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On the Preparation of Bimetallic Rh–Co Hydroformylation Catalysts from $[Rh(CO)_2Cl]_2$ and Cobalt Carbonyls on the Surface of SiO_2

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The preparation of bimetallic Rh–Co catalysts from $[Rh(CO)_2Cl]_2$ and cobalt carbonyls ($Co_2(CO)_8$ and $Co_4(CO)_{12}$) on the surface of SiO_2 has been investigated by IR spectroscopy and the ethylene hydroformylation reaction. The reaction of $Co_2(CO)_8$ with $[Rh(CO)_2Cl]_2$ (Rh : Co = 1 : 3.5 atomic ratio) yields spontaneously and promptly $RhCo_3(CO)_{12}$ on the surface. The $RhCo_3(CO)_{12}$ thus synthesized is characterized by in situ IR monitoring and extraction from the surface into *n*-hexane. This chemistry parallels that in solution. In *n*-hexane solution, the reaction proceeds very slowly and is complete after approximately 1 d. The results show that the surface of SiO_2 exerts an unusual promoting effect on this organometallic synthesis. When $Co_2(CO)_8$ is replaced by $Co_4(CO)_{12}$, no reaction takes place either in solution or on the surface. However, a bimetallic Rh–Co catalyst may efficiently result from $([Rh(CO)_2Cl]_2+Co_4(CO)_{12})/SiO_2$ (Rh : Co = 1 : 3 atomic ratio) by thermal treatment under a reducing atmosphere. In particular, $(Rh^++Co^{2+})/SiO_2$ (Rh : Co = 1 : 3 atomic ratio) derived from $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ likewise may be efficiently transformed to bimetallic Rh–Co clusters or particles under an ethylene hydroformylation atmosphere at 423 K. All the catalysts derived from $[Rh(CO)_2Cl]_2$ and cobalt carbonyls in this work have catalytic performances close to those of $RhCo_3(CO)_{12}/SiO_2$ in ethylene hydroformylation.

Surface-mediated organometallic synthesis has become an increasingly fascinating branch in the area of surface organometallic chemistry, from the viewpoint of simple and efficient synthesis of supported complex catalysts or supported catalyst precursors.[1)] Since pioneering syntheses of ruthenium and osmium carbonyl cluster anions $[Ru_6C(CO)_{16}]^{2-}$ and $[Os_{10}C(CO)_{24}]^{2-}$ from appropriate inorganic salts or carbonyl clusters of low nuclearity on the basic surfaces of MgO and γ-Al_2O_3 were reported,[2—4)] numerous successes have been achieved in the synthesis of various transition metal neutral and anionic clusters on the surfaces of inorganic supports with different properties.[1,5—9)] Nevertheless, there are only a couple of examples of the surface-mediated synthesis of bimetallic clusters among them.[5—7)] Very recently, we performed a success for preparation of $RhCo_3(CO)_{12}$ from the coordinatively saturated clusters $Rh_4(CO)_{12}$ and $Co_2(CO)_8$ on the surface of SiO_2 via decarbonylation of the monometallic clusters.[10,11)] This work implied that the surface reaction that produces the bimetallic Rh–Co cluster could proceed easily from coordinatively unsaturated monometallic complexes. In this paper, we report an easy synthesis of $RhCo_3(CO)_{12}$ from $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ on SiO_2 that is much faster than the reaction in solution, and we simultaneously describe a preparation of the same SiO_2-supported bimetallic Rh–Co catalysts from $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ by thermal treatment under reducing conditions.

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 Ref. 12. $[Rh(CO)_2Cl]_2$, $Rh_4(CO)_{12}$, and $RhCo_3(CO)_{12}$ were synthesized from $RhCl_3\cdot nH_2O$ and $NaCo(CO)_4$ as described in Refs. 13, 14, and 15. SiO_2 was a silica 'Aerosil' supplied by Degussa with a surface area of 380 m^2/g *n*-hexane used as the solvent was distilled over P_2O_5 and stored under Ar over 5 A molecular sieves. The gases H_2, CO, C_2H_4, and Ar had a purity of 99.99%. Before introduction into a sample vessel, a reactor and an IR cell, they were further purified by passage through traps of activated 5 A molecular sieves and Mn/MnO to eliminate traces of water and oxygen.

