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Catalytic studies of aminated MCM-41-tethered rhodium complexes for hydroformylation of 1-octene and styrene

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Abstract

The performances of aminated MCM-41-tethered rhodium complex catalysts in hydroformylation of 1-octene and styrene have been shown by comparison with the catalytic results of corresponding untethered rhodium complex catalysts. For 1-octene hydroformylation, the tethered PPh_3-free rhodium complex is of no advantages in activity, selectivity and *n*/*i* aldehyde ratio over the corresponding untethered one, whereas the tethered PPh_3-containing rhodium complex is of enormous advantages in activity and selectivity except for *n*/*i* aldehyde ratio over the untethered one. Adding excess PPh_3 increases strongly all catalytic performances, especially for the tethered PPh_3-free rhodium complex. For styrene hydroformylation, similar effects of donor ligands on catalytic performances are more evident.

Keywords: Aminated MCM-41; Tethered rhodium complex; 1-Octene; Styrene; Hydroformylation

1. Introduction

The exploitation of catalytic hydroformylation of higher olefins to produce higher aldehydes/alcohols has attracted wide interest, since higher aldehydes/alcohols are of high commercial value for fine chemicals [1]. Important examples are the hydroformylation of octenes to give C_9-aldehydes and the hydroformylation of styrene to obtain phenylpropanals. C_9-aldehydes are the raw materials of diiso-nonyl phthalate which is a high performance plasticizer. Phenylpropanals are the intermediate products for phenylpropionic acid derivatives which are highly valuable pharmaceuticals.

Recently, we investigated the preparation of rhodium complexes tethered to MCM-41 or SiO_2 via donor ligands and the heterogeneous cyclohexene hydroformylation in the presence of the MCM-41- or SiO_2-tethered rhodium complexes [2–5]. We have found that the aminated MCM-41- or SiO_2-tethered rhodium complex catalysts possess the advantages of both activity and resistance to rhodium leaching over the phosphinated and thiolated MCM-41- or SiO_2-tethered ones. Therefore, we chose amines as tethering ligands to further prepare and study tethered rhodium complex catalysts derived from $Rh_4(CO)_{12}$ and $RhCl(PPh_3)_3$ for olefin hydroformylation. $Rh_4(CO)_{12}$ and $RhCl(PPh_3)_3$ were used as catalyst precursors in the present work, in that they are typical rhodium complexes that contain no sterically demanding ligand and sterically demanding ligands, respectively, which can create distinct catalytic characteristics in olefin hydroformylation.

The present paper reports our continued work on the catalysis of aminated MCM-41-tethered rhodium complexes derived from $Rh_4(CO)_{12}$ and $RhCl(PPh_3)_3$ for hydroformylation of 1-octene and styrene. We compare the catalytic results obtained over the aminated MCM-41-tethered rhodium complexes to those produced over the corresponding untethered rhodium complexes. The catalytic performances of aminated MCM-41-tethered rhodium complex catalysts are displayed. The roles of PPh_3 ligand in the catalytic results including activity, selectivity and *n*/*i* aldehyde ratio are revealed. The effects of excess PPh_3 on the catalytic properties of the tethered catalysts derived from $Rh_4(CO)_{12}$ and $RhCl(PPh_3)_3$ in 1-octene hydroformylation are described.

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2. Experimental

PPh_3 (99%), 1-octene (98%), styrene (99%) and $H_2N(CH_2)_3Si(OEt)_3$ (99%) were purchased from Aldrich. $Rh_4(CO)_{12}$ (98%) and $RhCl(PPh_3)_3$ (99%) 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%.

Silicate MCM-41 was synthesized as described elsewhere [2]. As-synthesized MCM-41 was calcined at 560 °C for 10 h. In order to regenerate sufficient amounts of OH groups on the MCM-41 surface, the calcined MCM-41 was exposed to air at room temperature for 2 days followed by dehydration at 200 °C for 5 h. Aminated MCM-41 was prepared by reacting MCM-41 (2.0 g) with a toluene (150 ml) solution of $H_2N(CH_2)_3Si(OEt)_3$ (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, which contained 1.1% N. Aminated MCM-41 is denoted as MCM-41(NH_2).

Tethered rhodium complexes were prepared as follows. In the case with $Rh_4(CO)_{12}$, MCM-41(NH_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 turned brown in color and the red solution became colorless rapidly after stirring. 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 $RhCl(PPh_3)_3$, MCM-41(NH_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. The solid powder 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. The rhodium contents of $Rh_4(CO)_{12}$/MCM-41(NH_2) and $RhCl(PPh_3)_3$/MCM-41(NH_2) were 1.91 and 1.96%, respectively.

The materials thus obtained were characterized by X-ray diffraction (XRD) and N_2 adsorption–desorption, as described elsewhere [6]. The tethering of the rhodium complexes substantially did not result in the change in the mesoporous structural ordering of MCM-41, although the resultant materials exhibited reduced pore sizes, total pore volumes and BET surface areas.

Hydroformylation of olefins was conducted under 10–20 bar of an equimolar CO and H_2 mixture at 80 °C in an autoclave. 150 mg of tethered rhodium complex sample, 6 ml of olefin and 50 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 was 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. In 1-octene hydroformylation, 1-nonanal and 2-methyloctanal were yielded as the hydroformylation products, *cis*-2-octene and *trans*-2-octene as the isomerization products, and *n*-octane as the hydrogenation product. No hydrogenation products of aldehydes were detected. In styrene hydroformylation, only 2-phenylpropanal and 3-phenylpropanal were formed.

XRD of MCM-41 and MCM-41-based materials was performed on a Shimadzu XRD-6000 spectrometer with Cu Kα monochromatic radiation. The rhodium contents of the samples were determined by atomic absorption spectroscopy. The content of nitrogen in MCM-41(NH_2) was estimated by thermogravimetric analysis.

