SiO_2-supported bimetallic Rh–Co catalysts derived from $[Rh(CO)_2Cl]_2$ and cobalt carbonyls

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Received 25 February 1998; accepted 26 May 1998

According to the results of IR characterization and catalytic study in ethylene hydroformylation, bimetallic Rh–Co catalysts can be efficiently prepared from $[Rh(CO)_2Cl]_2$ and cobalt carbonyls by co-impregnation on SiO_2. The reaction of $Co_2(CO)_8$ with $[Rh(CO)_2Cl]_2$ (Rh : Co = 1 : 3 atomic ratio) gives rapidly $RhCo_3(CO)_{12}$ on the surface of SiO_2. Although $Co_4(CO)_{12}$ is not reactive with $[Rh(CO)_2Cl]_2$ on SiO_2 to form directly $RhCo_3(CO)_{12}$, an equivalent bimetallic catalyst can be easily obtained from $([Rh(CO)_2Cl]_2 + Co_4(CO)_{12})/SiO_2$ or its derivative $(Rh^+ + Co^{2+})/SiO_2$ (Rh : Co = 1 : 3 atomic ratio) under reducing conditions.

Keywords: $[Rh(CO)_2Cl]_2$, cobalt carbonyl, SiO_2, bimetallic catalyst, co-impregnation

1. Introduction

It is well known that bimetallic catalysts are able to play unusual roles in catalytic activity and selectivity for a variety of reactions. Since a dozen of years, the preparation of inorganic-material-supported bimetallic catalysts has received further attention in heterogeneous catalysis [1–22]. The preparative methods for bimetallic supported catalysts from monometallic compounds usually involve the incipient wetness co-impregnation of inorganic salts and the co-impregnation of organometallic complexes in organic solvents followed by H_2 thermal treatment. As a result of rapid development of surface organometallic chemistry, surface-mediated organometallic synthesis has covered over a wide range of transition metals and inorganic supports [13,23–27]. It provides an efficient and simple method for preparation of supported metal clusters from mononuclear metal compounds on the surfaces of inorganic oxides and zeolites. In this area, only a limited number of surface-mediated syntheses of bimetallic clusters have been published [13,24,25]. In this letter, we report studies of the preparation and ethylene hydroformylation performances of SiO_2-supported bimetallic $RhCo_3$ clusters from $[Rh(CO)_2Cl]_2$ and cobalt carbonyls ($Co_2(CO)_8$ and $Co_4(CO)_{12}$).

2. Experimental

$RhCl_3{\cdot}nH_2O$, $Co_2(CO)_8$ and $Co_4(CO)_{12}$ were purchased commercially. $NaCo(CO)_4$ was synthesized from $Co_2(CO)_8$ according to [28]. $[Rh(CO)_2Cl]_2$, $Rh_4(CO)_{12}$ and $RhCo_3(CO)_{12}$ were synthesized from $RhCl_3{\cdot}nH_2O$ and $NaCo(CO)_4$ as described in [29–31].

$[Rh(CO)_2Cl]_2$, $Rh_4(CO)_{12}$, $Co_2(CO)_8$, $Co_4(CO)_{12}$ and $RhCo_3(CO)_{12}$ were employed as starting materials to prepare $[Rh(CO)_2Cl]_2/SiO_2$ (1% Rh loading), $Rh_6(CO)_{16}/SiO_2$ (1% Rh loading), $Co_4(CO)_{12}/SiO_2$ (1.7% Co loading), $([Rh(CO)_2Cl]_2 + Co_4(CO)_{12})/SiO_2$ (1% Rh loading, Rh : Co = 1 : 3 atomic ratio) and $RhCo_3(CO)_{12}/SiO_2$ (1% Rh loading). SiO_2 (60–80 mesh granule) was partially dehydroxylated at 623 K under vacuum for 5 h and subsequently impregnated with a solution of complex or a mixture solution of complexes in n-hexane under Ar. After 2 h of contact of the liquid and solid phases, the solvent was removed by evacuation at room temperature and the resulting solid sample was further treated under vacuum (1.3×10^{-3} kPa) for 1 h. The catalyst precursor thus obtained was carefully preserved under Ar prior to use.

Hydroformylation of ethylene was conducted under atmospheric pressure at 423 K in a glass tubing flow reactor (i.d. = 7 mm), to which 0.10 g of catalyst precursor was transferred under Ar. The catalyst precursor was decarbonylated in flowing H_2 at 623 K for 2 h, after which H_2 was replaced by a gas mixture of C_2H_4, CO and H_2 (20 : 20 : 20 ml/min) at 423–473 K. In order to make the catalytic reaction proceed possibly under a differential condition, the conversion of C_2H_4 was controlled to below 15%. Data were taken 7 h after the initiation of reaction. Both hydrocarbon and oxygenated products were analyzed on line with a gas chromatograph, using a 2 m length column of Porapak R and a flame ionization detector.

