Effects of supported donor ligands on the activity and stability of tethered rhodium complex catalysts for hydroformylation

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Abstract

Functionalized SiO_2-tethered rhodium complexes derived from $Rh_4(CO)_{12}$, $RhCl(PPh_3)_3$ and $RhHCl(PPh_3)_3$ have been studied by infrared spectroscopy (IR) and solid state ^{31}P NMR. $Rh_4(CO)_{12}$ and phosphinated or aminated SiO_2 are suggested to form $Rh_4(CO)_{12-x}L_x$ (L: supported PPh_2 or NH_2; $x = 2$ or 3). $Rh_4(CO)_{12}$ reacts with thiolated SiO_2 to give $[Rh(\mu\text{-}L)(CO)_2]_2$ (L: supported SH). The reaction of $RhCl(PPh_3)_3$ or $RhH(CO)(PPh_3)_3$ with functionalized SiO_2 is assumed to result in $RhCl(PPh_3)_2L$ or $RhH(CO)(PPh_3)_2L$ (L: supported PPh_2 or NH_2 or SH).

The catalytic activity and stability of a tethered rhodium complex catalyst in cyclohexene hydroformylation shows the supported donor ligand and the catalyst precursor dependences. The aminated SiO_2-tethered catalyst derived from $Rh_4(CO)_{12}$ or $RhCl(PPh_3)_3$ displays good catalytic activity and good resistance to rhodium leaching. The thiolated SiO_2-tethered catalyst derived from $RhH(CO)(PPh_3)_3$ exhibits the highest catalytic activity and good resistance to rhodium leaching. The effects of supported donor ligands on the activity and stability of tethered rhodium complex catalysts for hydroformylation are described.
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1. Introduction

Over the past few decades, development and application of immobilized homogeneous hydroformylation catalysts have been attracting widespread interest [1–4], since such catalysts can combine the high activity and selectivity of homogeneous catalysts and the long lifetime and ease of separation of heterogeneous catalysts. Rhodium complex catalysts are the most active for hydroformylation and are widely used. Much work has been devoted to studying the preparation and performance of immobilized rhodium complex hydroformylation catalysts [2–14]. In order to efficiently heterogenize homogeneous catalysts and prevent metal leaching during reaction, the most common method is to tether metal complexes to organic polymers and inorganic supports with the aid of ligand silane coupling reagents. SiO_2 is most widely used as a typical inorganic support, as surface hydroxy groups of SiO_2 react easily with alkoxy or chloro groups of a silane that has a donor ligand coordinated

to the metal complex, to form surface silanol species. It is documented that various donor ligands have been employed to prepare SiO_2-tethered rhodium compounds or complexes [14–37]. Some of these SiO_2-tethered rhodium compounds or complexes have been investigated in the catalysis for olefin hydroformylation [14,15,18,19,25,26,31–33,36,37].

The typical donor ligands for use in the research of heterogeneous hydroformylation are phosphines, amines and thiols. They play some roles in promoting the catalysis of rhodium compounds or complexes as well as in anchoring rhodium compounds or complexes to the supports. Earlier studies made use of simple rhodium complexes such as $[Rh(CO)_2Cl]_2$ and $Rh(acac)(CO)_2$ to prepare SiO_2-tethered rhodium complexes via phosphine, amine and thiol ligands [16,18,19]. These catalysts were found to possess different heterogeneously catalytic properties and different resistance to rhodium leaching in hexene-1 hydroformylation at 80–150 °C and 42 atm depending on the donor ligand [18,19]. In the 1980s, a rhodium thiolate complex like $Rh_2(CO)_2(PBu^t_3)_2(\mu\text{-}Cl)(\mu\text{-}SR)$ (R = $(CH_2)_3Si(OEt)_3$) was chemically linked to SiO_2 [27]. The resultant immobilized catalyst was used to catalyze cyclohexene hydroformylation at 80 atm and 120 °C with fair recycling [38]. In

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recent years, tethered rhodium complex hydroformylation catalysts were further developed [33–37]. SiO_2-tethered catalysts prepared from $Rh_2[\mu\text{-}S(CH_2)_3Si(OMe)_3]_2(CO)_4$ and $Rh_2[\mu\text{-}S(CH_2)_3Si(OMe)_3]_2[Ph_2P(CH_2)_3Si(OEt)_3]_2(CO)_2$ displayed high activity and good stability for octene-1 hydroformylation in the presence of phosphine ligands under the mild conditions of 60 °C and 1 atm [33]. Also, $Rh_2[\mu\text{-}S(CH_2)_3Si(OMe)_3]_2(CO)_4$ was tethered to phosphinated Pd-SiO_2 and $Rh_2[\mu\text{-}S(CH_2)_3Si(OMe)_3]_2[Ph_2P(CH_2)_3Si(OEt)_3]_2(CO)_2$ to several SiO_2-supported metal catalysts M-SiO_2 [36]. The obtained tethered catalysts were found to be even more active and well stable for octene-1 hydroformylation in the presence of phosphorus-containing ligands under the mild conditions of 60 °C and 1 atm [36].

Although the previous studies illustrated that some specific tethered rhodium complex catalysts via donor ligands are effective for heterogeneous olefin hydroformylation [18,19,33,36,38], little has been revealed about the comparative effects of different donor ligands on the catalytic activity and stability of a rhodium complex and the synergistic promotion of two different ligands on the catalysis of a rhodium complex. The relationship between the catalytic properties and the nature of a tethered rhodium complex has not been established. In the present paper, we report systematic studies of the preparation of a variety of rhodium complexes tethered to the surface of SiO_2 via phosphine-, amine- and thiol-containing silane coupling reagents and of heterogeneous cyclohexene hydroformylation catalyzed by these tethered rhodium complex-derived catalysts. We briefly describe the surface behaviours of the rhodium complexes on donor ligand-functionalized SiO_2 during the preparation processes of tethered rhodium complexes by IR and solid state ^{31}P NMR studies, in order to gain an insight into the nature of rhodium complexes tethered to SiO_2. We wish to demonstrate the effects of different supported donor ligands on the activity and stability of tethered rhodium complex catalysts by comparing the activities and resistance to rhodium leaching of different tethered rhodium complex catalysts in cyclohexene hydroformylation.

2. Experimental

SiO_2 that is a silica "Aerosil" with a surface area of 380 m^2/g, was purchased from Degussa. Cyclohexene (99%) was purchased from Merck. $Cl(CH_2)_3Si(OMe)_3$, (97%), $H_2N(CH_2)_3Si(OEt)_3$, (99%), $HS(CH_2)_3Si(OMe)_3$, (96%) and $KPPh_2$ (0.5 M solution in tetrahydrofuran (THF)) were supplied by Aldrich. $Rh_4(CO)_{12}$ (98%), $RhCl(PPh_3)_3$ (99%) and $RhH(CO)(PPh_3)_3$ (98%) were supplied by Strem. All other reagents were purchased commercially. Organic solvents were distilled and dried prior to use. The gases $CO + H_2$ and N_2 had a purity of 99.999%.