3. Results and discussion

3.1. 1-Octene hydroformylation

1-Octene hydroformylation was conducted at 10 bar (H_2/CO = 1) and 80 °C with the homogeneous and heterogeneous catalyst systems. In Figs. 1–7 are presented all the comparative catalytic results as a function of reaction time. For total reaction, $Rh_4(CO)_{12}$ was much more active than $Rh_4(CO)_{12}$/MCM-41(NH_2) while $RhCl(PPh_3)_3$/MCM-41(NH_2) was much more active than $RhCl(PPh_3)_3$, as seen in Fig. 1. In the first hour, $Rh_4(CO)_{12}$ gave nearly total conversion of the 1-octene and $Rh_4(CO)_{12}$/MCM-41(NH_2) converted only 16.1% of the 1-octene. The latter did not convert 70.8% of the 1-octene until 4 h. The inverse comparative results were noted for $RhCl(PPh_3)_3$ and $RhCl(PPh_3)_3$/MCM-41(NH_2). The 1-octene was nearly entirely converted after 4 h over $RhCl(PPh_3)_3$/MCM-41(NH_2) and after 10 h over $RhCl(PPh_3)_3$. The magnitude of the activity for total reaction over the catalyst systems has the order as $Rh_4(CO)_{12}$ > $RhCl(PPh_3)_3$/MCM-41(NH_2) > $Rh_4(CO)_{12}$/MCM-41(NH_2) > $RhCl(PPh_3)_3$.

From Fig. 2, it is seen that for the formation of aldehydes, $Rh_4(CO)_{12}$, $Rh_4(CO)_{12}$/MCM-41(NH_2) and $RhCl(PPh_3)_3$ present low catalytic activities while $RhCl(PPh_3)_3$/MCM-41(NH_2) shows a high catalytic activity. The yields of total aldehyde were 23.3, 21.0, 41.3 and 83.5%, respectively, after 22 h. Careful comparison at 1 h shows that $RhCl(PPh_3)_3$ and $Rh_4(CO)_{12}$/MCM-41(NH_2) have smaller rates of 1-octene hydroformylation than $Rh_4(CO)_{12}$. After 1 h, all of the 1-octene almost reacted over $Rh_4(CO)_{12}$. The increase of total aldehyde in this system is attributed to the hydroformylation of 2-octene isomerized from 1-octene. Likewise, the increase of total aldehyde after 10 h over $RhCl(PPh_3)_3$, after 7 h over $Rh_4(CO)_{12}$/MCM-41(NH_2) and after 4 h over $RhCl(PPh_3)_3$/MCM-41(NH_2) are ascribed to the hydroformylation of 2-octene. From Figs. 2–4, it is obvious that 2-octene hydroformylation produces both 1-nonanal and 2-methyloctanal with $Rh_4(CO)_{12}$ and $Rh_4(CO)_{12}$/MCM-41(NH_2), and only 2-methyloctanal with $RhCl(PPh_3)_3$ and $RhCl(PPh_3)_3$/MCM-41(NH_2).

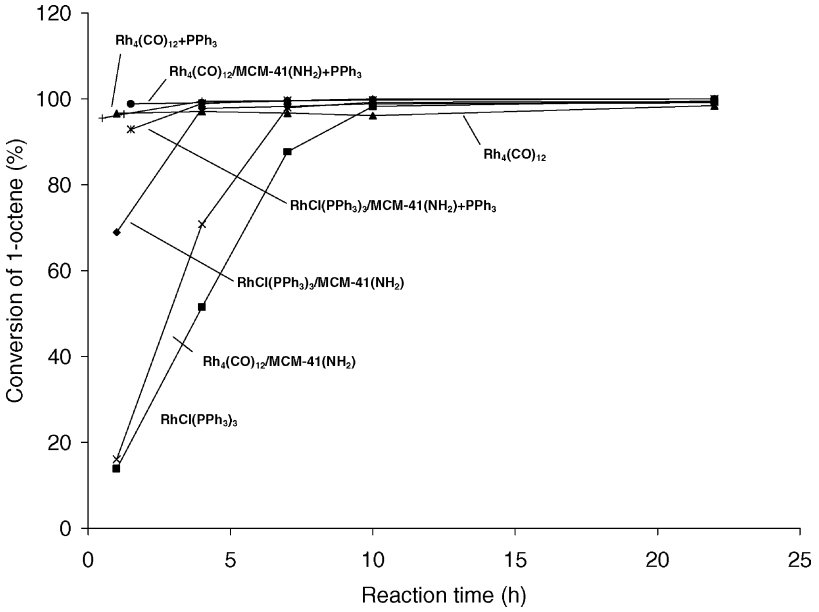

Fig. 1. Conversions of 1-octene as a function of reaction time in 1-octene hydroformylation over different catalyst systems.