IR experiments were carried out using a KBr cell for liquid samples and using a single beam cell with CaF_2 windows for solid samples. The solid samples (catalyst precursor and SiO_2) were pressed into wafers of 20 mg each in air and placed in the IR cell where the wafers were subjected to the desired treatments. *In situ* IR characterization of catalyst precursors was performed, using wafers of SiO_2 which were dripped with the carbonyl complexes

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in n-hexane under Ar in the IR cell. All IR spectra were recorded on a Bio-Rad FTS-7 spectrometer at room temperature. Adsorbed IR spectra were measured in the presence of gas phases by subtracting the contributions of solid and gas phases.

The metal contents of the samples studied were determined by X-ray fluorescence (XRF) and atomic emission (AE) spectroscopies. According to elemental analytical results, the metal contents of all the samples studied remained unchanged before and after catalytic tests.

3. Results and discussion

3.1. Reactivity between $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ on SiO_2

Martinengo et al. reported earlier that a mixture of $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ at an atomic ratio of Rh : Co = 2 : 3 in n-hexane transforms progressively to $Rh_2Co_2(CO)_{12}$ at ambient temperature and the reaction is complete after 3 days [31]. In order to investigate the surface-mediated synthesis of bimetallic Rh–Co clusters on SiO_2 from $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$, we were first interested in determining the reactivity between $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ at an atomic ratio of Rh : Co = 1 : 3 in n-hexane solution.

In a Schlenk tube, a mixture of $[Rh(CO)_2Cl]_2$ (7.6 mg) and $Co_2(CO)_8$ (22.8 mg) was dissolved in n-hexane (3 ml) under Ar. Figure 1 displays the IR spectral variations in the ν(CO) region in solution under Ar as a function of reaction time at ambient temperature. After dissolution of the mixture of $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$, the solution spectrum instantly displayed two additional carbonyl bands at 2056 and 1890 cm^{-1} in low intensity as well as characteristic carbonyl bands of $[Rh(CO)_2Cl]_2$ at 2106, 2091 and 2035 cm^{-1} and of $Co_2(CO)_8$ at 2071, 2044, 2023, 2003, 1993, 1867 and 1857 cm^{-1} in high intensity (figure 1(a)). The bands at 2056 and 1890 cm^{-1} in the complex spectrum may be assigned to $Rh_2Co_2(CO)_{12}$ [31] which was formed in small amounts. As the reaction proceeded, these two bands developed gradually at the expense of the reactant bands in view of the relative spectral intensity. A shoulder band toward 1873 cm^{-1} emerged, which may be attributed to a typical bridged carbonyl feature of $Rh_2Co_2(CO)_{12}$ [31]. Meanwhile, the 2056 cm^{-1} band slightly shifted upward to 2060 cm^{-1} with increasing intensity. An intense band at 2060 cm^{-1} was noted to progressively take the place of the 2071 cm^{-1} band. After 9 h of reaction, the linear CO bands at 2066 and 2060 cm^{-1} were dominantly present over the others in the spectra. These two bands are reasonably attributed to $RhCo_3(CO)_{12}$ [31]. The bands for $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ decreased regularly in intensity with reaction time. By 23.5 h, they had nearly disappeared in the spectrum, as shown in figure 1(d). At this stage, the spectrum of the reaction mixture substantially exhibited a set of bands at 2066s, 2060s, 2038m, 2033mm, 1913w, 1887m and 1860m cm^{-1}, which is characteristic of $RhCo_3(CO)_{12}$ [31]. This significantly shows that the reaction between $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ at an atomic ratio of Rh : Co = 1 : 3 preferably produces $RhCo_3(CO)_{12}$ in solution at ambient temperature and this reaction is nearly comlete within 1 day. The presence of the 1873 cm^{-1} shoulder indicates the coexistence of a negligible amount of $Rh_2Co_2(CO)_{12}$ as the by-product in the reaction mixture. During the whole reaction process, it was also observed that the reaction proceeded with the concomitant increase in the amount of precipitate in the Schlenk tube. This may be indicative of the simultaneous formation of $CoCl_2$ in the reaction.

