An active and stable Wilkinson's complex-derived SiO_2-tethered catalyst via an amine ligand for cyclohexene hydroformylation

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A Wilkinson's complex-derived SiO_2-tethered catalyst via an amine ligand is not only fairly effective and stable for cyclohexene hydroformylation under the milder conditions of 100 °C and 28 bar of equimolar CO and H_2 but also prevailing over the corresponding homogeneous catalyst. This catalyst has the advantage of resistance to rhodium leaching or/and high activity over homologous tethered catalysts via phosphine and thiol ligands.

KEY WORDS: Wilkinson's complex; SiO_2-tethered catalyst; amine ligand; cyclohexene hydroformylation.

1. Introduction

Although Wilkinson's complex, $RhCl(PPh_3)_3$ is famous for hydrogenation, its and its analogues' studies as catalyst precursors for hydroformylation have seldom been reported [1,2], unlike those of other phosphine-containing rhodium complexes such as $RhH(CO)(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$ and their analogues [1–24]. Only one paper reported on hydroformylation of pentene-1 with Wilkinson's complex in homogeneous catalysis [1]. Only one report has described hydroformylation of hexene-1 carried out with a SiO_2-supported analogue of Wilkinson's complex, $RhCl(Ph_2P(CH_2)_2Si(O_s)_3)_3$ (O_s: surface oxygen) under 43 atm of equimolar CO and H_2 at 140 °C in heterogeneous catalysis [2]. The interests in choosing Wilkinson's complex as a hydroformylation catalyst precursor lie in its lower cost than conventionally used hydroformylation rhodium catalyst precursors such as $RhH(CO)(PPh_3)_3$, $RhCl(CO)(PPh_3)_3$ and $Rh_4(CO)_{12}$ on the one hand, and its much less air sensitivity for experimental handling on the other hand.

$RhCl(PPh_3)_3$ was earlier tethered to the surface of SiO_2 via $HS(CH_2)_3Si(OMe)_3$ [25]. The tethered complex was used as a catalyst precursor for hydrogenations of hexene-1 and cyclohexene [25]. Recently, $RhCl(PPh_3)_3$ was tethered to the surface of silicate MCM-41 via $(OEt)_3Si(CH_2)_3PPh_2$ [26] using the same preparative method [25]. The resulting immobilized catalyst was studied for cyclohexene hydrogenation [26]. Here, we communicate the preparation of $RhCl(PPh_3)_3$ tethered to the SiO_2 surface via phosphine, amine and thiol ligands and the catalytic application of the tethered complexes in cyclohexene hydroformylation. For the first time, an immobilized $RhCl(PPh_3)_3$ is reported, which has effectiveness and stability for hydroformylation under milder conditions.

2. Experimental

SiO_2, which 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. $RhCl(PPh_3)_3$ (99%) was 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. Tethered Wilkinson's complex was prepared following the approach described in [25]. SiO_2 was first functionalized 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. The resulting phosphinated SiO_2 was filtered off, washed with methanol (100 mL) and dried in vacuum. Phosphinated, aminated and thiolated SiO_2 samples are denoted as $SiO_2(PPh_2)$, $SiO_2(NH_2)$ and $SiO_2(SH)$ respectively. Then, functionalized SiO_2 (1.0 g) was refluxed

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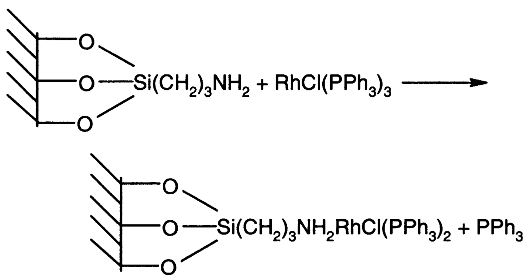
with a toluene (50 mL) solution of $RhCl(PPh_3)_3$ (0.183 g) under N_2 for 16 h. In all the cases, the solid color turned deep brown, and the red solution became colorless at the end of the reaction, indicative of the linkage of $RhCl(PPh_3)_3$ to the support via complexation of supported amine. Afterward, 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. The rhodium contents of $SiO_2(PPh_2)$-, $SiO_2(NH_2)$- and $SiO_2(SH)$-tethered catalyst precursors were 1.90, 1.87 and 1.90% respectively.