From the curve values at 1 h in Fig. 5, it is noted that the magnitude of the rate of 1-octene isomerization over the catalyst systems has the order as $Rh_4(CO)_{12}$ > $RhCl(PPh_3)_3/MCM\text{-}41(NH_2)$ > $Rh_4(CO)_{12}/MCM\text{-}41(NH_2)$ > $RhCl(PPh_3)_3$. After 22 h, the yields of 2-octene were 56.3, 10.2, 62.2 and 46.3%, respectively. The consumption of 2-octene during the reactions is ascribed to the hydroformylation and hydrogenation of 2-octene. 2-Octene hydroformylation proceeded with the concomitant diminution of *n*/*i* aldehyde ratios (Fig. 6). Estimation of the changes in product composition in Figs. 2–5 and 7 demonstrates that 2-octene experiences both hydroformylation and hydrogenation over $Rh_4(CO)_{12}$ and $Rh_4(CO)_{12}/MCM\text{-}41(NH_2)$, and only hydroformylation over $RhCl(PPh_3)_3$ and $RhCl(PPh_3)_3/MCM\text{-}41(NH_2)$. With $Rh_4(CO)_{12}$, conversion of the 2-octene yielded 5.6% 1-nonanal, 11.3% 2-methyloctanal and 13.8% *n*-octane, approximately. With $Rh_4(CO)_{12}/MCM\text{-}41(NH_2)$, conversion of the 2-octene produced 4.2% 1-nonanal, 10.4% 2-methyloctanal and 13.3% *n*-octane, approximately. With $RhCl(PPh_3)_3$ and $RhCl(PPh_3)_3/MCM\text{-}41(NH_2)$, 2-octene was converted only to 2-methyloctanal.

The curve values at 1 h in Fig. 7 indicate that the magnitude of the rate of 1-octene hydrogenation over the catalyst systems follows the order as $Rh_4(CO)_{12}$ > $RhCl(PPh_3)_3/MCM\text{-}41(NH_2)$ > $Rh_4(CO)_{12}/MCM\text{-}41(NH_2)$ > $RhCl(PPh_3)_3$. After 22 h, the yields of *n*-octane were

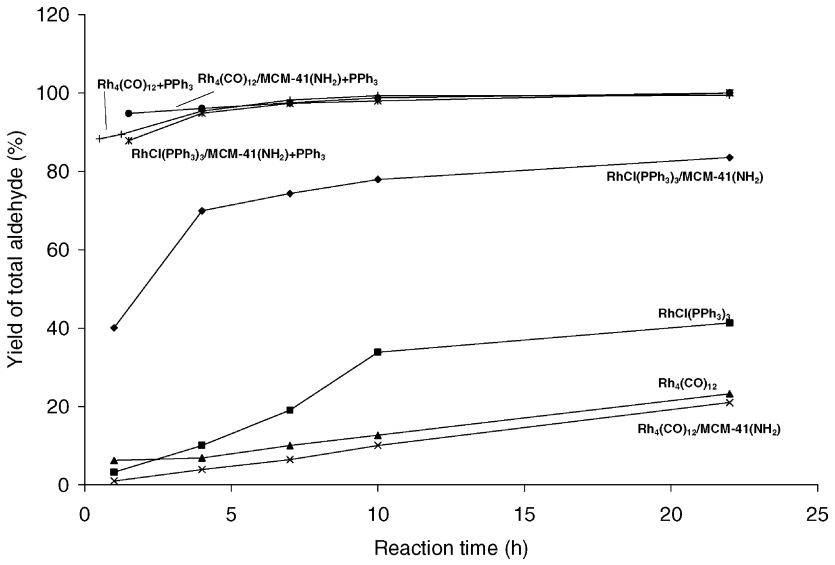

Fig. 2. Yields of total aldehyde as a function of reaction time in 1-octene hydroformylation over different catalyst systems.

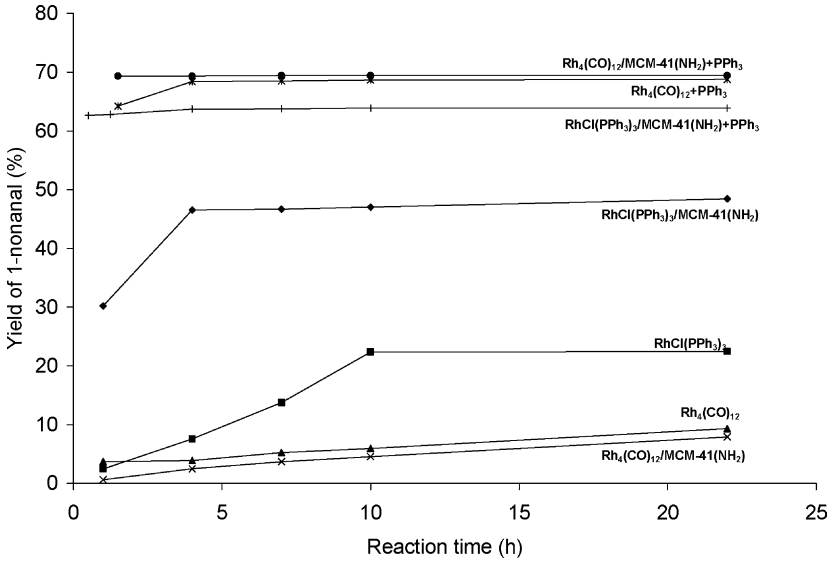

Fig. 3. Yields of 1-nonanal as a function of reaction time in 1-octene hydroformylation over different catalyst systems.

18.9, 5.4, 16.1 and 12.9%, respectively. With $Rh_4(CO)_{12}$ and $Rh_4(CO)_{12}$/MCM-41(NH_2) *n*-octane was formed by hydrogenation of 1-octene and 2-octene, whereas with $RhCl(PPh_3)_3$ and $RhCl(PPh_3)_3$/MCM-41(NH_2) *n*-octane was obtained merely by hydrogenation of 1-octene, as demonstrated above.