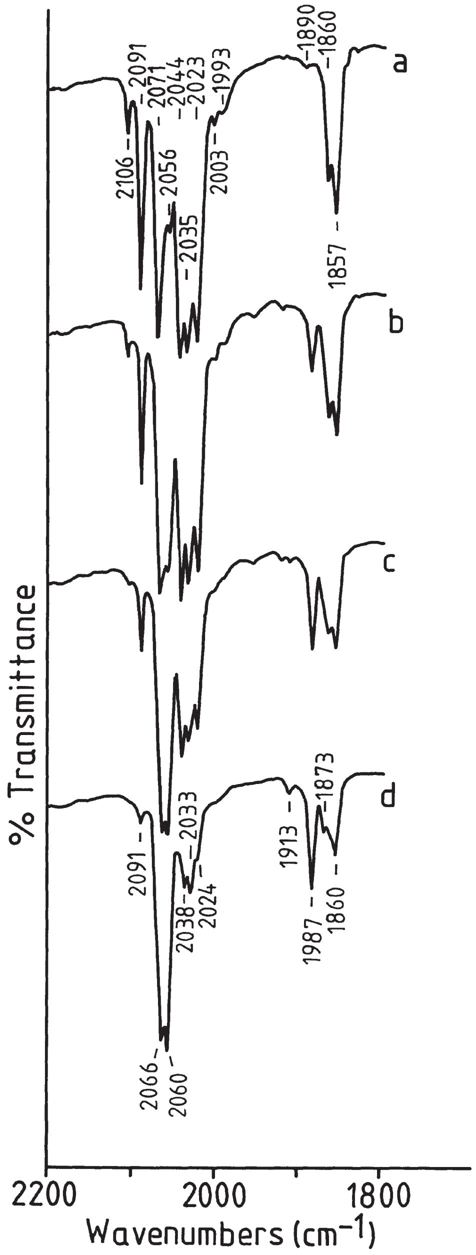

Figure 1. Solution IR spectral evolution during the reaction between $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ (Rh : Co = 1 : 3 atomic ratio) in n-hexane at ambient temperature. (a) 5 min; (b) 3 h; (c) 9 h; (d) 23.5 h.

The above IR spectroscopic results allow us to put forward the following organometallic reaction between $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ at an atomic ratio of Rh : Co = 1 : 3 at ambient temperature:

$$2[Rh(CO)_2Cl]_2 + 7Co_2(CO)_8 \xrightarrow[293\ K]{n\text{-hexane}} 4RhCo_3(CO)_{12} + 2CoCl_2 + 16CO \qquad (1)$$

Based on the reactivity between $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ in solution, we used the surface of SiO_2 as the reaction medium in place of the organic solvent and, hence, studied the surface chemistry of a mixture of $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$.

Immediately after a mixture of $[Rh(CO)_2Cl]_2$ (6.3 mg) and $Co_2(CO)_8$ (18 mg) (Rh : Co = 1 : 3.5 atomic ratio) had been dissolved in n-hexane (3 ml) in a Schlenk tube under Ar, the resultant solution was transferred onto a wafer of SiO_2 predehydroxylated at 623 K by a syringe under Ar. As soon as the solution was brought in contact with the surface, the surface spectrum exhibited carbonyl bands at 2067s, 2035sh, 1922w, 1860m and 1834m cm^{-1} in the presence of the solvent, as shown in figure 2(b). This spectrum exhibited a great change as compared with the mixture spectrum of $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ in solution shown in figure 2(a). Evidently, the bands at 2106, 2091 and 2035 cm^{-1} for $[Rh(CO)_2Cl]_2$ disappeared and a new band at 1834 cm^{-1} appeared. It is difficult to assign these observed broad bands in figure 2(b). But the bands at 2067, 1922 and 1860 cm^{-1} closely resemble those of $RhCo_3(CO)_{12}/SiO_2$ in the presence of n-hexane [32]. The band at 1834 cm^{-1} may be ascribed to one of the bridged carbonyl features of $Co_2(CO)_8$ adsorbed on SiO_2 [33]. Within 10 min, further contact with the surface in the presence of the solvent led to decrease in intensity of the 1834 cm^{-1} band. Meanwhile, the broad linear band became somewhat narrow in favor of the appearance of the 2069 cm^{-1} band. It was found that there was a significant increase in the relative intensity of linear CO bands to that of bridged CO bands with contact time. These observations suggest that the mixture of $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ has strong tendency to produce the bimetallic cluster $RhCo_3(CO)_{12}$ on the SiO_2 surface.

Removal of the solvent by evacuation resulted in a downward shift and a broadening of the bridged CO band center. The linear CO band at 2069 cm^{-1} depleted in favor of the appearance of another linear CO band at 2033 cm^{-1}. After 2 h of evacuation treatment, the resulting wafer displayed a dominant linear CO band and a very broad bridged CO band centered at 1836 cm^{-1}, as shown in figure 5(a). The pattern of this surface spectrum is similar to that of $RhCo_3(CO)_{12}$ strongly physisorbed on SiO_2 [32]. Accordingly, the bimetallic carbonyl cluster resulting from the surface reaction between $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ probably undergoes the same interaction with the SiO_2 surface under vacuum. It is necessary to mention that neither $[Rh(CO)_2Cl]_2/SiO_2$ nor $Co_4(CO)_{12}/SiO_2$ can result in such a spectral pattern following treatment under vacuum.