Hydroformylation of cyclohexene was conducted under 28 bar of an equimolar CO and H_2 mixture at 100 °C in an autoclave. 300 mg of catalyst precursor, 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. Sampling of the reaction mixture was done during the course of reaction. The samples were analyzed by gas chromatography.

^{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

Figure 1 shows the solid-state ^{31}P NMR spectra 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 δ 48.7, 32.2, 29.9, 23.9 and 21.7, while the spectrum of $RhCl(PPh_3)_3/SiO_2(NH_2)$ displayed only one broad signal at δ 28.9. 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 in figure 1(b) is quite similar to that of the MCM-41(PPh_2)-tethered $RhCl(PPh_3)_3$ reported recently [26]. The main signal at δ 28.9 is present in both spectra. It is generally admitted that the reaction of a complex on the surface is favored with only one supported ligand to form a simple product [27]. As is the case with immobilization of $RhCl(PPh_3)_3$ on MCM-41(PPh_2), the spectral evolution in figure 1 may be closely related to the coordination of a supported amine to the rhodium center of $RhCl(PPh_3)_3$. 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.



Likewise, similar results may be speculated without spectroscopic evidence with the formation of

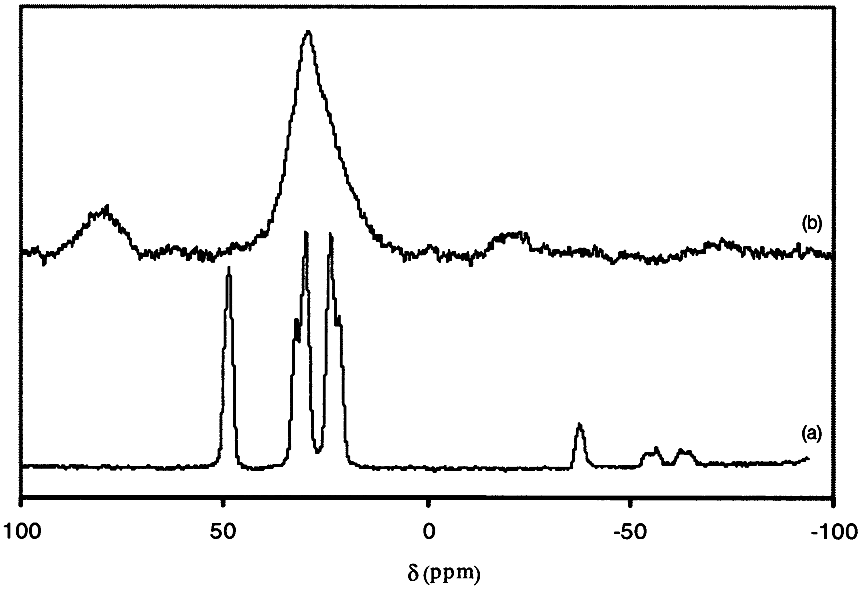


Figure 1. Solid-state ^{31}P NMR spectra of (a) $RhCl(PPh_3)_3$ and (b) $RhCl(PPh_3)_3/SiO_2(NH_2)$.

Table 1
Catalytic properties of $RhCl(PPh_3)_3$-derived catalysts[a] in cyclohexene hydroformylation[b]

Catalyst precursor	Cyclohexene conversion (%)	Turnover[c] (mol/mol Rh)	Selectivity (mol%)	
			Cyclohexane	Cyclohexane carboxaldehyde
$RhCl(PPh_3)_3$[d]	89.4	1915	0.8	99.2
$RhCl(PPh_3)_3/SiO_2(NH_2)$				
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
$RhCl(PPh_3)_3/SiO_2(SH)$				
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
$RhCl(PPh_3)_3/SiO_2(PPh_2)$	30.3	649	0.5	99.5

[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/cycle.
[c] For conversion of cyclohexene.
[d] 0.051 g.