$[Rh(CO)_2Cl]_2$, $Rh_4(CO)_{12}$, $Co_2(CO)_8$, $Co_4(CO)_{12}$, and $RhCo_3(CO)_{12}$ were used 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) and $RhCo_3(CO)_{12}/SiO_2$ (1% Rh loading). For the study of reactivities between $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ and between $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$, the Rh : Co atomic ratio was set to 1 : 3.5 according to chemical stoichiometry in Eq. 1. For the study of catalytic properties of Rh–Co catalysts derived from $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$, and from $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ in ethylene hydroformylation, an atomic ratio of Rh : Co = 1 : 3 was chosen so that the catalytic results could be compared to that of the $RhCo_3(CO)_{12}$-derived catalyst. SiO_2 (60—80 mesh granule) was partially dehydroxylated at 623 K under a 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 before use.

Hydroformylation of ethylene was done 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 mixture of C_2H_4, CO, and H_2 (20 : 20 : 20 ml min^{-1}) at 423—473 K. To make the catalytic reaction proceed, possibly under different conditions, the conversion of C_2H_4 was kept to below 15%. Data were taken 7 h after the start of reaction. Both hydrocarbon and oxygenated products were analyzed on line with gas chromatography, using a 2-m length column of Porapak R and a flame ionisation detector.

IR experiments were done 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 treated as desired. In situ IR characterization of catalyst precursors was done using wafers of SiO_2 which were dripped with the carbonyl complexes in *n*-hexane under Ar in the IR cell. In situ IR study during ethylene hydroformylation was also done with this static IR cell, to which an equimolar mixture of C_2H_4, CO, and H_2 was admitted. All IR spectra were recorded on a Bio-Rad FTS-7 spectrometer at room temperature. Surface 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 measured 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.

Results and Discussion

Studies of the Reactivity between $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$. Martinengo et al. reported earlier that an 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 room temperature and the reaction is complete after 3 d.[15] 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 measuring the reactivity between $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ at an atomic ratio of Rh : Co = 1 : 3.5 in 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 hexane (3 ml) under Ar. Figure 1 shows the IR spectral variation in the ν(CO) region in solution under Ar with reaction time at room temperature. Immediately after dissolution of the mixture of $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$, the solution spectrum displayed two additional carbonyl bands at 2056 and 1890 cm^{-1} in low intensity as well as characteristic carbonyl ones 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 (Fig. 1(a)). The bands at 2056 and 1890 cm^{-1} in the complex spectrum may be assigned to $Rh_2Co_2(CO)_{12}$[15] 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 $Rh_2Co_2(CO)_{12}$.[15] 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 bands at 2066 and 2060 cm^{-1} were predominant over the others in the spectra. These two bands are reasonably attributed to $RhCo_3(CO)_{12}$.[15] The bands for $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ decreased regularly in intensity with reaction time.