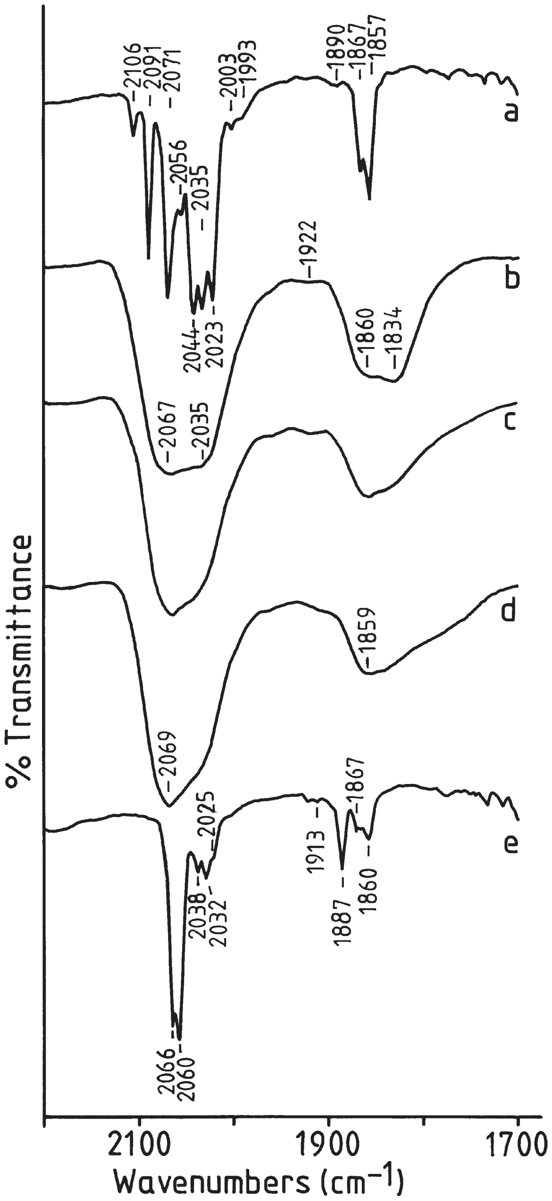

Figure 2. IR spectral evolution during the reaction between $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ (Rh : Co = 1 : 3 atomic ratio) at room temperature. (a) 5 min in n-hexane; after impregnation of SiO_2 predehydroxylated at 623 K with the mixture of $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ in n-hexane: (b) 5 min, (c) 10 min, (d) 1.5 h; (e) n-hexane extract from the surface (1% Rh loading) immediately after impregnation of SiO_2 predehydroxylated at 623 K with the n-hexane mixture solution of $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ followed by removal of the solvent under vacuum.

To verify the formation of $RhCo_3(CO)_{12}$ from $Rh_2(CO)_4Cl_2$ and $Co_2(CO)_8$ promoted by the SiO_2 surface, extraction of the reaction products from the surface was conducted. In a Schlenk tube, a mixture of $Rh_2(CO)_4Cl_2$ (9.8 mg) and $Co_2(CO)_8$ (27.1 mg) at an atomic ratio of Rh : Co = 1 : 3 was quickly dissolved in n-hexane (2 ml) under Ar. Immediately after dissolution, 0.5 g of SiO_2 predehydroxylated at 623 K was impregnated with this solution in another Schlenk tube. It was noticed that the solid phase instantaneously turned brown. The solvent was then removed by evacuation within 5 min. Onto the brown solid sample (1% Rh loading) was added n-hexane under Ar. The liquid phase turned deep brown at once, indicative of the extraction of adspecies from the surface. The solvent extract exhibited a representative IR spectrum of $RhCo_3(CO)_{12}$ except shoulder bands toward 2025 and 1873 cm^{-1}, as shown in figure 2(e). The shoulder at 2025 cm^{-1} may correspond to trace amounts of $Co_4(CO)_{12}$ formed from $Co_2(CO)_8$ on SiO_2. The shoulder at 1873 cm^{-1} may be due to trace amounts of $Rh_2Co_2(CO)_{12}$. This IR result of the extract clearly shows that $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ are effectively transformed to $RhCo_3(CO)_{12}$ upon co-impregnation on the surface of SiO_2. Based on the elemental analysis for rhodium by AE spectroscopy, the percent of extraction of $RhCo_3(CO)_{12}$ from the SiO_2 surface into n-hexane was 60–70.

In the present work, the surface-mediated synthesis of $RhCo_3(CO)_{12}$ from $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ parallels the corresponding organometallic synthesis. Reaction (1) is strongly accelerated on the SiO_2 surface. It is very likely that the surface of SiO_2 plays an effective catalytic role in the formation of the bimetallic cluster, although there is very little understanding of the mechanism of surface-mediated synthesis.

3.2. *Reactivity between $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ on SiO_2*

In place of $Co_2(CO)_8$, the reactivity of $Co_4(CO)_{12}$ with $[Rh(CO)_2Cl]_2$ was examined both in n-hexane solution and on the SiO_2 surface.