$SiO_2(PPh_2RhCl(PPh_3)_2)$ and $SiO_2(SHRhCl(PPh_3)_2)$ on $SiO_2(PPh_2)$ and $SiO_2(SH)$.

Table 1 presents the comparative catalytic results after 20 h of cyclohexene hydroformylation over the catalyst systems studied. All the catalyst systems displayed selectivity as high as above 94% to cyclohexane carboxaldehyde without activity to alcohols. $RhCl(PPh_3)_3/SiO_2(NH_2)$ 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 2088 (mol/mol Rh) in the third reaction cycle, which surpassed that of a homogeneous catalyst derived from $RhCl(PPh_3)_3$. When the 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. 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 weak leaching of the rhodium from the support occurs relative to the initial rhodium loading (1.87%) during a longer reaction. By contrast, $RhCl(PPh_3)_3/SiO_2(SH)$ and $RhCl(PPh_3)_3/SiO_2(PPh_2)$ led to rather low turnovers for conversion of cyclohexene. The former showed better resistance to rhodium leaching like $RhCl(PPh_3)_3/SiO_2(NH_2)$. 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 $RhCl(PPh_3)_3/SiO_2(SH)$ system. Only 1.12% of Rh remained on the support after the first cycle, starting from a 1.90% rhodium loading.

In the cases of both $RhCl(PPh_3)_3/SiO_2(NH_2)$ and $RhCl(PPh_3)_3/SiO_2(SH)$, the catalysts displayed a fluctuating catalytic behavior on reuse, namely, the second cycle was worse than the first cycle and the following cycles were better than the first cycle as seen in table 1. The data are significant according to our experimental accuracy. This phenomenon remains unclear and needs to be understood with further investigations. Two factors can be considered. One is that the catalysts are somewhat oxidized when exposed to air from cycle to cycle, as demonstrated by an earlier study [10]. This causes a slight decrease in the total catalytic activity in the second cycle. The other is that Wilkinson's complex must undergo an induction period prior to becoming an active species under catalytic conditions. It can be seen from figure 2 that a longer induction time is required for a tethered catalyst precursor than for the homogeneous catalyst precursor. This leads us to assume that the amount of active species derived from a tethered catalyst precursor increases more slowly with reaction time. Hence, the catalytic activity increases significantly in the third and fourth cycles. The increased catalytic activity does not seem to arise from leaching of the active species from the surface based on the rhodium contents of the solid catalysts after use, on the one hand. On the other hand, the maximum activity that the tethered catalysts are able to attain on steady state after the second cycle is comparable to that of the $RhCl(PPh_3)_3$-derived homogeneous catalyst. A portion of the active species leached from the surface is unlikely to result in a considerable catalytic turnover in every cycle. The observed close catalytic turnovers in the third and fourth cycles can reasonably account for a good stability of each tethered catalyst.