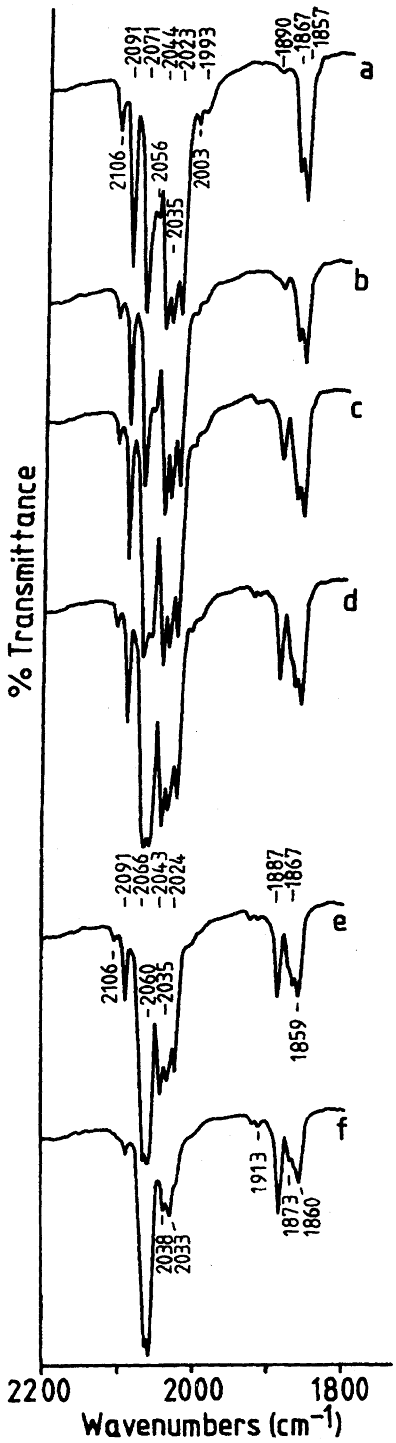


Fig. 1. Solution IR spectral evolution during the reaction between $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ (Rh : Co = 1 : 3.5 atomic ratio) in hexane at room temperature. (a) 5 min; (b) 1 h; (c) 3 h; (d) 6 h; (e) 9 h; (f) 23.5 h.

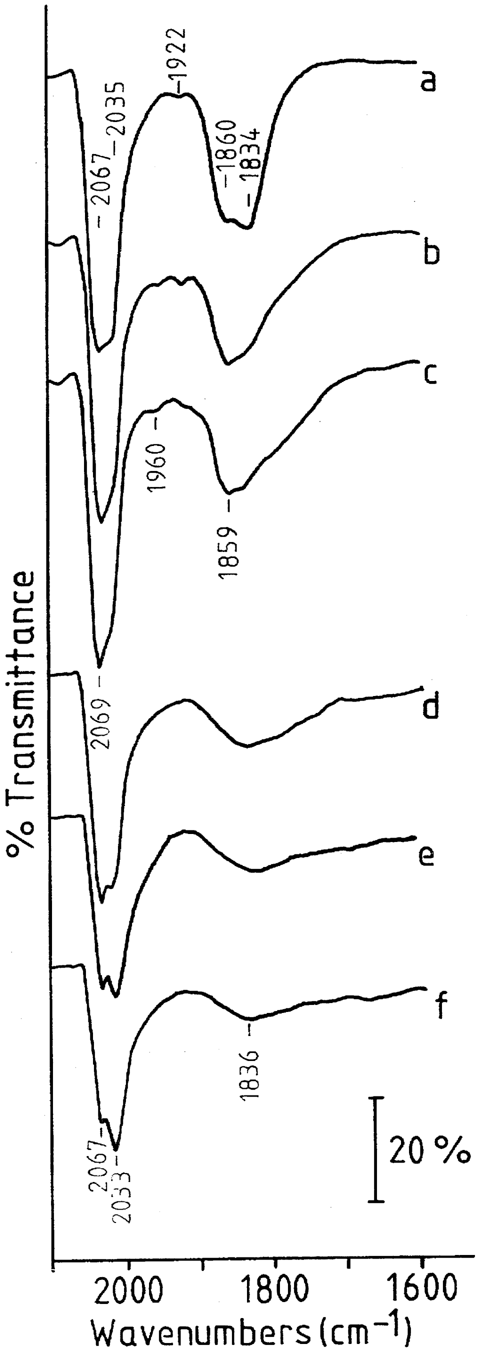


Fig. 2. Surface IR spectra evolution during the reaction between $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ (Rh : Co = 1 : 3.5 atomic ratio) on SiO_2 at room temperature. After impregnation of SiO_2 predehydroxylated at 623 K with the mixture of $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ in *n*-hexane: (a) 5 min; (b) 10 min; (c) 1.5 h; After treatment under vacuum (1.3×10^{-6} kPa): (d) 20 min; (e) 1 h; (f) 2 h.

By 23.5 h, they had nearly disappeared in the spectrum as shown in Fig. 1(f). At this stage, the spectrum of the reaction mixture had a set of bands at 2066s, 2060s, 2038m, 2033m, 1913w, 1887m, and 1860m cm^{-1}, which is characteristic of $RhCo_3(CO)_{12}$.[15] This significantly shows that the reaction between $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ at an atomic ratio of Rh : Co = 1 : 3.5 preferably gives rise to $RhCo_3(CO)_{12}$ in solution at roon temperature and that this reaction is nearly total within 1 d. The presence of the 1873 cm^{-1} shoulder indicates the coexistence of a negligible amount of $Rh_2Co_2(CO)_{12}$ as a by-product in the reaction mixture. During the whole reaction process, it was also noted that the reaction proceeded concomitant with the continuous increase in the amount of precipitate in the Schlenk tube. This may be indicative of the simultaneous formation of $CoCl_2$ in the reaction.