SiO_2 was subjected to dehydration at 200 °C prior to the following experiments. Donor ligand-functionalized SiO_2 was prepared by reacting SiO_2 (2.0 g) with a toluene

(150 ml) solution of organosilane (10 ml) under refluxing under N_2 for 16 h. The resulting solid was filtered off, washed with chloroform (200 ml) and dried in vacuum. The chlorinated, aminated and thiolated SiO_2 samples thus prepared contained 1.6% Cl, 1.1% N and 1.3% S, respectively. The chlorinated SiO_2 was further refluxed with $KPPh_2$ (1 ml) in THF (25 ml) under N_2 for 1 h. After filtration, washing with 100 ml of methanol and drying in vaccum, the resulting phosphinated SiO_2 contained 0.1% Cl and 0.8% P. Phosphinated, aminated and thiolated SiO_2 samples are denoted as $SiO_2(PPh_2)$, $SiO_2(NH_2)$ and $SiO_2(SH)$, respectively.

Tethered rhodium complexes were prepared as follows. In the case with $Rh_4(CO)_{12}$, functionalized SiO_2 (1.0 g) was impregnated with a *n*-hexane (50 ml) solution of $Rh_4(CO)_{12}$ (37 mg) under N_2. The system was stirred at room temperature under N_2 for 5 h. The solid powder colorated and the red solution became colorless rapidly after stirring. $SiO_2(PPh_2)$, $SiO_2(NH_2)$ and $SiO_2(SH)$ turned deep brown, brown and yellow in color, respectively after reacting with $Rh_4(CO)_{12}$. Afterward, the liquid was drawn off with a syringe under N_2 and the resulting solid was washed three times with *n*-hexane under N_2 followed by drying under vacuum (10^{-2} Torr). In the case with $RhCl(PPh_3)_3$, functionalized SiO_2 (1.0 g) was refluxed with a toluene (50 ml) solution of $RhCl(PPh_3)_3$ (0.183 g) under N_2 for 16 h. All the functionalized SiO_2 samples turned deep brown in color and the red solution became colorless at the end of reaction. Afterward the liquid was drawn off with a syringe under N_2, and the solid was washed three times with toluene under N_2 followed by drying in vacuum. In the case with $RhH(CO)(PPh_3)_3$, functionalized SiO_2 (1.0 g) was stirred with a toluene (50 ml) solution of $RhH(CO)(PPh_3)_3$ (0.180 g) at 70 °C under N_2 for 16 h. All the functionalized SiO_2 samples turned green in color and the green solution became almost colorless at the end of reaction. Afterward the liquid was drawn off with a syringe under N_2, and the solid was washed three times with toluene under N_2 followed by drying in vacuum.

Hydroformylation of cyclohexene was conducted under 28 bar of an equimolar CO and H_2 mixture at 100 °C in an autoclave. Three hundred milligrams of tethered rhodium complex sample, 12 ml of cyclohexene and 55 ml of THF were first transferred to the autoclave inside a glove box. Subsequently the $CO + H_2$ mixture was charged after the reaction system had been purged with this reaction gas mixture. When a reaction cycle of 20 h ceased, the solid catalyst was filtered off from the reaction mixture in air for the next cycle and elemental analysis. Sampling of the reaction mixture was done during the course of reaction. The samples were analyzed by gas chromatography.

IR experiments were carried out on a Shimadzu 8700 FTIR spectrometer at a resolution of 4 cm^{-1}. The solid samples studied were pressed into wafers of 15 mg each and placed in a single beam IR cell where the wafers could be subjected to the desired treatments. In situ IR studies of the reactivities between $Rh_4(CO)_{12}$ and unfunctionalized or functionalized SiO_2 were performed by dripping $Rh_4(CO)_{12}$

solution on unfunctionalized or functionalized SiO_2 wafers under N_2. IR spectra of supported rhodium complexes were recorded by subtracting the support contribution.

^{31}P NMR spectra were recorded on a 300 MHz Bruker ACF 300 FT-NMR spectrophotometer. Chemical shifts were referenced to Na_2HPO_4 at 0 ppm. The rhodium contents of the samples were determined by atomic absorption spectroscopy. The chlorine, sulphur and phosphorus contents of the samples were analyzed by X-ray fluorescence. Thermogravimetric analysis was used to estimate the contents of chlorine, nitrogen and sulphur in SiO_2(Cl), SiO_2(NH_2) and SiO_2(SH).

3. Results and discussion

3.1. Tethering of rhodium complexes to SiO_2

3.1.1. $Rh_4(CO)_{12}$

In Table 1, are presented the IR spectroscopic data after the interactions of $Rh_4(CO)_{12}$ with the surfaces of unfunctionalized and functionalized SiO_2. After impregnation of a wafer of SiO_2 predehydrated at 200 °C with a red solution of $Rh_4(CO)_{12}$ in *n*-hexane under N_2 followed by evacuation of the solvent, the wafer color turned red and the surface spectrum exhibited carbonyl bands at 2080s, 2049m(sh) and 1802m(br) cm^{-1}. This spectrum is explicitly assigned to $Rh_6(CO)_{16}$ supported on SiO_2 [41].

As soon as a wafer of SiO_2(PPh$_2$) predehydrated at 200 °C was impregnated with a *n*-hexane solution of $Rh_4(CO)_{12}$ under N_2, the wafer color turned deep brown. After removal of the solvent, the surface spectrum gave three linear carbonyl bands at 2067s(br), 2031m(br) and 2005m(br) cm^{-1} and two bridged carbonyl bands at 1871w(br) and 1801m(br) cm^{-1}. We attribute it to a new grafted rhodium carbonyl cluster not identified, since bridged carbonyl bands are still retained.

Upon addition of a *n*-hexane solution of $Rh_4(CO)_{12}$ under N_2 onto a wafer of SiO_2(NH_2) predehydrated at 200 °C,

the wafer color turned brown. After removal of the solvent, the surface spectrum showed three linear carbonyl bands at 2088m, 2053m(sh) and 2015s cm^{-1}, and two broad bridged carbonyl bands at 1858m(br) and 1802w(br) cm^{-1}. It may be related to a new supported rhodium carbonyl cluster, since bridged carbonyl ligands were still observed.

Alternatively, a *n*-hexane solution of $Rh_4(CO)_{12}$ was reacted with 4 eq. of $H_2N(CH_2)_3Si(OEt)_3$ under stirring and under N_2 at room temperature. The solution color turned deep red immediately after contact of the two reactants. By nearly 3.5 h, the reaction was stopped. A solution of the reaction mixture was transferred under N_2 onto a SiO_2 wafer predehydrated at 200 °C. The wafer color turned brown at once. After 1 h of treatment under vacuum (10^{-5} Torr), the surface spectrum presented carbonyl bands at 2088m(sh), 2059s, 2019m, 1855w(br) and 1805m(br) cm^{-1}. This spectrum resembles that obtained by impregnating SiO_2(NH_2) with $Rh_4(CO)_{12}$, which suggests the formation of the identical SiO_2-tethered rhodium complex.