On the basis of the above catalytic results in 1-octene hydroformylation, we added excess PPh_3 to $Rh_4(CO)_{12}$, $Rh_4(CO)_{12}$/MCM-41(NH_2) and $RhCl(PPh_3)_3$/MCM-41(NH_2) (PPh_3:Rh = 5:1 molar ratio) and checked the effects of PPh_3 at 10 bar ($H_2/CO = 1$) and 80 °C. It is clearly seen from Figs. 1–7 that addition of excess PPh_3 systematically leads to great increases in the rates of total reaction and hydroformylation and in the ratio of *n*/*i* aldehydes, and great decreases in the rates of isomerization and hydrogenation of 1-octene. With $Rh_4(CO)_{12} + PPh_3$, the conversion of 1-octene and the yield of total aldehyde went up to 95.5 and 88.3% after 0.5 h, the *n*/*i* aldehyde ratio reached 1.8 after 22 h, only a yield of 7.2% 2-octene was detected after 0.5 h and subsequently it progressively disappeared, only a yield of 0.6% *n*-octane was found after 22 h. With $Rh_4(CO)_{12}$/MCM-41(NH_2) + PPh_3, the conversion of 1-octene and the yield of total aldehyde already attained to 98.9 and 94.8% after 1.5 h, the *n*/*i* aldehyde ratio reached 2.3 after 22 h, only a yield of 4.1% 2-octene was observed after 1.5 h and it gradually reacted, no *n*-octane was discerned during the reaction. With $RhCl(PPh_3)_3$/MCM-41(NH_2) + PPh_3, the conversion of 1-octene and the yield of total aldehyde ascended to 92.9 and 87.8% after 1.5 h, the *n*/*i* aldehyde ratio went up to 2.2 after 22 h, only a yield of

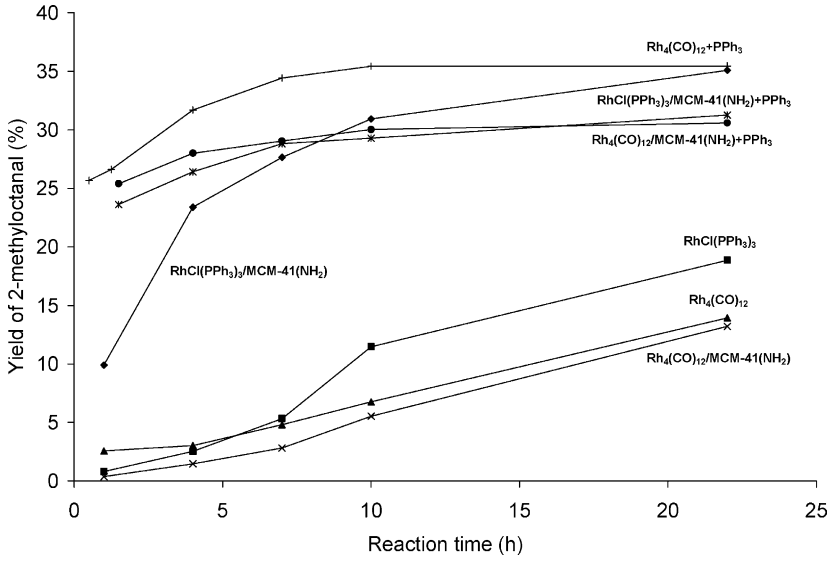

Fig. 4. Yields of 2-methyloctanal as a function of reaction time in 1-octene hydroformylation over different catalyst systems.

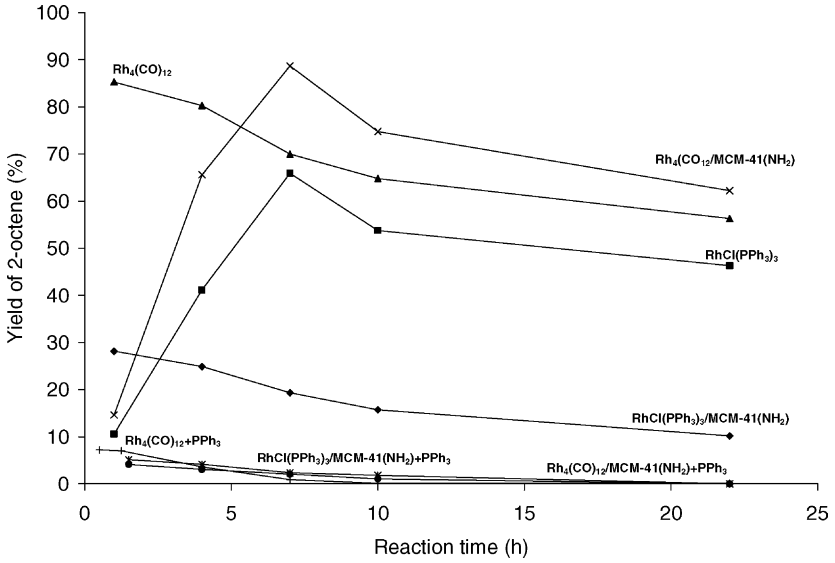

Fig. 5. Yields of 2-octene as a function of reaction time in 1-octene hydroformylation over different catalyst systems.

5.1% 2-octene was obtained after 1.5 h, no *n*-octane was detected during the reaction.

Table 1 lists the significant and comparative catalytic data of all the catalyst systems in the absence and presence of PPh_3 after 1.5 h reaction at 10 bar ($H_2/CO = 1$) and 80 °C. It is evident that $Rh_4(CO)_{12}$/MCM-41(NH_2) presents lower activity and selectivity for the formation of total aldehyde than $Rh_4(CO)_{12}$, while $RhCl(PPh_3)_3$/MCM-41(NH_2) gives remarkably higher activity and selectivity for the formation of total aldehyde than $RhCl(PPh_3)_3$. Meanwhile, all the catalyst systems display enormous increases of activity and selectivity for the formation of 1-nonanal in the presence of excess PPh_3.