These IR spectroscopic monitoring results allow us to put forward the following organometallic chemistry for the reaction between $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ at an atomic ratio of Rh : Co = 1 : 3.5 at room temperature:

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

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 and hence studied the surface chemistry of a mixture of $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$. Figure 2 shows the in situ surface IR spectra collected during the reaction between $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ (Rh : Co = 1 : 3.5 atomic ratio) on SiO_2. At first, a mixture of $[Rh(CO)_2Cl]_2$ (6.3 mg) and $Co_2(CO)_8$ (18 mg) was quickly dissolved in hexane (3 ml) in a Schlenk tube under Ar. Immediately after dissolution, the resultant solution was transferred onto a wafer of SiO_2 predehydroxylated at 623 K by a syringe under Ar. Before contact with the SiO_2 surface, the reaction between $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ in solution was known not to occur significantly, as indicated above. As soon as the solution was brought in contact with the surface, the surface spectrum developed carbonyl bands at 2067s, 2035sh, 1922w, 1860m, and 1834m cm^{-1} in the presence

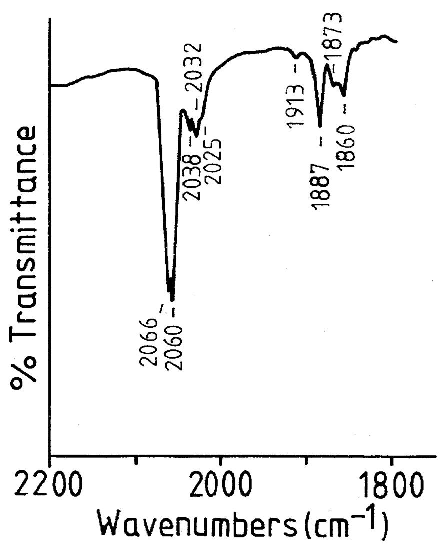


Fig. 3. IR spectrum of a hexane extract from the surface (1% Rh loading) immediately after impregnation of SiO_2 predehydroxylated at 623 K with a *n*-hexane mixture solution of $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ (Rh : Co = 1 : 3 atomic ratio) followed by removal of the solvent under vacuum.

of the solvent, as shown in Fig. 2(a). This spectrum was a great change from the mixture spectrum of [Rh(CO)$_2$Cl]$_2$ and Co$_2$(CO)$_8$ in solution shown in Fig. 1(a). Evidently, the bands at 2106, 2091, and 2035 cm^{-1} for [Rh(CO)$_2$Cl]$_2$ disappeared and a new band at 1834 cm^{-1} appeared. It is difficult to assign these observed broad bands in Fig. 2(a). 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.[16] The band at 1834 cm^{-1} may be ascribed to one of the bridged carbonyl features of Co$_2$(CO)$_8$ adsorbed on SiO$_2$.[17] Within 10 min, further contact with the surface in the presence of the solvent led to a decrease of the 1834 cm^{-1} band in intensity. 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 terminal carbonyl bands to that of bridged bands with contact time. These observations suggest that the mixture of [Rh(CO)$_2$Cl]$_2$ and Co$_2$(CO)$_8$ has strong tendancy to give rise to the bimetallic cluster RhCo$_3$(CO)$_{12}$ on the SiO$_2$ surface. During this transformation, there was little emergence of the band toward 1960 cm^{-1} due to a mononuclear cobalt subcarbonyl species.[16] This species has been assumed to be obviously present concomitant with the conversion of Co$_2$(CO)$_8$ to Co$_4$(CO)$_{12}$ on SiO$_2$.[16] The negligible production of this species indicates that upon introduction of the carbonyl mixture onto the SiO$_2$ surface, Co$_2$(CO)$_8$ reacts quite selectively with [Rh(CO)$_2$Cl]$_2$ to give RhCo$_3$(CO)$_{12}$.