When a *n*-hexane solution of $Rh_4(CO)_{12}$ was dripped under N_2 onto a wafer of SiO_2 (SH) predehydrated at 200 °C, the wafer color turned yellow immediately. The surface spectrum displayed four linear carbonyl bands at 2079m, 2059s, 2013s and 1972(sh) cm^{-1}. Both position and relative intensity of these three bands are quite similar to those for $[Rh(\mu\text{-}S(CH_2)_3Si(O_s)_3)(CO)_2]_2$ on SiO_2 (2081m, 2064s and 2020s cm^{-1}), which was reported by Gao and Angelici to be formed from $[Rh(CO)_2Cl]_2$ and $HS(CH_2)_3Si(OMe)_3$ [33]. Thus, we suggest that an identical rhodium carbonyl dimer is formed. In order to conform this hypothesis, we run a homogeneous reaction of $Rh_4(CO)_{12}$ with $HS(CH_2)_3Si(OMe)_3$ in *n*-hexane. $Rh_4(CO)_{12}$ and 4 eq. of $HS(CH_2)_3Si(OMe)_3$ produced a deep-red mixture under N_2 which gave an IR spectrum containing four linear carbonyl bands at 2071m, 2052s, 2003s and 1972vw cm^{-1}. We assign this spectrum to $[Rh(\mu\text{-}S(CH_2)_3Si(OMe)_3)(CO)_2]_2$ as this spectrum matches with that of $[Rh(\mu\text{-}S(CH_2)_3Si(OMe)_3)(CO)_2]_2$ in toluene (2074m, 2056s and 2004s cm^{-1}) and the spectral pattern of

Table 1
IR spectroscopic data of rhodium carbonyl complexes

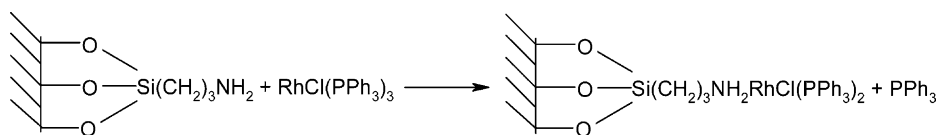| Complex	v(CO) (cm^{-1})	Reference
$Rh_4(CO)_{12}$/*n*-hexane	2069s, 2044m, 1886m	This work
$Rh_6(CO)_{16}$/KBr	2073s, 2026m, 1800s	[39]
$Rh_6(CO)_{16}$/SiO_2	2083s, 2051m(sh), 1804m(br)	[40]
$Rh_6(CO)_{16}$/SiO_2	2080s, 2049m(sh), 1802m(br)	This work[a]
$Rh_4(CO)_{12}$/SiO_2(PPh$_2$)	2067s(br), 2031m(br), 2005m(br), 1871w(br), 1801m(br)	This work[a]
$Rh_4(CO)_{12}$/SiO_2(NH_2)	2088m, 2053m(sh), 2015s, 1858m(br), 1802w(br)	This work[a]
($Rh_4(CO)_{12}$ + $4H_2N(CH_2)_3Si(OEt)_3$)	2088m(sh), 2059s, 2019m, 1855w(br), 1805m(br)	This work[b]
$Rh_4(CO)_{12}$/SiO_2(SH)	2079m(sh), 2063s, 2017s, 1978w(sh)	This work[a]
$[Rh(\mu\text{-}S(CH_2)_3Si(OMe)_3)(CO)_2]_2$/$SiO_2$	2081m, 2064s, 2020s	[33]
$[Rh(\mu\text{-}S(CH_2)_3Si(OMe)_3)(CO)_2]_2$/*n*-hexane	2071m, 2052s, 2003s, 1972vw	This work[c]
$[Rh(\mu\text{-}S(CH_2)_3Si(OMe)_3)(CO)_2]_2$/toluene	2074m, 2056s, 2004s	[42]

[a] By impregnation of support with $Rh_4(CO)_{12}$/*n*-hexane under N_2 followed by 1 h of treatment under vacuum (10^{-5} Torr).

[b] By impregnation of SiO_2 with a ($Rh_4(CO)_{12}$ + $4H_2N(CH_2)_3Si(OEt)_3$) reaction solution in *n*-hexane under N_2 followed by 1 h of treatment under vacuum (10^{-5} Torr).

[c] By 2 h of reaction between $Rh_4(CO)_{12}$ and 4 eq. of $HS(CH_2)_3Si(OMe)_3$ in *n*-hexane.

$[Rh(\mu\text{-}SR)_2(CO)_2]_2$ (R = Me, C_6H_5, p-FC_6H_4) in solvents reported before [33,42]. This solution spectrum is entirely compatible with the surface spectrum.

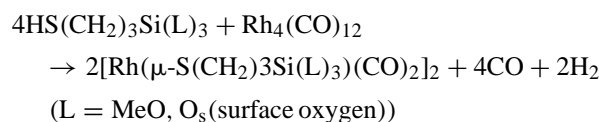The organometallic chemistry of $Rh_4(CO)_{12}$ with phosphine ligands is well documented [43,44], whereas that of $Rh_4(CO)_{12}$ with amine and thiol ligands is unavailable. Treatment of $Rh_4(CO)_{12}$ with PPh_3 under mild conditions yields $Rh_4(CO)_{11}PPh_3$, $Rh_4(CO)_{10}(PPh_3)_2$, $Rh_4(CO)_9$ $(PPh_3)_3$ and $Rh_4(CO)_8(PPh_3)_4$, in which the basic structure of the parent rhodium cluster is retained [43,44]. $Rh_4(CO)_{12}$ and 4 eq. of PPh_3 produce a mixture of $Rh_4(CO)_{10}(PPh_3)_2$ and $Rh_4(CO)_9(PPh_3)_3$ at room temperature under N_2, and $Rh_4(CO)_8(PPh_3)_4$ at 70 °C under N_2 [43]. Nevertheless, the reactivity between $Rh_4(CO)_{12}$ and supported phosphine ligands has not yet been reported. It may be expected that similar substitution reactions of $Rh_4(CO)_{12}$ with supported phosphine ligands occur, despite that the surface medium inhomogeneity causes the complicated chemistry. According to our IR observation during the reaction of $Rh_4(CO)_{12}$ with $SiO_2(PPh_2)$, the ligand substitution product appears to preserve the rhodium cluster since it shows the two bridged carbonyl bands at 1871w(br) and 1801m(br) cm^{-1}. A similar reaction result is suggested between $Rh_4(CO)_{12}$ with $SiO_2(NH_2)$ based on our IR data. We thus deduce that supported phosphine and amine do not make the Rh_4 cluster break down when coordinated to the rhodium atoms. These two supported donor ligands seem to possess comparable reactivity toward a rhodium complex, which is embodied in their reactions with $[Rh(CO)_2Cl]_2$ resulting both in a splitting of the chloride bridge [16]. However, it is difficult to determine, on steric grounds, the number of supported ligands on the surface accessible to $Rh_4(CO)_{12}$ although excess ligands are present on the surface in the present work. Based on the known reactivity between $Rh_4(CO)_{12}$ and PPh_3 in solution at room temperature under N_2, the substituted CO number is limited to less than four. It is thus

complex after grafting to SiO_2. This implies that at least two supported amine ligands are coordinated to $Rh_4(CO)_{12}$ to form a tethered rhodium cluster.

