tethered rhodium complex. One possible role for the supported metal is to adsorb H_2 and activate it to spill over onto the silica surface. Thus, the supported metal provides a very active form of hydrogen on the SiO_2 where the Rh complex is tethered. At the same time, the arene substrate binds to the Rh complex where it is activated to react with the spillover hydrogen.

The results in Table 1 show that the activity of $Rh{-}NEt_2/Pd{-}SiO_2$ is much higher than that of $Rh{-}NEt_2/Ni{-}SiO_2$ and $Rh{-}NEt_2/Au{-}SiO_2$. The low activity of $Rh{-}NEt_2/Au{-}SiO_2$ may be related to the fact that gold is a very poor metal for adsorbing and activating H_2.[20] The lower activity of $Rh{-}NEt_2/Ni{-}SiO_2$ compared to $Rh{-}NEt_2/Pd{-}SiO_2$ may be due to the slow reduction of the oxided nickel surface under the reaction conditions. In addition, supported nickel is a poorer hydrogen spillover initiator compared to palladium, which is among the most active metals for providing spillover hydrogen.[5]

IR(DRIFT) spectra of used TCSM catalysts $Rh{-}NEt_2/M{-}SiO_2$ (M = Pd, Ni, Au) isolated from reaction mixtures show that the two CO ligands are removed from the rhodium center during the hydrogenation. Since $Rh{-}NEt_2/Pd{-}SiO_2$ is active for at least three cycles and much of the CO is removed after the first cycle, the active form of the catalyst presumably does not contain the CO ligands.

Although the TCSM catalysts were designed to function with the tethered complex as an active site, it is necessary to consider the possibility that some form of SiO_2-supported Rh is responsible for the TCSM catalyst activity. Rhodium on SiO_2 is known[11–13] to adsorb CO to give IR absorptions at 2093–2100, 2058–2065, 2023–2030 and 1830–1890 cm^{-1}; two CO absorptions at 2090–2097 and 2023–2030 cm^{-1}, which are characteristic of the $Rh(CO)_2$ species, are observed for Rh/SiO_2 at lower Rh loadings and high dispersion. The ν(CO) bands of fresh and CO-treated, used $Rh{-}NEt_2/Pd{-}SiO_2$ catalysts occur at 2080–2085 and 2005–2010 cm^{-1} and no other ν(CO) absorptions are observed. A similar IR spectroscopic study of the $Rh(COD)(N{-}N)/Pd{-}SiO_2$ catalyst shows IR bands at 2092(s) and 2020(s) cm^{-1}. All of these bands can be attributed to $Rh^{I}(CO)_2$ species, either in tethered complexes or on the SiO_2 surface.

Assuming the catalysts do contain active tethered complexes, we attempted to deactivate the used TCSM catalysts, $Rh{-}NEt_2/Pd{-}SiO_2$ and $Rh(COD)(N{-}N)/Pd{-}SiO_2$, by removing the Rh with a more strongly binding ligand. These catalysts were stirred with dppe ($Ph_2PCH_2CH_2PPh_2$) in toluene at 60 °C for 4 h, and then washed with toluene and dichloromethane several times. The activities of the resulting catalysts were indeed low (0.58 mmol H_2 uptake in a 24 h period) and about the same as that of $Pd{-}SiO_2$ treated with dppe in the same way; the activity (0.47 mmol H_2 uptake in a 25 h period) of dppe-treated $Pd{-}SiO_2$ was substantially less than that (1.05 mmol H_2 uptake in a 23 h period) of untreated $Pd{-}SiO_2$. This result is consistent with the suggestion that rhodium on the used catalysts was removed by the strongly coordinating dppe ligand and that the resulting catalyst has a low toluene hydrogenation activity. However, if Rh were present on the silica surface, it might also be deactivated by the dppe treatment.

One of the tests[21] for the presence of catalytically active Rh nanoclusters is an induction period during which the nanoclusters are formed. The kinetic curves in Fig. 2, however, show that all of the TCSM catalysts are active from the outset and no induction period is observed. In fact, as the reaction proceeds, the rate decreases very slightly for $Rh{-}NEt_2/M{-}SiO_2$ and markedly for $Rh(COD)(N{-}N)/Pd{-}SiO_2$ and $Rh{-}NH_2/Pd{-}SiO_2$. This kinetic behavior does not support the possibility that the catalytically active species is a reduced rhodium(0) metal colloid or cluster.[21] It should also be noted that the tethered Rh complex on just SiO_2, $Rh(COD)(N{-}N)/SiO_2$, has a very low catalytic activity (Table 1), which indicates that catalytically active nanoclusters are not formed. Only if Pd catalyzes the formation of nanoclusters could such species be involved in the high activity of the Rh(COD)- $(N{-}N)/Pd{-}SiO_2$ TCSM catalyst. It should also be noted that the mixed $Rh/Pd{-}SiO_2$-supported metal catalyst is much less active than $Rh{-}NEt_2/Pd{-}SiO_2$ (Table 1). All of the above results lead to the conclusion that it is not possible to state definitively whether the Rh in these TCSM catalysts remains coordinated to the tethered amine ligand [which is most likely for $Rh(COD)(N{-}N)/Pd{-}SiO_2$] or it is adsorbed on the silica.

Exposure of the TCSM catalysts to air for one month strongly affects their activities. At least for the $Rh{-}NEt_2/Pd{-}SiO_2$ catalyst, it appears to be the water in air that causes an increase in activity and loss of the CO groups. A similar loss of CO ligands upon exposure to air was also reported by Bartholin *et al.* for $[RhCl(CO)_2]_2$ immobilized on phosphinated silica.[22] The effect of air/H_2O is complicated because it does not always lead to an increase in activity as noted in the Results. For example, air-aged Rh(COD)-$(N{-}N)/Pd{-}SiO_2$ has a lower activity and it gives a DRIFT spectrum after CO treatment that is quite different from the spectrum of the fresh $Rh(COD)(N{-}N)/Pd{-}SiO_2$ that has been treated with CO.

Summary

The TCSM catalysts, $Rh{-}NEt_2/M{-}SiO_2$ (M = Pd, Ni, Au) and $Rh(COD)(N{-}N)/Pd{-}SiO_2$, are very active for the hydrogenation of arenes under the mild conditions of 40 °C and 1 atm. The activities of the TCSM catalysts are strongly affected by the nature of both the tethered complex and the supported metal. Among these TCSM catalysts, $Rh{-}NEt_2/Pd{-}SiO_2$ exhibits the highest activity, while $Rh(COD)(N{-}N)/Pd{-}SiO_2$ exhibits the highest stability through several catalytic cycles. It is not known whether the Rh remains coordinated to the tethered ligands during the hydrogenation reactions or is adsorbed to the SiO_2 surface. If the Rh is on the SiO_2, it must be in a much more active form than it is in the mixed metal catalyst $Rh/Pd{-}SiO_2$ prepared by classical impregnation methods (Table 1). In addition, if the active form of the catalyst is Rh on SiO_2, it must be generated only when Pd is present because the rhodium amine complexes tethered on just silica have much lower activities than those tethered on $Pd{-}SiO_2$. Although the nature of these catalysts requires further study, it is clear that they are very active for arene hydrogenation.

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