In a Schlenk tube, a mixture of $Co_4(CO)_{12}$ (23.2 mg) and $[Rh(CO)_2Cl]_2$ (9.2 mg) at an atomic ratio of $Rh:Co = 1:3.5$ was dissolved in n-hexane (3 ml) under Ar. In contrast with the reactivity between $Co_2(CO)_8$ and $[Rh(CO)_2Cl]_2$, there was no reaction occurring between these two complexes at ambient temperature. Figure 3(a) presents the IR spectrum of the reaction mixture after 2 days: 2106w, 2091s, 2064s, 2057s, 2037m, 2029w, 1900w and 1867s cm^{-1}, which has no bands for new species except those for the starting complexes. This result shows that $Co_4(CO)_{12}$ is much less reactive with $[Rh(CO)_2Cl]_2$ than $Co_2(CO)_8$ to form a bimetallic complex.

After a pretreated wafer of SiO_2 had been impregnated with a n-hexane mixture solution of $Co_4(CO)_{12}$ and $[Rh(CO)_2Cl]_2$ ($Rh:Co = 1:3.5$ atomic ratio) under Ar, the resulting surface spectrum displayed a set of carbonyl bands at 2103m, 2062s, 2038sh, 1902w, 1860m and 1843m cm^{-1} in the presence of the solvent, as presented in figure 3(b). The band at 2103m and 2038sh cm^{-1} can be regarded as the gem-dicarbonyl features for $[Rh(CO)_2Cl]_2/SiO_2$. The bands at 2062s, 1902w, 1860m and 1843m cm^{-1} resemble those for $Co_4(CO)_{12}/SiO_2$ [32,33]. The whole spectrum which seems to be a result of the superimposition of the bands for $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ adsorbed on SiO_2, remained the same in the presence of the solvent under Ar at ambient temperature. Removal of the solvent under vacuum did not lead to a significant change in the above spectrum, except a broadening of each band, as shown in figure 6(a). This essentially differs from the case with the sample surface derived from $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$. Similarly, extraction following impregnation was done. 0.6 g of pretreated SiO_2 was impregnated with a n-hexane mixture solution (4 ml) of $Co_4(CO)_{12}$ (25.4 mg) and $[Rh(CO)_2Cl]_2$ (10.4 mg) at an atomic ratio of $Rh:Co = 1:3$ in a Schlenk tube under Ar. After 2 h of stirring, the solvent was removed by evacuation, followed by 2 h of treatment under vacuum (1.3×10^{-3} kPa). Onto a portion of the resulting solid sample (1% Rh loading) was added n-hexane under Ar. Subsequently the extract solution clearly gave an identical IR spectrum (figure 3(c)) with that of the mixture solution of $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ shown in figure 3(a). This spectrum is consistent with that observed on the surface of SiO_2.

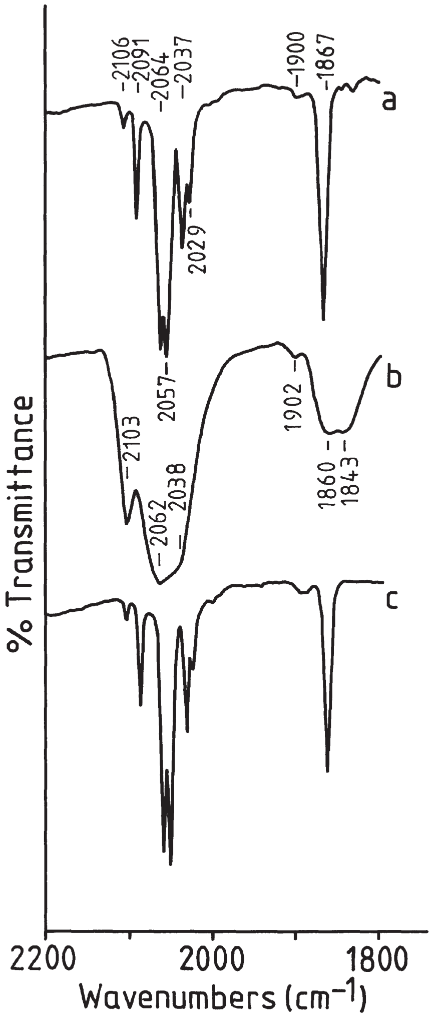

Figure 3. IR spectra of a mixture of $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ ($Rh:Co = 1:3.5$ atomic ratio). (a) In n-hexane for 2 days; (b) adsorbed on SiO_2 in the presence of n-hexane for 0.5 h; (c) n-hexane extract from the surface (1% Rh loading) after impregnation of SiO_2 predehydroxylated at 623 K with the n-hexane mixture solution of $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ followed by 2 h of treatment under vacuum.

Combination of the *in situ* observation and the extraction result reveals that no reaction occurs between $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ on SiO_2 at ambient temperature, just as is the case in n-hexane.

3.3. Catalysis in ethylene hydroformylation

On the basis of the above surface behaviors of monometallic complexes by IR study, a catalytic study was performed to help understand the rhodium–cobalt interaction on SiO_2 at elevated temperatures and the nature of supported catalysts.