When a catalytic reaction over a tethered rhodium complex was ceased, the solid catalyst was filtered off from the reaction solution in air. In each case, the solid sample remained unchanged in color before and after reaction, and the liquid phase was almost colorless. Elemental analysis indicated that the rhodium content of each solid sample varied little before and after reaction, which signifies very weak rhodium leaching from MCM-41 during 1-octene hydroformylation. On the other hand, the observed distinct catalytic behaviours over the tethered rhodium complexes compared to those over the untethered rhodium complexes suggest the heterogeneously catalytic characteristics of the tethered rhodium complexes.

After catalytic reactions, the XRD patterns of the MCM-41-tethered rhodium complex catalysts were retained unchanged. This implies that the mesoporous structure of MCM-41 is stable under operating catalytic conditions.

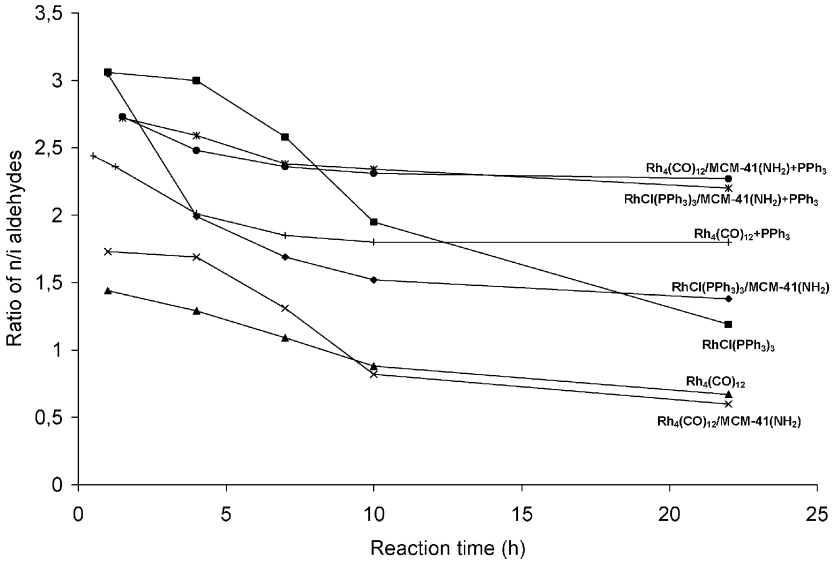

Fig. 6. Ratios of *n*/*i* aldehydes as a function of reaction time in 1-octene hydroformylation over different catalyst systems.

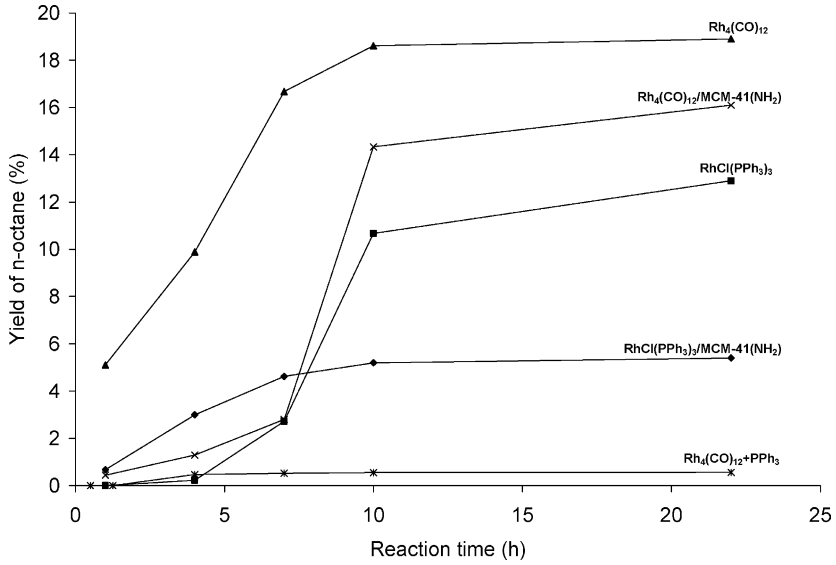

Fig. 7. Yields of *n*-octane as a function of reaction time in 1-octene hydroformylation over different catalyst systems.

The observations of the differences in catalytic behaviour between a phosphine-free rhodium complex and a phosphine-containing rhodium complex, and between a MCM-41-tethered rhodium complex and an untethered rhodium complex, can be interpreted in terms of electronic and steric factors of donor ligands. PPh_3 is a strong σ-electron donor and a poor π-electron acceptor. It is a strong sterically demanding ligand as well. Under hydroformylation conditions, $RhCl(PPh_3)_3$ may be said to be transformed to an active hydridic species like $RhH(CO)(PPh_3)_2$ [7]. In $RhH(CO)(PPh_3)_2$, the CO ligand is bonded more strongly to the rhodium center since the rhodium tends to transfer the increased negative charge from the phosphorus to the CO ligand by π-back donation. This can lead to increased stability of the Rh–CO bond which slows down the CO migratory insertion step, and thus decreased catalytic activity for hydroformylation compared to the $Rh_4(CO)_{12}$-derived homogeneous catalyst. Besides electronic factor, steric considerations are equally important in ligand-modified rhodium complex catalysts. The presence of PPh_3 can generate substantial steric inhibition to the coordination of 1-octene to the rhodium center and thus decrease the rates of all the 1-octene reactions, as summarized by Evans et al. [7]. Such a steric hindrance cannot arise in the pure carbonyl systems [7]. Such a steric hindrance also favours anti-Markownikov addition of the Rh–H bond to the 1-octene to produce 1-nonanal and thus leads to a higher *n*/*i* aldehyde ratio and the formation of less 2-octene [7]. Comparatively, $(O_s)_3Si(CH_2)_3NH_2$ (O_s: surface oxygen) is a weak sterically demanding ligand although a strong σ-electron donor. In the case of $Rh_4(CO)_{12}/MCM\text{-}41(NH_2)$, $Rh_4(CO)_{12}$ and $(O_s)_3Si(CH_2)_3NH_2$ are suggested to form $((O_s)_3Si(CH_2)_3NH_2)_xRh_4(CO)_{12-x}$ ($x = 2, 3$) [2]. On the one hand the strong σ-electron donation makes CO ligands being bonded more strongly to the rhodium center, on the other hand the steric hindrance renders 1-octene coordinated