Removal of the solvent by evacuation resulted in a downward shift and a broadening of the bridged band center at 1859 cm^{-1}. Moreover the linear band at 2069 cm^{-1} was depleted progressively in favor of the appearance of another linear band at 2033 cm^{-1}. After completion of evacuation treatment, the resulting wafer had a dominant linear band at 2033 cm^{-1} and a very broad bridged band centered at 1836 cm^{-1}, as shown in Fig. 2(f). The pattern of this surface spectrum is similar to that of RhCo$_3$(CO)$_{12}$ strongly physisorbed on SiO$_2$.[16] Accordingly, the bimetallic carbonyl cluster resulting presumably from the surface reaction between [Rh(CO)$_2$Cl]$_2$ and Co$_2$(CO)$_8$ probably undergoes the same interaction with the SiO$_2$ surface under vacuum.

To confirm the rapid formation of RhCo$_3$(CO)$_{12}$ from [Rh(CO)$_2$Cl]$_2$ and Co$_2$(CO)$_8$ promoted by the SiO$_2$ surface, the reaction products were extracted from the surface. In a Schlenk tube, a mixture of [Rh(CO)$_2$Cl]$_2$ (9.8 mg) and Co$_2$(CO)$_8$ (27.1 mg) at an atomic ratio of Rh : Co = 1 : 3 was quickly dissolved in 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 had a representative IR spectrum of RhCo$_3$(CO)$_{12}$ except shoulder bands toward 2025 and 1873 cm^{-1}, as shown in Fig. 3. The shoulder at 2025 cm^{-1} may correspond to traces of Co$_4$(CO)$_{12}$ formed from Co$_2$(CO)$_8$ on SiO$_2$. The shoulder at 1873 cm^{-1} may be due to traces of Rh$_2$Co$_2$(CO)$_{12}$.

The IR result of the extract clearly demonstrates that the monometallic complexes [Rh(CO)$_2$Cl]$_2$ and Co$_2$(CO)$_8$ are effectively transformed to the bimetallic cluster RhCo$_3$(CO)$_{12}$ upon contact with the surface of SiO$_2$. This is in good accord with the suggestion made by the in situ surface IR study. 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. The surface-mediated synthesis of RhCo$_3$(CO)$_{12}$ fully parallels the corresponding organometallic synthesis. The reaction that needs 1 d in solution can be completed within a few minutes on SiO$_2$. In a sense, the surface of SiO$_2$ plays a quite effective catalytic role in the formation of RhCo$_3$(CO)$_{12}$, although there is very little understanding of the mechanism of surface-mediated synthesis. The IR result of the extract also implies that the Rh : Co atomic ratio set to either 1 : 3 or 1 : 3.5 has no significant influence on the formation of RhCo$_3$(CO)$_{12}$ from [Rh(CO)$_2$Cl]$_2$ and Co$_2$(CO)$_8$ on SiO$_2$.

Studies of the Reactivity between [Rh(CO)$_2$Cl]$_2$ and Co$_4$(CO)$_{12}$. In place of Co$_2$(CO)$_8$, the reactivity of Co$_4$(CO)$_{12}$ with [Rh(CO)$_2$Cl]$_2$ 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)$_2$Cl]$_2$ (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)$_2$Cl]$_2$, there was no reaction occurring between these two complexes at room temperature, even after prolonged stirring of the solution.

The surface chemistry was studied by impregnation of SiO$_2$ predehydroxylated at 623 K with a *n*-hexane mixture solution of Co$_4$(CO)$_{12}$ and [Rh(CO)$_2$Cl]$_2$. In a type in situ IR experiment, a mixture of Co$_4$(CO)$_{12}$ (17.1 mg) and [Rh-

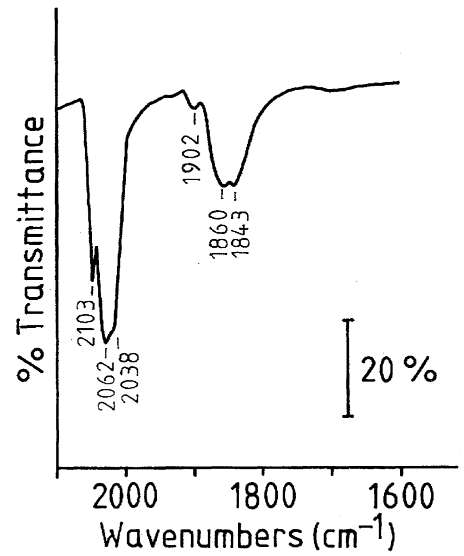


Fig. 4. IR spectrum of a mixture of [Rh(CO)$_2$Cl]$_2$ and Co$_4$(CO)$_{12}$ (Rh : Co = 1 : 3.5 atomic ratio) adsorbed on SiO$_2$ in the presence of *n*-hexane for 0.5 h.