In table 1 are given the results of ethylene hydroformylation over the related SiO_2-supported catalysts under atmospheric pressure at 423 K. Following the same pretreatment, the catalyst derived from $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ displayed excellent catalytic performances which are close to those of the $RhCo_3(CO)_{12}$-derived catalyst. The activity to oxygenates was 15 times more than that of the $Rh_4(CO)_{12}$-derived catalyst. The selectivity to oxygenates was also remarkably improved. The results, which apparently show the properties of a bimetallic catalyst [34], further support the suggested facile synthesis of $RhCo_3(CO)_{12}$ from $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ on SiO_2 according to the IR observations. Moreover, this catalyst had a fairly good stability over 106 h of catalytic reaction, as shown in figure 4. However, it was surprisingly found that the catalyst derived from $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ had close catalytic performances to those of the $RhCo_3(CO)_{12}$-derived catalyst under the same conditions as well, although the direct reaction between $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ to synthesize $RhCo_3(CO)_{12}$ was thought not to take place on SiO_2. The observed unusual catalysis for ethylene hydroformylation may be related to the presence of bimetallic Rh–Co particles or clusters on the surface [34]. In another recent

Table 1
Catalytic properties of SiO_2-supported catalysts[a] in atmospheric ethylene hydroformylation ($C_2H_4:CO:H_2 = 20:20:20$ ml/min) at 423 K.

Starting material	Co : Rh (atomic ratio)	Activity[b] C_2H_6	Activity[b] Oxygenates[c]	Selectivity (mol%) C_2H_5CHO	Selectivity (mol%) n-C_3H_7OH	Selectivity (mol%) C_2H_6
$Co_2(CO)_8$		0	0	–	–	–
$Rh_4(CO)_{12}$		0.62	0.31	34	0	66
$RhCo_3(CO)_{12}$		3.63	6.56	58	6	36
$[Rh(CO)_2Cl]_2 + Co_2(CO)_8$	3 : 1	3.85	5.00	51	5	34
$[Rh(CO)_2Cl]_2 + Co_4(CO)_{12}$	3 : 1	9.43	5.61	48	5	47
$([Rh(CO)_2Cl]_2 + Co_4(CO)_{12})$[d]	3 : 1	5.05	5.27	48	3	49

[a] With 1% Rh and 1.7% Co loadings, pretreated under H_2 at 623 K for 2 h.

[b] Expressed by (mol/Co mol/min) for Co/SiO_2 and (mol/Rh mol/min) for Rh containing catalysts, data were taken 7 h after the initiation of reaction.

[c] $C_2H_5CHO + n$-C_3H_7OH.

[d] Preoxidized in air at room temperature for 24 h and subsequently baked under Ar at 623 K for 2 h.

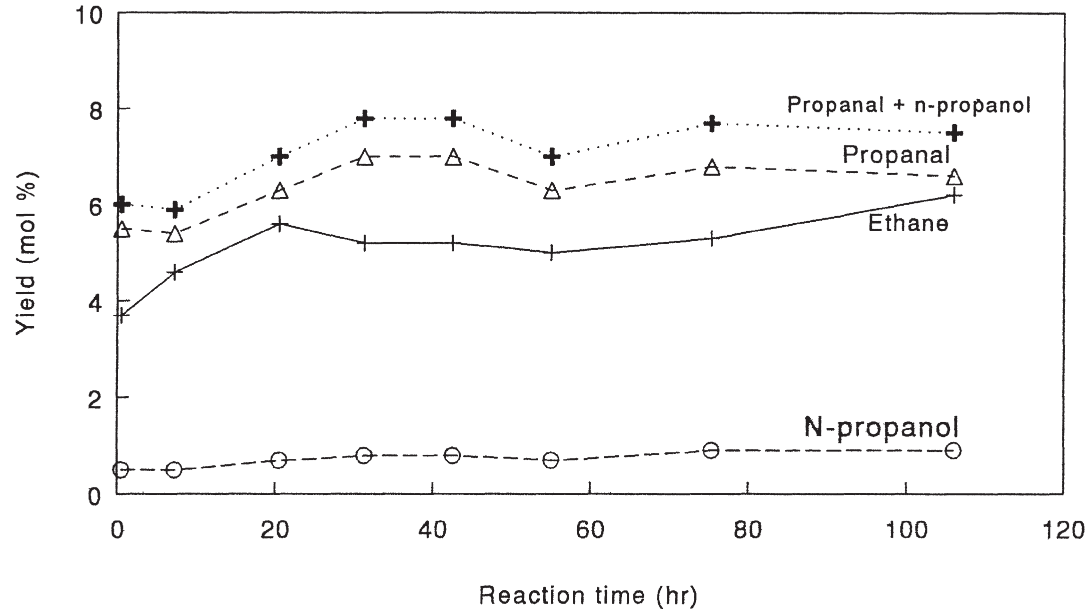

Figure 4. Dynamic atmospheric ethylene hydroformylation ($C_2H_4:CO:H_2 = 20:20:20$ ml/min) at 423 K over a SiO_2-supported catalyst (1% Rh loading) derived from $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ (Rh : Co = 1 : 3 atomic ratio).