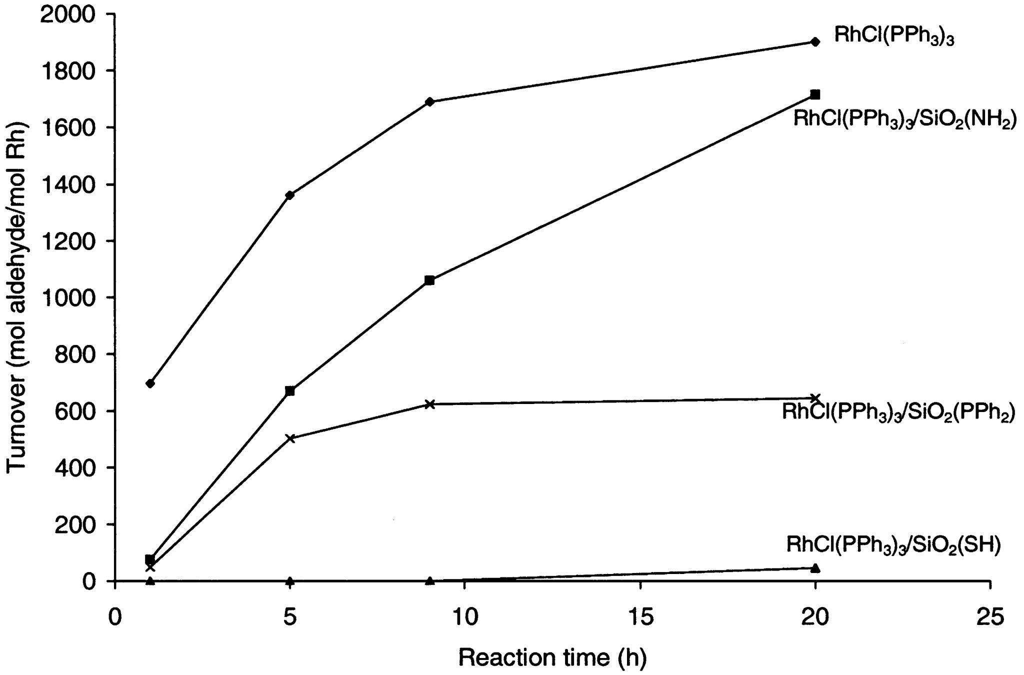


Figure 2. Turnovers of cyclohexane carboxaldehyde formed as a function of reaction time over $RhCl(PPh_3)_3$-derived catalysts.

Figures 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 the 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 exceed that of the homogeneous system (figure 3). This signifies that the $RhCl(PPh_3)_3/SiO_2(NH_2)$-derived catalyst can

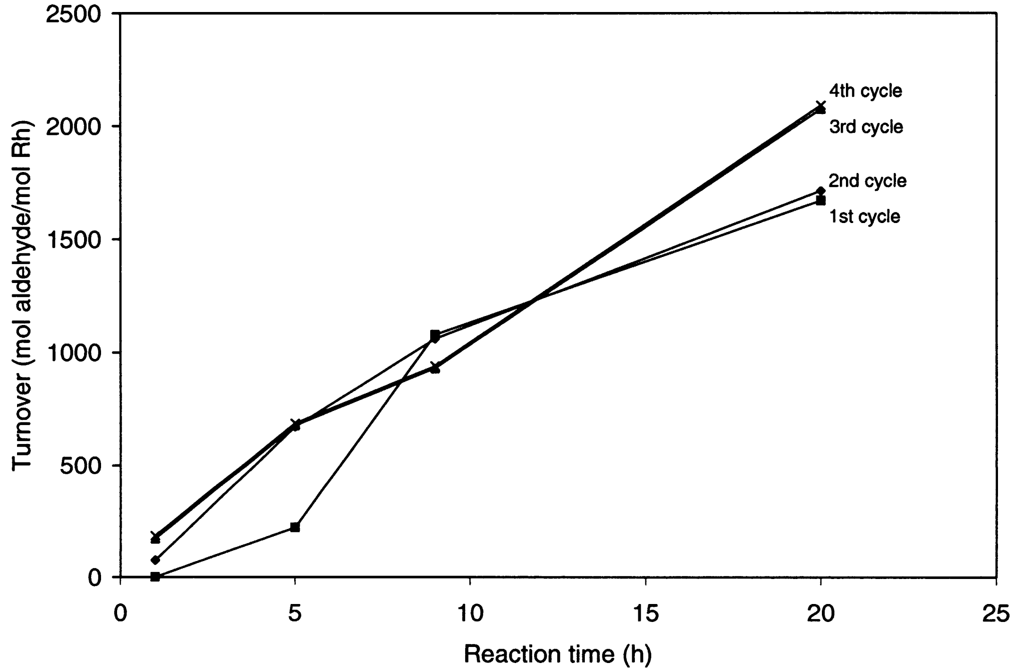


Figure 3. Turnovers of cyclohexane carboxaldehyde formed as a function of reaction time over a $RhCl(PPh_3)_3/SiO_2(NH_2)$-derived catalyst.

maintain its activity unchanged in a prolonged hydroformylation, prevailing over the homogeneous catalyst.