$(CO)_2Cl]_2$ (4.6 mg) at an atomic ratio of Rh : Co = 1 : 3.5 was dissolved in *n*-hexane (3 ml) under Ar in a Schlenk tube. Then the mixture solution was carefully dropped onto a pretreated wafer of SiO_2 in the IR cell by syringe 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 Fig. 4. The bands 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 $Co_4(CO)_{12}/SiO_2$.[16,17]

To study the above surface behavior by IR spectroscopy, extraction following impregnation was done. A sample (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 : 3.5 in a Schlenk tube under Ar. After 2 h of stirring, the solvent was removed by evacuation followed by 2 h of treatment under a vacuum (1.3×10^{-3} kPa). Onto a portion of the resulting solid sample (1% Rh loading) was added *n*-hexane under Ar. The extract solution clearly gave an identical IR spectrum (Fig. 5(a)) with that of the mixture solution of $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$. This spectrum is consistent with that observed on the surface. Combination of the in situ observation and the extraction result shows that no reaction occurs between $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ on the SiO_2 surface at room temperature, just as is the case in solution.

Another portion of the sample was heated under a static vacuum (1.3×10^{-3} kPa). The extracted species following heating treatments were also characterized by IR spectroscopy. From the corresponding spectra given in Fig. 5(b, c, and d), it can easily be concluded that it is impossible to synthesize bimetallic Rh–Co clusters from $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ on SiO_2 till the decomposition of the monometallic complexes under inert conditions.

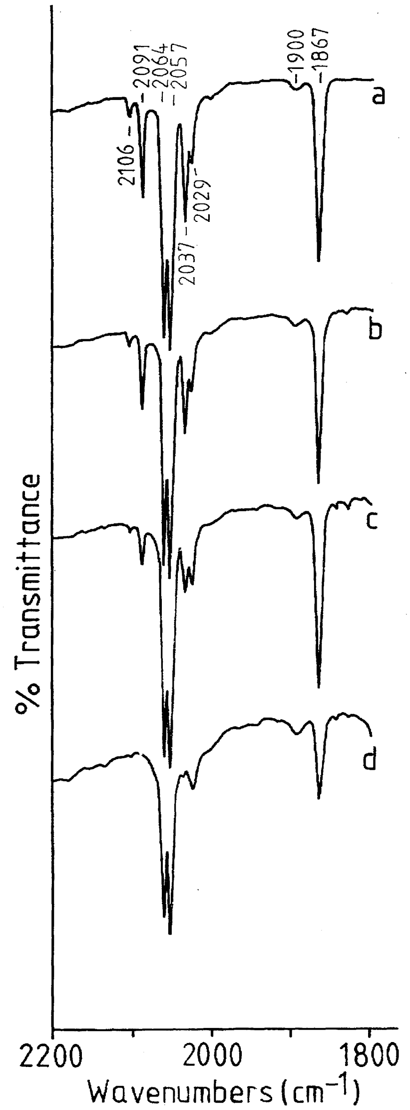
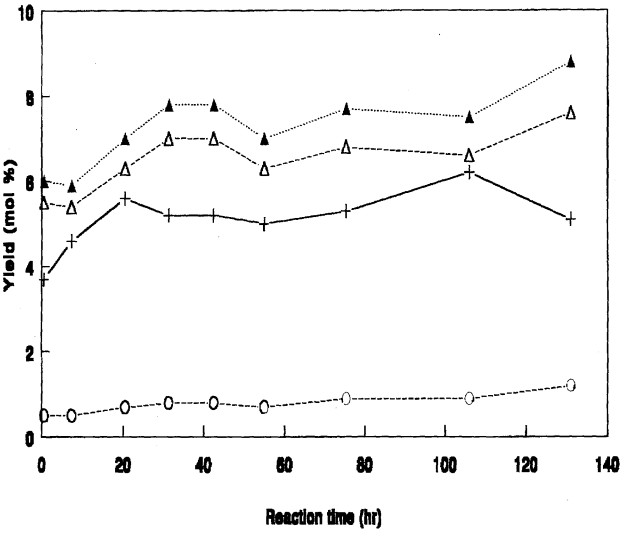