work, we have demonstrated that the bimetallic $RhCo_3$ cluster may be formed from $(Rh_6(CO)_{16} + Co_4(CO)_{12})/SiO_2$ by treatment under H_2 at a high temperature, whereas no reaction occurs between $Rh_6(CO)_{16}$ and $Co_4(CO)_{12}$ on SiO_2 at room temperature [35]. In the case of $([Rh(CO)_2Cl]_2 + Co_4(CO)_{12})/SiO_2$, the same explanation may be made that highly dispersed rhodium and cobalt atoms on the surface derived from $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ under reducing conditions interact to produce Rh–Co particles or clusters at elevated temperatures. Furthermore, it was also noticed that much the same catalytic results were obtained when the catalyst precursor $([Rh(CO)_2Cl]_2 + Co_4(CO)_{12})/SiO_2$, following long exposure to air, was directly submitted to the catalytic test at 423 K without prereductive treatment under H_2. During exposure to air, the zerovalent cobalt atoms in the catalyst precursor are known to be quickly oxidized to Co^{2+} ions [36]. This result seems to account for the facile reduction of both Rh^+ and Co^{2+} in the binary system and the efficient formation of bimetallic Rh–Co particles or clusters under a hydroformylation atmosphere at 423 K.

Furthermore, we checked the IR spectra of the two binary catalysts during ethylene hydroformylation. Figure 5 shows comparative IR spectra before and after the reaction over the catalyst derived from $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$. In a type experiment, the catalyst precursor derived from $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$, which displayed a representative spectrum in figure 5(a), was first pressed into a wafer. Afterward, the wafer underwent H_2 treatment at 623 K for 2 h followed by heating treatment under a static atmosphere of gas mixture of C_2H_4, CO and H_2 (26 : 26 : 26 kPa) at 423 K. After 1.5 h of hydroformylation, the surface spectrum exhibited mainly bands at 2036, 1821, 1722, 1465, 1400 and 1348 cm^{-1}, as shown in figure 5(b). The pattern of carbonyl bands resembles that of the catalyst precursor. The bands at 1722, 1465, 1400 and 1348 cm^{-1} are ascribed to propanal adsorbed on SiO_2 which was produced from ethylene hydroformylation. Although it is difficult to conclude from this spectrum that $RhCo_3(CO)_{12}$ is present as the actual catalyst for ethylene hydroformylation, the carbonyl spectrum is not a simple superimposition of those for CO adsorbed on Rh^0/SiO_2 and CO adsorbed Co^0/SiO_2. Under equivalent conditions, the bands of CO adsorbed, especially bridged CO on Rh/SiO_2 (1% Rh loading), are situated at higher wavenumbers and almost no bands of CO adsorbed Co/SiO_2 (1.7% Co loading) were observed, as indicated in our previous studies [37,38]. The IR result in figure 5 is consistent with the observations on a $RhCo_3(CO)_{12}/SiO_2$-derived catalyst under identical conditions which suggested the preservation of the bimetallic $RhCo_3$ cluster on the surface during ethylene hydroformylation [39]. On the one hand, the observed both linear and bridged carbonyl bands at lower wavenumbers (toward 3036 and 1821 cm^{-1}) may be due to a strong interaction between $RhCo_3(CO)_{12}$ and the SiO_2 surface that causes a strong spectral modification of $RhCo_3(CO)_{12}/SiO_2$, as described before [32]; on the other hand, this phenomenon may tentatively be interpreted in terms of the electron-donating effect of cobalt atoms on rhodium atoms when they remain in intimate contact on the surface, as proposed by Ichikawa [40].