Table 1
Catalytic properties of rhodium complex catalysts[a] for 1-octene hydroformylation[b] at 10 bar

Catalyst precursor	1-Octene conversion (%)	Turnover[c] (mol/mol Rh)	Selectivity (mol%)			Aldehyde ratio (*n*/*i*)
			n-Octane	2-Octene	Total aldehyde	
$Rh_4(CO)_{12}$[d]	96.7	1257	6.1	87.4	6.5	1.4
$Rh_4(CO)_{12}$[d] + PPh_3	97.7	1270	0	6.9	93.1	2.4
$Rh_4(CO)_{12}/MCM\text{-}41(NH_2)$	25.2	346	2.4	91.7	5.9	1.7
$Rh_4(CO)_{12}/MCM\text{-}41(NH_2)$ + PPh_3	98.9	1360	0	4.1	95.9	2.7
$RhCl(PPh_3)_3$[e]	20.1	279	0.5	78.1	21.4	3.0
$RhCl(PPh_3)_3/MCM\text{-}41(NH_2)$	73.6	986	1.5	37.5	61.0	2.9
$RhCl(PPh_3)_3/MCM\text{-}41(NH_2)$ + PPh_3	92.9	1245	0	5.5	94.5	2.7

[a] 0.15 g of catalyst precursor with nearly 2.0% Rh loading, PPh_3:Rh = 5:1 molar ratio.
[b] Reaction conditions: 6 ml of 1-octene, $H_2/CO = 1$, 80 °C, 1.5 h.
[c] For conversion of 1-octene.
[d] 0.011 g, 12 ml of 1-octene.
[e] 0.051 g, 12 ml of 1-octene.

to the rhodium center more difficultly. They both can lead to lower rates of 1-octene hydroformylation and all the other 1-octene reactions than those with $Rh_4(CO)_{12}$. The lesser steric hindrance that $(O_s)_3Si(CH_2)_3NH_2$ presents than PPh_3 results in a higher rate of total reaction than that with $RhH(CO)(PPh_3)_2$. The lesser steric hindrance also causes a weaker anti-Markownikov addition to give the intermediate *n*/*i* aldehyde ratio in the first 7 h and the intermediate rate of 2-octene formation compared to those with $Rh_4(CO)_{12}$ and $RhH(CO)(PPh_3)_2$, as seen in Figs. 5 and 6. However, after all of the 1-octene has almost reacted at the end of 7 h, 2-octene hydroformylation speeds up with $Rh_4(CO)_{12}$/MCM-41(NH_2), which produces more 2-methyloctanal than the same reaction with $Rh_4(CO)_{12}$ owing to favourable steric factor. Therefore, the *n*/*i* aldehyde ratio is slightly lower over $Rh_4(CO)_{12}$/MCM-41(NH_2) than over $Rh_4(CO)_{12}$ after 7 h. In the case of $RhCl(PPh_3)_3$/MCM-41(NH_2), $(O_s)_3Si(CH_2)_3NH_2RhCl(PPh_3)_2$ is assumed to result by ligand substitution [8]. Under catalytic conditions, $(O_s)_3Si(CH_2)_3NH_2RhCl(PPh_3)_2$ may be believed to be transformed to an active species such as $(O_s)_3Si(CH_2)_3NH_2RhH(CO)(PPh_3)$ [7]. Because of the strong electronegativity of the nitrogen, the increased negative charge may be only partially transferred to the CO ligands via the rhodium by π-back donation. Consequently, the Rh–CO bond is weaker in $(O_s)_3Si(CH_2)_3NH_2RhH(CO)(PPh_3)$ than in $RhH(CO)(PPh_3)_2$ so that the former can be catalytically more active than the latter for hydroformylation. At the same time, $(O_s)_3Si(CH_2)_3NH_2$ presents a lesser steric hindrance than PPh_3 for the coordination of 1-octene to the rhodium center and thus can lead to greater rates of all the 1-octene reactions. It is worth pointing out that such a supported amine bring about a tremendous enhancement of the activity of the $RhCl(PPh_3)_3$-derived catalyst for 1-octene hydroformylation. The lesser steric hindrance relatively disfavours anti-Markownikov addition, which can produce more 2-methyloctanal and 2-octene. Accordingly, the observed *n*/*i* aldehyde ratio is lower with $(O_s)_3Si(CH_2)_3NH_2RhCl(PPh_3)_2$ than with $RhCl(PPh_3)_3$ in the first 10 h. After 10 h, however, all of the 1-octene is converted and 2-octene is formed in high selectivity over $RhCl(PPh_3)_3$. 2-Octene hydroformylation gives more 2-methyloctanal with $RhCl(PPh_3)_3$ than with $RhCl(PPh_3)_3$/MCM-41(NH_2) because of higher 2-octene concentration and beneficial steric condition. Hence, the *n*/*i* aldehyde ratio over $RhCl(PPh_3)_3$ tends to fall and becomes inferior to that over $RhCl(PPh_3)_3$/MCM-41(NH_2) at the end of 22 h. As compared with the two PPh_3-free rhodium complexes, the two PPh_3-containing rhodium complexes give rise to high *n*/*i* aldehyde ratios and low yields of 2-octene. Furthermore, 2-octene is only hydroformylated to 2-methyloctanal with the two PPh_3-containing rhodium complexes, in contrast with the two PPh_3-free rhodium complexes with which 2-octene is converted to 1-nonanal, 2-methyloctanal and *n*-octane. This is fully due to the steric effect of PPh_3.