Fig. 5. IR spectra of *n*-hexane extracts from the surface (1% Rh loading) after impregnation of SiO_2 predehydroxylated at 623 K with a *n*-hexane mixture solution of $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ (Rh : Co = 1 : 3.5 atomic ratio) followed by the following treatments: (a) 2 h under vacuum (1.3×10^{-3} kPa) at 293 K; (b) 2 h under static vacuum at 333 K; (c) 3 h under static vacuum at 378 K; (d) 3 h under static vacuum at 433 K.

Catalytic Study in Ethylene Hydroformylation. In Table 1 are given the catalytic results of the related SiO_2-supported catalysts in this work in ethylene hydroformylation under atmospheric pressure at 423 K. Following the same H_2 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 18 times more than that of the $[Rh(CO)_2Cl]_2$-derived catalyst. The selectivity to oxygenates was also improved. Moreover this catalyst had a fairly good stability over 131 h of catalytic reaction, as shown in Fig. 6. The results which apparently show the properties of a bimetallic catalyst,[11] further support the suggested easy synthesis of $RhCo_3(CO)_{12}$ from $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ on SiO_2 according to the IR observations. However, it was surprisingly found that the catalyst derived from $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ had catalytic performances chose 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 is obviously related to the presence of bimetallic Rh–Co particles or clusters on the surface.[11] In another recent work, we have demonstrated that the bimetallic $RhCo_3$ cluster can be formed from $(Rh_6(CO)_{16}+Co_4(CO)_{12})/SiO_2$ by treatment under H_2 at a high temperature, but no reaction occurs between $Rh_6(CO)_{16}$ and $Co_4(CO)_{12}$ on SiO_2 at room temperature.[10] In the case of $([Rh(CO)_2Cl]+Co_4(CO)_{12})/SiO_2$, the same explanation can 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 $RhCo_3$ clusters at elevated temperatures. Furthermore, it was also noticed that much the same catalytic results were obtained when the catalyst precursor $(Rh(CO)_2Cl]_2+Co_4(CO)_{12})/SiO_2$ fol-



+: C_2H_6; △: C_2H_5CHO; O: $n\text{-}C_3H_7OH$; ▲: $C_2H_5CHO + n\text{-}C_3H_7OH$

Fig. 6. Dynamic atmospheric hydroformylation ($C_2H_4 : CO : H_2 = 20:20:20$ ml min^{-1}) at 423 K over a SiO$_2$-supported catalyst (1% Rh loading) derived from [Rh(CO)$_2$Cl]$_2$ and Co$_2$(CO)$_8$ (Rh : Co = 1 : 3 atomic ratio) by 2 h of decarbonylation under H$_2$ at 623 K.

lowing long exposure to air was directly submitted to the catalytic test at 423 K without pre-reductive 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.[18] The result seems to account for the easy reduction of both Rh$^+$ and Co^{2+} in the binary system and the efficient formation of bimetallic RhCo$_3$ clusters under a hydroformylation atmosphere at 423 K. The catalytic data appear to substantiate the existence of RhCo$_3$ clusters in both the ([Rh(CO)$_2$Cl]$_2$+Co$_2$(CO)$_8$)- and the ([Rh(CO)$_2$Cl]$_2$+Co$_4$(CO)$_{12}$)-derived catalysts, by comparison with the catalytic properties of the RhCo$_3$(CO)$_{12}$-derived catalyst.