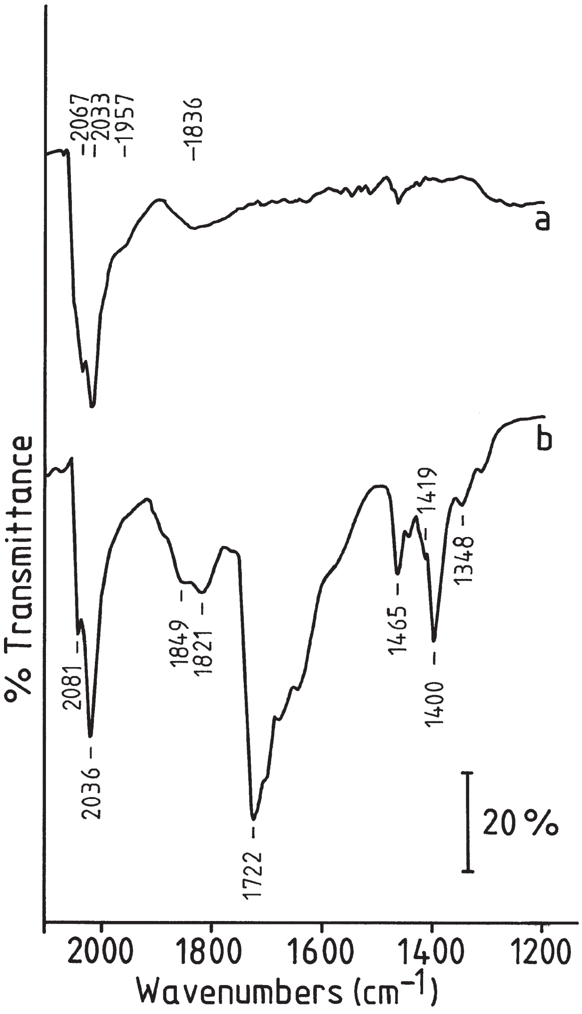

Figure 5. Comparative surface IR spectra before and after ethylene hydroformylation ($C_2H_4 : CO : H_2 = 26 : 26 : 26$ kPa) at 423 K over a SiO_2-supported catalyst (1% Rh loading) derived from $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ (Rh : Co = 1 : 3 atomic ratio). (a) After impregnation of SiO_2 predehydroxylated at 623 K with a mixture of $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ in n-hexane followed by 2 h of treatment under vacuum (1.3×10^{-6} kPa); (b) after 1.5 h of reaction.

A similar IR spectrum was obtained during ethylene hydroformylation over the catalyst derived from $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$, as shown in figure 6(b), which indicates that bimetallic $RhCo_3$ clusters or Rh–Co particles may be formed from $([Rh(CO)_2Cl]_2 + Co_4(CO)_{12})/SiO_2$.

4. Conclusions

The present work has shown that bimetallic Rh–Co particles or clusters can be obtained by co-impregnation of $[Rh(CO)_2Cl]_2$ and cobalt carbonyls on SiO_2. IR study reveals that $Co_2(CO)_8$ reacts rapidly with $[Rh(CO)_2Cl]_2$ to produce $RhCo_3(CO)_{12}$ upon co-impregnation on the surface, whereas $Co_4(CO)_{12}$ does not at all at ambient temperature. The surface-mediated synthesis of $RhCo_3(CO)_{12}$

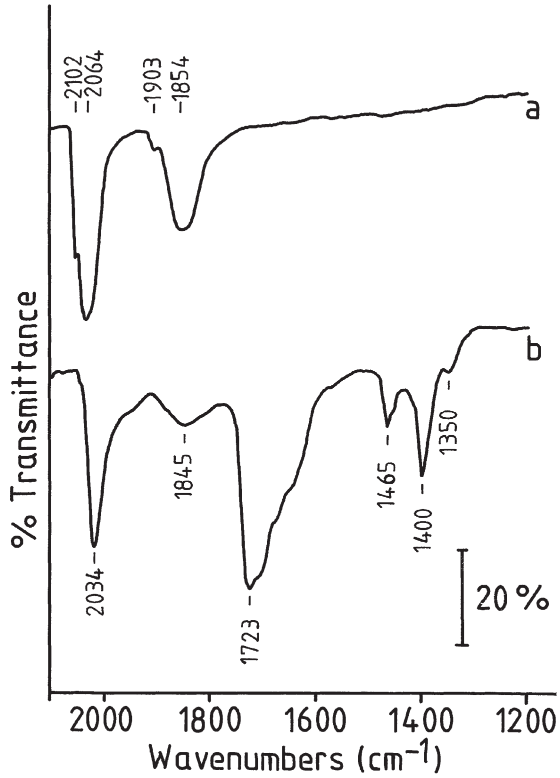

Figure 6. Comparative surface IR spectra before and after ethylene hydroformylation ($C_2H_4 : CO : H_2 = 26 : 26 : 26$ kPa) at 423 K over a SiO_2-supported catalyst (1% Rh loading) derived from $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ (Rh : Co = 1 : 3.5 atomic ratio). (a) After impregnation of SiO_2 predehydroxylated at 623 K with a mixture of $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ in n-hexane followed by 2 h of treatment under vacuum (1.3×10^{-6} kPa); (b) after 1.5 h of reaction.

from $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ parallels the same reaction in solution. But the reaction proceeds much faster on the surface than in solution. Catalytic study of ethylene hydroformylation suggests that bimetallic Rh–Co particles or clusters are formed once the catalyst precursor ($[Rh(CO)_2Cl]_2 + Co_4(CO)_{12}$)/$SiO_2$ or its derivative ($Rh^+ + Co^{2+}$)/SiO_2 is subjected to reductive treatment under mild conditions. The combination of rhodium and cobalt carbonyl complexes appears to yield preferentially bimetallic Rh–Co particles or clusters on the SiO_2 surface under appropriate conditions

Acknowledgement

The authors acknowledge the support of this research by the Chinese Academy of Sciences.

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