On the surface of SiO_2, our IR results clearly account for that both unsupported and supported thiol react severely with $Rh_4(CO)_{12}$ to oxidize the rhodium and disintegrate the cluster. The following reaction readily takes place at room temperature both in solution and on the surface:

$$4HS(CH_2)_3Si(L)_3 + Rh_4(CO)_{12}$$
$$\rightarrow 2[Rh(\mu\text{-}S(CH_2)3Si(L)_3)(CO)_2]_2 + 4CO + 2H_2$$
$$(L = MeO, O_s(\text{surface oxygen}))$$

3.1.2. RhCl(PPh₃)₃ and RhH(CO)(PPh₃)₃
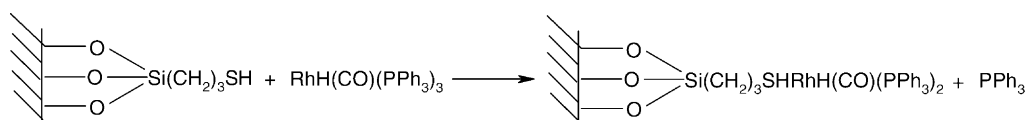
The solid state ^{31}P NMR spectra were measured before and after the reaction of $RhCl(PPh_3)_3$ with $SiO_2(NH_2)$. The spectrum of solid $RhCl(PPh_3)_3$ exhibited a set of signals at 48.7s, 32.2(sh), 29.9s, 23.9s and 21.7(sh) ppm, while the spectrum of $RhCl(PPh_3)_3/SiO_2(NH_2)$ displayed only one broad signal at 28.9 ppm. The reactivity between rhodium complexes and nitrogen donor ligands is still poorly documented and no ^{31}P NMR data of amino rhodium-phosphine complexes are available. However, the observed ^{31}P NMR signal position of supported complex significantly differs from those of solid $RhCl(PPh_3)_3$. The spectral pattern of $RhCl(PPh_3)_3/SiO_2(NH_2)$ is quite similar to that of a MCM-41(PPh_2)-tethered $RhCl(PPh_3)_3$ reported recently [45]. The main signal at 28.9 ppm is present in both spectra. As is the case with immobilization of $RhCl(PPh_3)_3$ on MCM-41(PPh_2), the spectral evolution in our case may be closely related to the coordination of a supported amine to the rhodium centre of $RhCl(PPh_3)_3$.

Therefore, the reaction between $RhCl(PPh_3)_3$ and $SiO_2(NH_2)$ is suggested to follow the same mechanism with the formation of $SiO_2(NH_2RhCl(PPh_3)_2)$ and the concomitant dissociation of a PPh_3 ligand:

assumed that the possible number of supported phosphine on $SiO_2(PPh_2)$ coordinated to $Rh_4(CO)_{12}$ should not exceed three. The fact that treatment of $Rh_4(CO)_{12}$ with 4 eq. of $H_2N(CH_2)_3Si(OEt)_3$ followed by grafting to SiO_2 leads to a surface IR spectrum similar to that obtained by reaction of $SiO_2(NH_2)$ with $Rh_4(CO)_{12}$, suggests that the possible number of supported amine ligands available to $Rh_4(CO)_{12}$ is not more than four. As the reactivity of $Rh_4(CO)_{12}$ with $H_2N(CH_2)_3Si(OEt)_3$ has not yet been elucidated, the product formed in our reaction remains unknown. The $v(CO)$ spectral difference observed between on the surface and in solution is explained by the change in the spectral symmetry of this

Likewise, similar results may be speculated without spectroscopic evidence with the formation of $SiO_2(PPh_2RhCl\text{-}(PPh_3)_2)$ and $SiO_2(SHRhCl(PPh_3)_2)$ on $SiO_2(PPh_2)$ and $SiO_2(SH)$.

The solid state ^{31}P NMR spectra were measured before and after the reaction of $RhH(CO)(PPh_3)_3$ with $SiO_2(SH)$. The spectrum of solid $RhH(CO)(PPh_3)_3$ exhibited a set of signals at 44.4m, 34.1(sh), 33.6s and 32.8(sh) ppm, while the spectrum of $RhH(CO)(PPh_3)_3/SiO_2(SH)$ presented a broad signal at 32.8s and a sharp signal at 0m ppm. The organometallic chemistry of phosphine-containing rhodium complexes with sulphur donor ligands is poorly established and there are no solid state ^{31}P NMP data available of phos-

phino rhodium thiolate complexes. However, the observed ^{31}P NMR signal positions of supported complex are significantly different from those of solid $RhH(CO)(PPh_3)_3$. This spectral evolution may be attributed to the coordination of a supported thiol to the rhodium center of $RhH(CO)(PPh_3)_3$. Refering to the case with immobilization of $Rh(PPh_3)_3Cl$ on MCM-41(PPh_2) reported recently [45], a similar ^{31}P NMR spectral evolution before and after immobilization has been explained by substitution of a PPh_3 with a supported phosphine with the formation of MCM-41($PPh_2RhCl(PPh_3)_2$). Thus, we infer without direct evidence that the reaction between $RhH(CO)(PPh_3)_3$ and $SiO_2(SH)$ would follow the same mechanism and form $SiO_2(SHRhH(CO)(PPh_3)_2)$ with the concomitant dissociation of a PPh_3:

and only 1.0% of which was hydrogenated to cyclohexane. In the second cycle, it was noticed that the turnover for cyclohexene converted went up to 1550 (mol/mol Rh). This turnover remained almost unchanged in the third cycle. The brown color of the catalyst remained unchanged during the three cycles. 1.67% of Rh was retained on the support according to the results of elemental analysis (Table 3) and the liquid phase color was light brown after the first cycle. The rhodium content of the catalyst almost no longer declined and the liquid phase was colorless from the second cycle. This indicates that only a weak leaching of the rhodium from the support occurs referring to the initial rhodium loading (1.89%) during reaction over $Rh_4(CO)_{12}/SiO_2$ (NH_2).

Similar results may be speculated without spectroscopic evidence with the formation of $SiO_2(PPh_2RhH(CO)(PPh_3)_2)$ and $SiO_2(NH_2RhH(CO)(PPh_3)_2)$ on $SiO_2(PPh_2)$ and $SiO_2(NH_2)$.

3.2. Catalytic cyclohexene hydroformylation with tethered rhodium complexes and effects of supported donor ligands

All the unsupported and supported rhodium complexes studied were tested in cyclohexene hydroformylation. The blank test showed no catalytic activities in the autoclave. All the catalysts displayed selectivities greater than 94% to cyclohexane carboxaldehyde with formation of no alcohols under operating reaction conditions.

Table 2 presents the catalytic results at the end of 20 h reaction over the $Rh_4(CO)_{12}$-derived catalysts. When $Rh_4(CO)_{12}/SiO_2(NH_2)$ was tested under catalytic conditions, a turnover of 950 (mol/mol Rh) for cyclohexene converted was obtained in the first reaction cycle, 99.0% of which was hydroformylated to cyclohexane carboxaldehyde

By contrast, $Rh_4(CO)_{12}/SiO_2(PPh_2)$ only led to a turnover of 585 (mol/mol Rh) for cyclohexene hydroformylation in the first reaction cycle. After the first cycle, the solid sample color turned light yellow and the liquid phase color became brown. The light yellow solid sample contained only 0.09% Rh referring to the initial rhodium loading (1.92%). This shows that a heavy rhodium leaching takes place from the support during reaction over $Rh_4(CO)_{12}/SiO_2(PPh_2)$. However, $Rh_4(CO)_{12}/SiO_2(SH)$ presented neither catalytic activities nor rhodium leaching.