The addition of excess PPh_3 makes a significant impact on the enhancement of catalytic activity and selectivity of rhodium complexes for 1-octene hydroformylation [9–11]. Consistent with the results reported with other rhodium complex systems for 1-octene hydroformylation [9–11], our catalyst systems show not only a marked increase in the *n*/*i* aldehyde ratio and great decreases in the activities for the formation of 2-octene and *n*-octane, but a great increase in the activity for the formation of aldehydes in the presence of excess PPh_3 (PPh_3:Rh = 5:1 molar ratio). The increase in the *n*/*i* aldehyde ratio and the suppression of the side reactions of 1-octene are mainly due to strong steric effect of excess PPh_3 [7,12]. However, the increase in the activity for the formation of aldehydes by addition of excess PPh_3 remains unclear. Moreover, this effect is profound in our case. It is interesting to note that adding excess PPh_3 to $RhCl(PPh_3)_3$/MCM-41(NH_2) decreases slightly the activity for the formation of 2-methyloctanal while it increases the activity for the formation of 1-nonanal, whereas adding PPh_3 to $Rh_4(CO)_{12}$/MCM-41(NH_2) or $Rh_4(CO)_{12}$ increases the activities for the formation of both 1-nonanal and 2-methyloctanal, as shown in Figs. 3 and 4. Moreover, the increase in the activity for the formation of total aldehyde is much greater with $Rh_4(CO)_{12}$/MCM-41(NH_2) or $Rh_4(CO)_{12}$ than with $RhCl(PPh_3)_3$/MCM-41(NH_2), as seen in Fig. 2. Adding PPh_3 to $Rh_4(CO)_{12}$/MCM-41(NH_2) results in the greatest increase in the *n*/*i* aldehyde ratio that is observed after 10 h [Fig. 6]. Interpretation of the unusual promotions of PPh_3 added on the catalysis of $Rh_4(CO)_{12}$-derived systems most likely involves the generation of new PPh_3-substituted rhodium complexes in the reaction systems. It is known that the reaction of $Rh_4(CO)_{12}$ with an excess of PPh_3 at room temperature under atmospheric CO gives almost quantitatively the dinuclear complex $[Rh(CO)_2(PPh_3)_2]_2$ [13]. Such dinuclear rhodium species have been demonstrated to be stable without fragmentation even under a high pressure of CO or ($CO + H_2$) ($H_2/CO = 1$) and over the hydroformylation temperature range [14]. We speculate that the catalytic species derived from such dinuclear rhodium complexes are more active than that derived from $RhCl(PPh_3)_3$ for hydroformylation. Similar examples have previously been reported that the presence of excess PPh_3 with $Rh_4(CO)_{12}$ or $Rh_6(CO)_{16}$ increases dramatically the rates of hydroformylation of propene and 1-hexene and decreases dramatically the rates of side reactions [13,15].

3.2. Styrene hydroformylation

Styrene hydroformylation was carried out at 20 bar ($H_2/CO = 1$) and 80 °C with the homogeneous and heterogeneous catalyst systems mentioned above. In Figs. 8 and 9 are presented the comparative catalytic yields of total aldehyde and *n*/*i* aldehyde ratios as a function of reaction time. The lack of competing reactions during styrene hydroformylation simplifies the understanding of catalytic

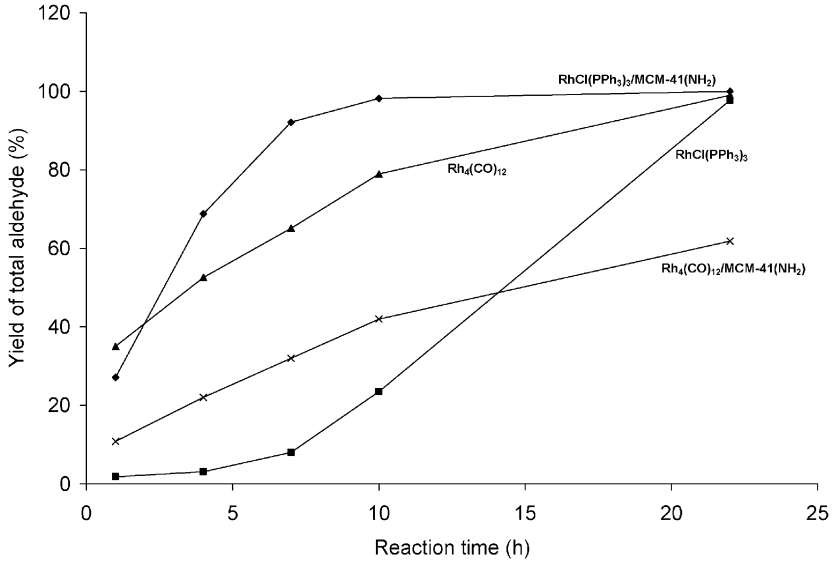

Fig. 8. Yields of total aldehyde as a function of reaction time in styrene hydroformylation over different catalyst systems.

processes and readily elucidates the effects of donor ligands on the catalytic activity and *n*/*i* aldehyde ratio. Because of the structural feature of styrene, Markownikov and anti-Markownikov additions of the Rh–H bond to give 3-phenylpropanal and 2-phenylpropanal, respectively.