The results reveal that the $SiO_2(NH_2)$-tethered catalyst is not only potentially highly active but also quite stable for recycling, that the $SiO_2(SH)$-tethered catalyst is much less active, although fairly stable against rhodium leaching and that the $SiO_2(PPh_2)$-tethered catalyst is insignificant in heterogeneous catalysis because of high rhodium leaching. The $RhCl(PPh_3)_3/SiO_2(NH_2)$-derived catalyst preserves at least the turnover and selectivity of the homogeneous catalyst derived from $RhCl(PPh_3)_3$ as well as having the advantage of good immobility. To our knowledge, it evidently possesses higher activity than other heterogeneous catalysts reported before with comparable selectivity for cyclohexene hydroformylation [28]. The good performances of the $SiO_2(NH_2)$-tethered catalyst are assumed to consist in the promotion and stabilization of supported amine on the catalysis of a $RhCl(PPh_3)_3$-derived complex. The distinct properties of $RhCl(PPh_3)_3$-derived SiO_2-tethered catalysts via the three kinds of donor ligands in hydroformylation may be associated with the nature of chemical bonding of donor ligands with the rhodium center. Although all the three kinds of ligands are strong σ-electron donors, the electron transfer in the complexes and the strength of chemical bonds between the ligands and the rhodium center also relate to alternative properties of the ligands. $(O_s)_3Si(CH_2)_3PPh_2$ and $(O_s)_3Si(CH_2)_3SH$ are poor and strong π-electron acceptors respectively. The weak $d\pi$–$p\pi$ bonding between the phosphorus and the rhodium center results in a weak P–Rh bond, whereas the strong $d\pi$–$p\pi$ bonding between the sulfur and the rhodium center produces a strong S–Rh bond. Owing to the weak P–Rh bond, supported phosphine coordinated to the rhodium center is readily replaced by CO with the occurrence of rhodium leaching under hydroformylation conditions. Owing to the strong S–Rh bond, the rhodium leaching can be largely suppressed in hydroformylation on the one hand. However, the strong $d\pi$–$p\pi$ bonding leads to the transfer of the negative charge from the rhodium center to the sulfur, which probably impedes the formation of a hydridic complex necessary for hydroformylation by hydrogenolysis of the Rh–Cl bond under reaction conditions, thereby greatly influencing the catalytic activity on the other hand. In contrast, $(O_s)_3Si(CH_2)_3NH_2$ has no $d\pi$ orbitals. However, a strong N–Rh bond may be formed and the transfer of the negative charge from the rhodium center to other ligands may be controlled by the strong electronegativity of the nitrogen. It may be assumed that the presence of an amine ligand in the tethered complex makes the transformation of the Rh–Cl bond into the Rh–H bond proceed to a satisfactory extent. The complexation of a supported amine with $RhCl(PPh_3)_3$ not only produces a tight N–Rh bond to immobilize the complex but also ensures stable and high catalytic activity for hydroformylation. Such promotion and stabilization of supported amine on the catalysis of a $RhCl(PPh_3)_3$-derived complex may be regarded as the concerted effect of amine and phosphine on hydroformylation.

4. Conclusions

$RhCl(PPh_3)_3$ is tethered to $SiO_2(PPh_2)$, $SiO_2(NH_2)$ and $SiO_2(SH)$ possibly in the forms of $SiO_2(PPh_2RhCl(PPh_3)_2)$, $SiO_2(NH_2RhCl(PPh_3)_2)$ and $SiO_2(SHRhCl(PPh_3)_2)$ respectively. The $SiO_2(NH_2RhCl(PPh_3)_2)$-derived catalyst exhibits both high activity for cyclohexene hydroformylation under 28 bar of equimolar CO and H_2 at 100 °C and fair stability for recycling. Its activity prevails over that of the $RhCl(PPh_3)_3$-derived homogeneous catalyst in a longer reaction. The $SiO_2(PPh_2RhCl(PPh_3)_2)$-derived catalyst displays serious rhodium leaching. The $SiO_2(SHRhCl(PPh_3)_2)$-derived catalyst shows good resistance to rhodium leaching and low activity.

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