Fig. 1 shows the variation of turnovers of cyclohexane carboxaldehyde formed on these $Rh_4(CO)_{12}$-derived catalysts with reaction time. The homogeneous $Rh_4(CO)_{12}$ system was the most active in the first 9 h, after which it became inactive since its turnover stopped increasing. At the end of reaction, the liquid phase was noted to become colorless with the concomitant formation of black precipitate, which was indicative of the metallic aggregation of $Rh_4(CO)_{12}$ under pressurized CO + H_2. The

Table 2
Catalytic properties of $Rh_4(CO)_{12}$-derived catalysts[a] in cyclohexene hydroformylation[b]

Complex	Cyclohexene conversion (%)	Turnover[c] (mol/mol Rh)	Product distribution (mol%)	
			Cyclohexane	Cyclohexane carboxaldehyde
$Rh_4(CO)_{12}$[d]	86.5	1743	0	100
$Rh_4(CO)_{12}/SiO_2(NH_2)$				
1st cycle	44.1	950	1.0	99.0
2nd cycle	63.6	1550	0.6	99.4
3rd cycle	63.1	1547	0.6	99.4
$Rh_4(CO)_{12}/SiO_2(PPh_2)$	27.6	585	0.8	99.2
$Rh_4(CO)_{12}/SiO_2(SH)$	0	–	–	–

[a] 0.30 g of tethered complex sample with nearly 2.0% Rh loading.

[b] *Reaction conditions*: 12 ml of cyclohexene, 28 bar, 100 °C, H_2/CO = 1, 20 h per cycle.

[c] For conversion of cyclohexene.

[d] 0.011 g.

Table 3
Color and rhodium content changes of tethered rhodium complex samples before and after cyclohexene hydroformylation

Tethered complex	Before reaction		After reaction	
	Color	Rh (%)	Color	Rh (%)
$Rh_4(CO)_{12}/SiO_2(NH_2)$				
1st cycle	Brown	1.89	Brown	1.67
2nd cycle	Brown	1.67	Brown	1.66
3rd cycle	Brown	1.66	Brown	1.66
$Rh_4(CO)_{12}/SiO_2(PPh_2)$	Deep brown	1.92	Light yellow	0.09
$Rh_4(CO)_{12}/SiO_2(SH)$	Yellow		Yellow	1.94
$RhCl(PPh_3)_3/SiO_2(NH_2)$				
1st cycle	Deep brown	1.87	Deep brown	1.70
2nd cycle	Deep brown	1.70	Deep brown	1.70
3rd cycle	Deep brown	1.70	Deep brown	1.70
4th cycle	Deep brown	1.70	Deep brown	1.70
$RhCl(PPh_3)_3/SiO_2(PPh_2)$	Deep brown	1.90	Brown	1.12
$RhCl(PPh_3)_3/SiO_2(SH)$				
1st cycle	Deep brown	1.90	Deep brown	1.66
2nd cycle	Deep brown	1.66	Deep brown	1.66
3rd cycle	Deep brown	1.66	Deep brown	1.66
4th cycle	Deep brown	1.66	Deep brown	1.66
$RhH(CO)(PPh_3)_3/SiO_2(NH_2)$	Green	1.75	Brown	0.85
$RhH(CO)(PPh_3)_3/SiO_2(PPh_2)$	Green	1.75	Light yellow	0.12
$RhH(CO)(PPh_3)_3/SiO_2(SH)$				
1st cycle	Green	1.73	Green	1.65
2nd cycle	Green	1.65	Green	1.65
3rd cycle	Green	1.65	Green	1.65

turnovers over the tethered catalysts increased continuously throughout 20 h of reaction. From the second reaction cycle, the turnovers over $Rh_4(CO)_{12}/SiO_2(NH_2)$ increased linearly with reaction time after 5 h. This implies that the $Rh_4(CO)_{12}/SiO_2(NH_2)$-derived catalyst can maintain its activity stable in an extended hydroformylation.

From the above catalytic results based on $Rh_4(CO)_{12}$ as a catalyst precursor, it is demonstrated that the $SiO_2(NH_2)$-tethered catalyst is not only highly active but quite stable for recycling, that the $SiO_2(SH)$-tethered catalyst is inactive though very stable, and that the $SiO_2(PPh_2)$-tethered catalyst has heavy rhodium leaching. The $Rh_4(CO)_{12}/SiO_2(NH_2)$-derived catalyst displays a potential of high activity in a prolonged reaction, although it is less active than the $Rh_4(CO)_{12}$-derived homogeneous catalyst in a 20 h reaction. The $Rh_4(CO)_{12}$-derived
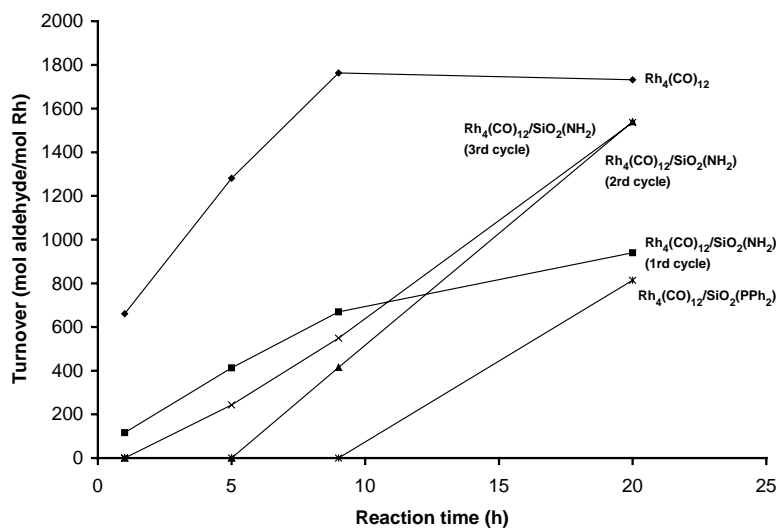

Fig. 1. Turnovers of cyclohexane carboxaldehyde formed as a function of reaction time over $Rh_4(CO)_{12}$-derived catalysts.

Table 4
Catalytic properties of RhCl(PPh₃)₃-derived catalysts[a] in cyclohexene hydroformylation[b]

Complex	Cyclohexene conversion (%)	Turnover (mol/mol Rh)[c]	Selectivity (mol%)	
			Cyclohexane	Cyclohexane carboxaldehyde
RhCl(PPh₃)₃[d]	89.4	1915	0.8	99.2
RhCl(PPh₃)₃/SiO₂(NH₂)				
1st cycle	80.6	1754	2.3	97.7
2nd cycle	70.3	1683	0.7	99.3
3rd cycle	87.2	2088	0.6	99.4
4th cycle	87.9	2104	0.6	99.4
RhCl(PPh₃)₃/SiO₂(PPh₂)	30.3	649	0.5	99.5
RhCl(PPh₃)₃/SiO₂(SH)				
1st cycle	2.3	49	6.0	94.0
2nd cycle	0	–	–	–
3rd cycle	17.5	429	1.2	98.2
4th cycle	18.3	449	1.2	98.2

[a] 0.30 g of catalyst precursor with nearly 2.0% Rh loading.
[b] *Reaction conditions*: 12 ml of cyclohexene, $H_2/CO = 1$, 28 bar, 100 °C, 20 h per cycle.
[c] For conversion of cyclohexene.
[d] 0.051 g.

homogeneous catalyst deactivates after 9 h of reaction, due to the metallic rhodium agglomeration under pressurized CO + H₂. The SiO₂(NH₂)-tethered catalyst is much more resistant to rhodium leaching than the SiO₂(PPh₂)-tethered catalyst.