From Fig. 8, it is seen that the reaction trends over $Rh_4(CO)_{12}$ and over $Rh_4(CO)_{12}$/MCM-41(NH_2) follow much the same pattern, and the reaction trends over $RhCl(PPh_3)_3$ and over $RhCl(PPh_3)_3$/MCM-41(NH_2) have roughly a similar mode. Throughout the reaction, the catalytic activity of $Rh_4(CO)_{12}$/MCM-41(NH_2) was remarkably lower than that of $Rh_4(CO)_{12}$, while the catalytic activity of $RhCl(PPh_3)_3$/MCM-41(NH_2) was much higher than that of $RhCl(PPh_3)_3$. This is mainly due to steric effect, as explained in the case of 1-octene hydroformylation. It is evident that the steric hindrance has a profound influence on the catalytic activity for styrene hydroformylation. $RhCl(PPh_3)_3$/MCM-41(NH_2) is the most active among the four catalyst systems. As a matter of fact, $RhCl(PPh_3)_3$/MCM-41(NH_2) had converted all of the styrene by 10 h, at which the yields of total aldehyde were 78.9% over $Rh_4(CO)_{12}$, 42.0% over $Rh_4(CO)_{12}$/MCM-41(NH_2) and 23.5% over $RhCl(PPh_3)_3$. After 22 h, $Rh_4(CO)_{12}$ and $RhCl(PPh_3)_3$ converted all of the styrene whereas $Rh_4(CO)_{12}$/MCM-41(NH_2) converted only 61.8% of the styrene. Meanwhile, the steric hindrance led to the increase in *n*/*i* aldehyde ratio as shown in Fig. 9.

As is the case of 1-octene hydroformylation, very weak rhodium leaching from MCM-41 occurs during styrene hydroformylation, based on elemental analysis. The

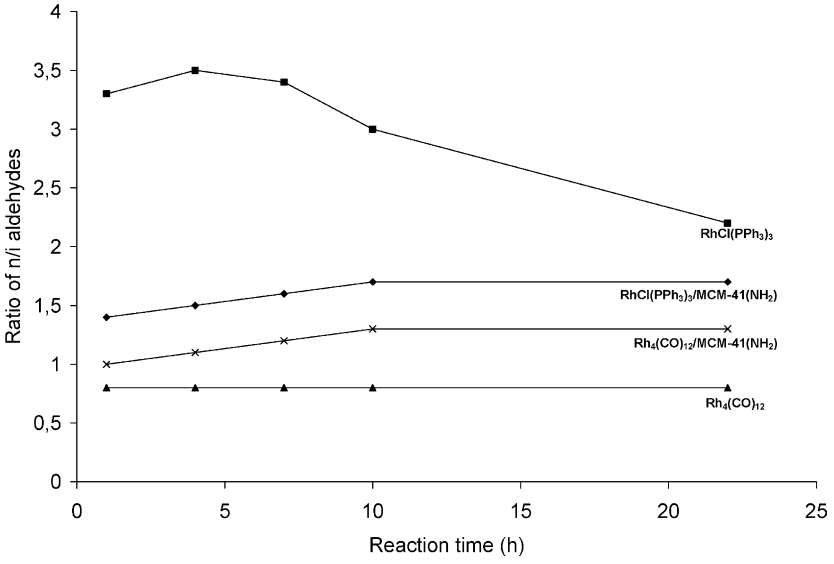

Fig. 9. Ratios of *n*/*i* aldehydes as a function of reaction time in styrene hydroformylation over different catalyst systems.

mesoporous structure of MCM-41 remains stable under operating catalytic conditions, according to XRD observations.

4. Conclusions

In this work, we have studied and compared the catalytic properties of $Rh_4(CO)_{12}$, $Rh_4(CO)_{12}$/MCM-41(NH_2), $RhCl(PPh_3)_3$ and $RhCl(PPh_3)_3$/MCM-41(NH_2) toward 1-octene hydroformylation at 10 bar ($H_2/CO = 1$) and 80 °C and styrene hydroformylation at 20 bar ($H_2/CO = 1$) and 80 °C. Possibly due to both electronic and steric factors of phosphine and amine ligands that affect CO migratory insertion and olefin coordination, $Rh_4(CO)_{12}$/MCM-41(NH_2) is less active than $Rh_4(CO)_{12}$ and $RhCl(PPh_3)_3$/MCM-41(NH_2) much more active than $RhCl(PPh_3)_3$ for 1-octene hydroformylation. Because of steric hindrance of phosphine and amine ligands that impedes olefin hydroformylation and favours anti-Markownikov addition of the Rh–H bond to the olefin, $Rh_4(CO)_{12}$/MCM-41(NH_2) has lower activities than $Rh_4(CO)_{12}$ for 1-octene isomerization and hydrogenation while $RhCl(PPh_3)_3$/MCM-41(NH_2) posseses higher activities than $RhCl(PPh_3)_3$ for 1-octene isomerization and hydrogenation and a lower *n*/*i* aldehyde ratio than $RhCl(PPh_3)_3$. The PPh_3-containing rhodium complexes result in higher *n*/*i* aldehyde ratios and lower yields of 2-octene than the PPh_3-free rhodium complexes. $RhCl(PPh_3)_3$/MCM-41(NH_2) displays the strong advantages of both activity and selectivity for 1-octene hydroformylation over the other catalyst systems. The presence of excess PPh_3 (PPh_3:Rh = 5:1 molar ratio) with the rhodium complexes not only markedly increases *n*/*i* aldehyde ratio but considerably enhances activity and selectivity for 1-octene hydroformylation. The greatest changes in *n*/*i* aldehyde ratio, activity and selectivity occur with $Rh_4(CO)_{12}$/MCM-41(NH_2). Similar steric effects of phosphine and amine ligands on activity and *n*/*i* aldehyde ratio are more evident in styrene hydroformylation.

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