Table 4 presents the catalytic results at the end of 20 h reaction over the RhCl(PPh₃)₃-derived catalysts. RhCl(PPh₃)₃/SiO₂(NH₂) resulted in the highest turnover for conversion of cyclohexene among three tethered catalyst systems. Its turnover was noticed to increase after the second reaction cycle and attained to 2088 (mol/mol Rh) in the third reaction cycle, which surpassed that of the homogeneous catalyst derived from RhCl(PPh₃)₃. The deep brown color of the catalyst remained unchanged during the four cycles. 1.70% of Rh was retained on the support and

the liquid phase color was light brown after the first cycle. The rhodium content of the catalyst no longer diminished and the liquid phase was colorless from the second cycle. This demonstrates that only a week leaching of the rhodium from the support occurs relative to the initial rhodium loading (1.87%) during a longer reaction. By contrast, RhCl(PPh₃)₃/SiO₂(SH) and RhCl(PPh₃)₃/SiO₂(PPh₂) led to rather low turnovers for conversion of cyclohexene. The former showed better resistance to rhodium leaching like RhCl(PPh₃)₃/SiO₂(NH₂). The detected rhodium content on the catalyst was 1.66% after the first cycle referring to the initial rhodium loading (1.90%) and no longer declined from the second cycle. The latter exhibited enormous rhodium leaching during the first cycle, although this system was catalytically more active than the RhCl(PPh₃)₃/SiO₂(SH)
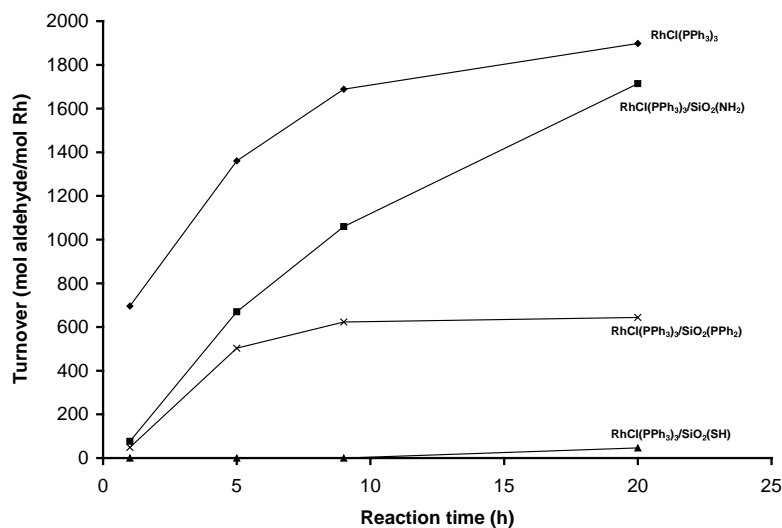

Fig. 2. Turnovers of cyclohexane carboxaldehyde formed as a function of reaction time over RhCl(PPh₃)₃-derived catalysts.

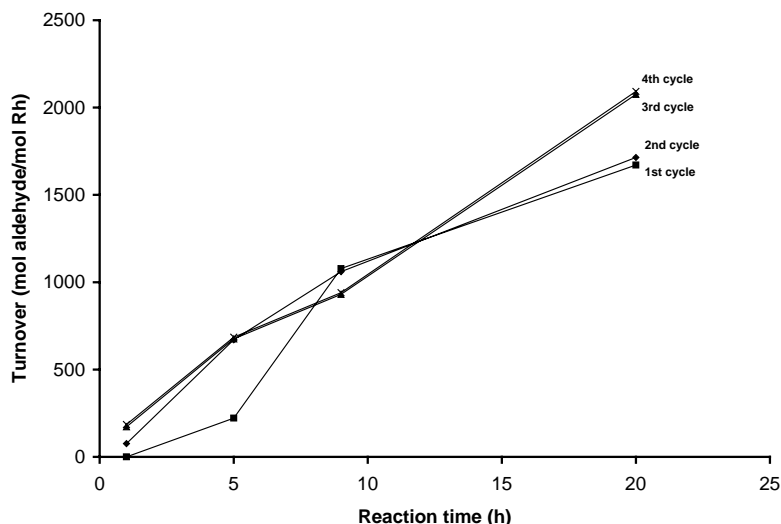Fig. 3. Turnovers of cyclohexane carboxaldehyde formed as a function of reaction time over a $RhCl(PPh_3)_3/SiO_2(NH_2)$-derived catalyst.

system. Only 1.12% of Rh remained on the support after the first cycle, starting from a 1.90% rhodium loading.

Figs. 2 and 3 show the variation of turnovers of cyclohexane carboxaldehyde formed on the three tethered catalyst systems with reaction time. All the catalyst systems maintained hydroformylation activity throughout 20 h reaction as their turnovers of aldehyde formed increased continuously with reaction time. Although the homogeneous $RhCl(PPh_3)_3$ system was most active within the first 17 h, its activity decreased progressively with reaction time. The $RhCl(PPh_3)_3/SiO_2(NH_2)$ system apparently tended to enhance its activity, having undergone the first two reaction cycles. In the third and fourth cycles, its turnover of aldehyde formed might be considered to increase almost linearly with reaction time and finally exceeded that of the homogeneous system (Fig. 3). This signifies that The $RhCl(PPh_3)_3/SiO_2(NH_2)$-derived catalyst can maintain its activity unchanged in a prolonged hydroformylation, prevailing over the homogeneous catalyst.

Table 5 presents the catalytic results at the end of 20 h reaction over the $RhH(CO)(PPh_3)_3$-derived catalysts. $RhH(CO)(PPh_3)_3/SiO_2(SH)$ resulted in continuously increased turnover for conversion of cyclohexene during three reaction cycles running. From the second cycle, it was noted that the activity of $RhH(CO)(PPh_3)_3/SiO_2(SH)$-derived catalyst was higher than that of the homogeneous catalyst derived from $RhH(CO)(PPh_3)_3$. In the third cycle, the turnover attained to 2400 (mol cyclohexene/mol Rh). The green color of the catalyst remained unchanged during the three cycles. 1.65% of Rh was retained on the support and the liquid phase color was light green after the first cycle. The rhodium content of the catalyst no longer declined and the liquid phase was colorless from the second cycle. This demonstrates that only a weak leaching of the rhodium from the support occurs relative to the initial rhodium loading (1.73%) under catalytic conditions. Comparatively, a considerable rhodium leaching was found from $RhH(CO)(PPh_3)_3/SiO_2(NH_2)$ during the first cycle, although it gave rise to a satisfactory

Table 5
Catalytic properties of $RhH(CO)(PPh_3)_3$-derived catalysts[a] in cyclohexene hydroformylation[b]

Complex	Cyclohexene converison (%)	Turnover[c] (mol/mol Rh)	Production distribution (mol%)	
			Cyclohexane	Cyclohexane carboxaldehyde
$RhH(CO)(PPh_3)_3$[d]	44.2	1632	0.5	99.5
$RhH(CO)(PPh_3)_3/SiO_2(NH_2)$	68.4	1590	2.1	97.9
$RhH(CO)(PPh_3)_3/SiO_2(PPh_2)$	13.6	316	0.7	99.3
$RhH(CO)(PPh_3)_3/SiO_2(SH)$				
1st cycle	56.6	1332	0.7	99.3
2nd cycle	81.9	2020	0.4	99.6
3rd cycle	97.3	2400	0.7	99.3

[a] 0.30 g of catalyst precursor with nearly 2.0% Rh loading.

[b] *Reaction conditions*: 12 ml of cyclohexene, $H_2/CO = 1$, 28 bar, 100 °C, 20 h per cycle.

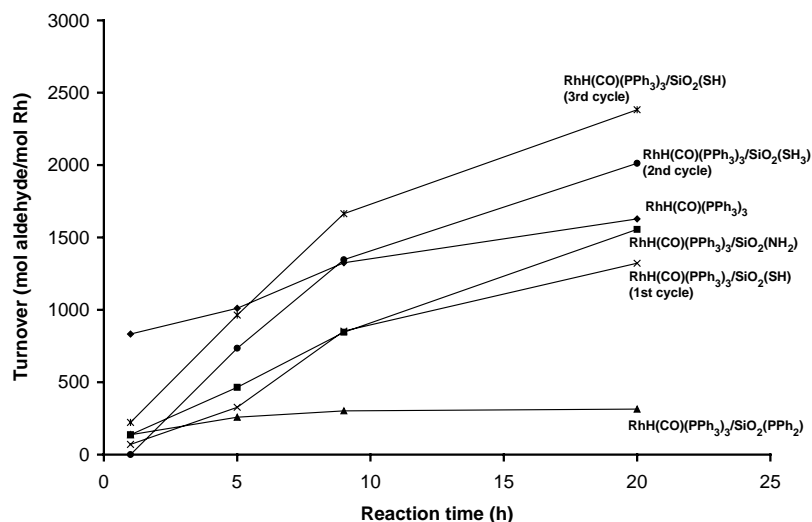[c] For conversion of cyclohexene.

[d] 0.030 g.

Fig. 4. Turnovers of cyclohexane carboxaldehyde formed as a function of reaction time over $RhH(CO)(PPh_3)_3$-derived catalysts.

turnover for conversion of cyclohexene at 1590 (mol cyclohexene/mol Rh). The liquid phase color became green and the detected rhodium content on the catalyst was 0.85% after the first cycle, referring to the initial rhodium loading (1.75%). An even heavier rhodium leaching was observed with $RhH(CO)(PPh_3)_3/SiO_2(PPh_2)$. The solid phase became nearly colorless and the remaining rhodium content on the catalyst was as low as 0.12% after the first cycle, starting from 1.75% of rhodium loading. Moreover, this catalyst system led to a worse turnover for conversion of cyclohexene at 316 (mol cyclohexene/mol Rh).

From the variation of turnovers of cyclohexane carboxaldehyde formed on these catalyst systems with reaction time shown in Fig. 4, it is seen that all the catalyst systems maintained hydroformylation activity throughout 20 h reaction since their turnovers of aldehyde formed increased continuously with reaction time. In the first hour, the homogeneous $RhH(CO)(PPh_3)_3$ system was the most active and all the supported catalyst systems were little active. Then the activity of the former greatly decreased so that the turnover of aldehyde on it became inferior to those on $RhH(CO)(PPh_3)_3/SiO_2(SH)$ (second and third cycles). Thus, the $SiO_2(SH)$-tethered catalyst is regarded as being stable for recycling and more active after undergoing a reaction period.

From the above catalytic results based on $RhCl(PPh_3)_3$ and $RhH(CO)(PPh_3)_3$ as catalyst precursors, we remark that the effects of supported donor ligands on the catalytic activity and stability are dependent on the complex used. In the case of $RhCl(PPh_3)_3$, the $SiO_2(NH_2)$-tethered catalyst is not only highly active but quite stable for recycling, and the $SiO_2(SH)$-tethered catalyst is much less active than the former though fairly stable against rhodium leaching. In the case of $RhH(CO)(PPh_3)_3$, however, the $SiO_2(SH)$-tethered catalyst is highly active as well as quite stable for recycling, and the $SiO_2(NH_2)$-tethered catalyst has high rhodium leaching although it is highly active in the first cycle. In both cases, the $SiO_2(PPh_2)$-tethered catalysts are insignificant in heterogeneous catalysis because of high rhodium leaching. The $RhCl(PPh_3)_3/SiO_2(NH_2)$- and $RhH(CO)(PPh_3)_3/SiO_2(SH)$-derived catalysts present higher activities than those of the corresponding homogeneous catalysts. Above all, the $RhH(CO)(PPh_3)_3/SiO_2(SH)$-derived catalyst shows the highest activity among all the tethered catalysts studied in this work. It is believed that so good performances of these two catalysts are ascribed to the promotion and stabilization of supported ligands on the catalysis of phosphine-containing rhodium complexes, because a $SiO_2(NH_2)$-tethered phosphine-free rhodium complex catalyst is less active than a $RhCl(PPh_3)_3/SiO_2(NH_2)$-derived catalyst and a $SiO_2(SH)$-tethered phosphine-free rhodium complex catalyst is inactive as shown in Tables 2 and 4.

Virtually, the catalytic properties and the immobility of a tethered metal complex are dependent on the nature of complexation of a supported donor ligand with the metal centre. Phosphine, amine and thiol ligands are all σ-electron donors. Meanwhile $(O_s)_3Si(CH_2)_3PPh_2$ and $(O_s)_3Si(CH_2)_3SH$ are poor and strong π-electron acceptors, respectively. In the case of $Rh_4(CO)_{12}$, CO ligands are bonded more strongly to the rhodium centre in a $(O_s)_3Si(CH_2)_3PPh_2$-containing rhodium complex since the rhodium tends to transfer the increased negative charge from the phosphorus to CO by π-back donation. This leads to increased stability of CO–Rh bond and thus decreased catalytic activity for hydroformylation compared to the phosphine-free rhodium complex. At the same time, the weaker $d\pi$–$p\pi$ bonding between the rhodium centre and the phosphorus results in decreased strength of P–Rh bond. In a $(O_s)_3Si(CH_2)_3SH$-containing rhodium complex, contrarily, coordination of thiol to the rhodium centre weakens the CO–Rh bond and in some cases causes the oxidation of rhodium centre, in favour of the enhancement of S–Rh bond strength because of the stronger $d\pi$–$p\pi$ bonding between the rhodium centre and the sulphur. The stronger S–Rh bond and the formation of

Rh^+ centre in $[Rh(\mu-S(CH_2)_3Si(O_s)_3)(CO)_2]_2/SiO_2$ without strong electron-donating ligands like phosphines lead to no catalytic activity for hydroformylation. As for an amine-coordinated rhodium complex, $(O_s)_3Si(CH_2)_3NH_2$ is only a strong σ-electron donor without dπ obitals. However, the nitrogen is one of the most electronegative elements. In the presence of coordinated amine, the rhodium centre may transfer only a part of the increased negative charge from the nitrogen to CO by π-back donation. This appropriate coordination of amine may not only produce a suitable strength of CO–Rh bond for hydroformylation but ensure the stability of N–Rh bond.

In the cases of $RhCl(PPh_3)_3$ and $RhH(CO)(PPh_3)_3$, the concerted action between a supported ligand and complex ligands on the activity and immobility of a tethered catalyst should be taken into consideration. Generally, the presence of phosphine in a complex results in the decreased negative charge transfer from a supported ligand to the complex and hence weakens the L–Rh bond strength (L = P, N, S), as compared with the case of a phosphine-free complex. But relatively, the weak P–Rh bond leads to the heavy rhodium leaching of the $SiO_2(PPh_2)$-tethered complexes, and the strong S–Rh bond largely suppresses the rhodium leaching of the $SiO_2(SH)$-tethered complexes under hydroformylation conditions. However, why the $SiO_2(PPh_2)$-tethered catalyst systems give the catalytic activities greatly lower than those of the corresponding homogeneous catalyst systems is not understood. Between $SiO_2(SHRhCl(PPh_3)_2)$ and $SiO_2(SHRhH(CO)(PPh_3)_2)$, a contrast in catalytic activity is observed when both are tested in cyclohexene hydroformylation. In $SiO_2(SHRhCl(PPh_3)_2)$, the strong dπ–pπ bonding leads to the transfer of the negative charge from the rhodium centre to the sulphur, which probably impedes the formation of a hydridic complex necessary for hydroformylation by hydrogenation of the Rh–Cl bond under hydroformylation conditions. Thus, a very low catalytic activity is produced. Since $SiO_2(SHRhH(CO)(PPh_3)_2)$ itself contains a rhodium hydridic complex $RhH(CO)(PPh_3)_2$ which is known to be an active species for hydroformylation [46], a high catalytic activity is easily achieved. As for the $SiO_2(NH_2)$-tethered complexes, the distinct results of rhodium leaching suggest that a stronger N–Rh bond is formed in $SiO_2(NH_2RhCl(PPh_3)_2)$ than in $SiO_2(NH_2RhH(CO)(PPh_3)_2)$. Meanwhile, the complexation of a supported amine may ensure that the rhodium centre gains the sufficient negative charge in $SiO_2(NH_2RhCl(PPh_3)_2)$ and thus may make the transformation of the Rh–Cl bond into the Rh–H bond proceed to some extent under hydroformylation conditions. The tethered rhodium hydridic complex so formed which is more stable may be $SiO_2(NH_2RhH(PPh_3)_2)$. It therefore gives rise to a high catalytic activity and a good immobility. Despite that $SiO_2(NH_2RhH(CO)(PPh_3)_2)$ also leads to a fairly high catalytic activity, the rhodium hydridic complex is readily leached into the liquid phase.

Interestingly, the influences of a supported ligand on the activity and immobility of a tethered complex catalyst vary with the catalyst precursor used. With a given SiO_2-supported ligand, different rhodium complexes give rise to different changes in catalytic activity with respect to homogeneous catalysts and different resistance to rhodium leaching, as shown in Tables 2–5. The representative complex dependences of activity and immobility are observed over the $SiO_2(SH)$-tethered catalysts. The understanding of promotion and immobilization of a supported ligand on a tethered complex catalyst essentially may involve the synergistic electronic effect of supported ligands and complex ligands on the metal centre. High activity and good immobility of a tethered complex catalyst can be obtained only when both the L–M bond strength and the transfer between the metal centre and ligands are appropriately adjusted.

4. Conclusions

Rhodium complexes derived from $Rh_4(CO)_{12}$, $RhCl(PPh_3)_3$ and $RhH(CO)(PPh_3)_3$ have been tethered to $SiO_2(PPh_2)$, $SiO_2(NH_2)$ and $SiO_2(SH)$. On $SiO_2(PPh_2)$ and $SiO_2(NH_2)$, $Rh_4(CO)_{12}$ reacts with supported donor ligands to give presumably $SiO_2(L_xRh_{12}(CO)_{12-x})$ (L = PPh_2, NH_2; $x = 2$ or 3) by ligand substitution, while on $SiO_2(SH)$, $Rh_4(CO)_{12}$ is dramatically attacked by thiol ligands to form $SiO_2([Rh(\mu-S)(CO)_2]_2)$. The same chemistry occurs between $Rh_4(CO)_{12}$ and 4 eq. of $HS(CH_2)_3Si(OMe)_3$ in solution, producing $[Rh(\mu-S(CH_2)_3Si(OMe)_3)(CO)_2]_2$. The reactions of $RhCl(PPh_3)_3$ or $RhH(CO)(PPh_3)_3$ with the three functionalized supports are presumed to yield $SiO_2(LRhCl(PPh_3)_2)$ or $SiO_2(LRhH(CO)(PPh_3)_2)$ (L = PPh_2, NH_2, SH).

These functionalized SiO_2-tethered rhodium complexes result in different catalytic behaviours and different catalyst immobility in cyclohexene hydroformylation at 28 bar of equimolar CO and H_2 and at 100 °C. Using $Rh_4(CO)_{12}$ as a catalyst precursor, the $SiO_2(NH_2)$-tethered catalyst exhibits potentially higher activity than that of the $Rh_4(CO)_{12}$-derived homogeneous catalyst and good stability for recycling; the $SiO_2(SH)$-tethered catalyst shows neither activity nor rhodium leaching; and the $SiO_2(PPh_2)$-tethered catalyst presents low activity as well as serious rhodium leaching. Using $RhCl(PPh_3)_3$ as a catalyst precursor, the $SiO_2(NH_2)$-tethered catalyst displays higher activity than that of the $RhCl(PPh_3)_3$-derived homogeneous catalyst and good stability for recycling; the $SiO_2(SH)$-tethered catalyst shows much lower activity than that of the former as well as low rhodium leaching; and the $SiO_2(PPh_2)$-tethered catalyst gives low activity as well as high rhodium leaching. Using $RhH(CO)(PPh_3)_3$ as a catalyst precursor, the $SiO_2(NH_2)$-tethered catalyst has high rhodium leaching although it exhibits high activity in the first reaction cycle; the $SiO_2(SH)$-tethered catalyst presents not only the highest activity among all the tethered catalysts studied, which greatly exceeds that of the $RhH(CO)(PPh_3)_3$-derived homogeneous catalyst, but very low rhodium leaching; and

the $SiO_2(PPh_2)$-tethered catalyst gives low activity as well as serious rhodium leaching.

Accordingly, the supported donor ligands do have notable effects on the activity and immobility of a SiO_2-tethered complex catalyst. Such effects actually consist in the synergistic electronic action of supported ligands and complex ligands on the rhodium centre. Since the nature of complexation of a supported ligand with the metal centre varies with the properties of complex ligands, the activity and immobility of a SiO_2-tethered complex catalyst closely relate to both the supported ligand and the catalyst precursor. A $SiO_2(NH_2)$-tethered catalyst is more active and immobile than a $SiO_2(PPh_2)$-tethered catalyst. A $SiO_2(SH)$-tethered catalyst derived from a rhodium carbonyl complex is inactive though most resistant to rhodium leaching. A $SiO_2(SH)$-tethered catalyst derived from a phosphine-containing rhodium complex possesses significant activity and certain rhodium leaching.

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