General Remarks. Thus far, we have successively explored the surface-mediated preparation of bimetallic Rh–Co cluster catalysts by impregnation of Rh$_4$(CO)$_{12}$+Co$_2$(CO)$_8$[10] and of [Rh(CO)$_2$Cl]$_2$+Co$_2$(CO)$_8$ (or Co$_4$(CO)$_{12}$) on SiO$_2$. It is of interest to compare the different reactivities between rhodium and cobalt complexes on the SiO$_2$ surface. In the study of surface chemistry of a mixture of Rh$_4$(CO)$_{12}$ and Co$_2$(CO)$_8$ on SiO$_2$, we found that no reaction can spontaneously occur between coordinatively saturated rhodium and cobalt complexes and instead, Rh$_4$(CO)$_{12}$ and Co$_2$(CO)$_8$ are independently chemisorbed on the SiO$_2$ surface in the forms of Rh$_6$(CO)$_{16}$ and Co$_4$(CO)$_{12}$ in the binary system.[10] In this work, the coordinatively unsaturated rhodium complex [Rh(CO)$_2$Cl]$_2$ is observed to behave differently in the reactivities versus Co$_2$(CO)$_8$ and Co$_4$(CO)$_{12}$ on SiO$_2$. Upon impregnation of SiO$_2$ with a mixture solution of [Rh(CO)$_2$Cl]$_2$ and Co$_2$(CO)$_8$ (Rh : Co = 1 : 3.5 atomic ratio), the carbonyl bands disappear in the surface IR spectrum as shown in Fig. 2. In contrast, the carbonyl bands of [Rh(CO)$_2$Cl]$_2$ and Co$_4$(CO)$_{12}$ are constantly present in the surface IR spectrum after impregnation of SiO$_2$ with a mixture solution of [Rh(CO)$_2$Cl]$_2$ and Co$_4$(CO)$_{12}$ (Rh : Co = 1 : 3.5 atomic ratio) as shown in Fig. 4. This can clearly demonstrate that Co$_2$(CO)$_8$ is very reactive with [Rh(CO)$_2$Cl]$_2$ on the SiO$_2$ surface while Co$_4$(CO)$_{12}$ is not reactive. According to the IR results, it is believed that the conversion of Co$_2$(CO)$_8$ to Co$_4$(CO)$_{12}$ does not take place on the SiO$_2$ surface in the presence of [Rh(CO)$_2$Cl]$_2$. The surface-mediated formation of RhCo$_3$(CO)$_{12}$ from [Rh(CO)$_2$Cl]$_2$ and Co$_2$(CO)$_8$ is substantiated by in situ IR observation and extraction of reaction product from the surface. This reaction not only parallels that occurring in solution, which is studied in this work, but also is much accelerated by the SiO$_2$ surface. Just as is the case in solution, bimetallic Rh–Co carbonyl clusters cannot be synthesized from [Rh(CO)$_2$Cl]$_2$ and Co$_4$(CO)$_{12}$ on the SiO$_2$ surface, either.

However, once the binary system ([Rh(CO)$_2$Cl]$_2$+Co$_4$(CO)$_{12}$)/SiO$_2$ or its derivative (Rh$^+$+Co^{2+})/SiO$_2$ is subjected to reductive treatment under mild conditions, the catalytic data show that a bimetallic catalyst is favorably obtained on the surface. This is identical with the case of another binary system (Rh$_6$(CO)$_{16}$+Co$_4$(CO)$_{12}$)/SiO$_2$.[10,11] Of course, these catalytic reaction data cannot account convincingly for the existence of bimetallic RhCo$_3$ clusters, because

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^{-1}) at 423 K

Starting material	Co : Rh	Activity[b]		Selectivity (mol %)	
	(atomic ratio)	C_2H_6	Oxygenates[c]	Oxygenates	$n\text{-}C_3C_7OH$
Co$_2$(CO)$_8$		0	0	—	—
[Rh(CO)$_2$Cl]$_2$		0.43	0.27	39	0
Rh$_4$(CO)$_{12}$		0.62	0.31	34	0
RhCo$_3$(CO)$_{12}$		3.63	6.56	64	6
[Rh(CO)$_2$Cl]$_2$+Co$_2$(CO)$_8$	3 : 1	3.85	5.00	56	5
[Rh(CO)$_2$Cl]$_2$+Co$_4$(CO)$_{12}$	3 : 1	9.43	5.61	53	5
([Rh(CO)$_2$Cl]$_2$+Co$_4$(CO)$_{12}$)[d]	3 : 1	5.05	5.27	51	3

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+$n\text{-}C_3H_7OH$. d) Preoxidized in air at room temperature for 24 h and baked under Ar at 623 K for 2 h.

the greatly increased catalytic activity in hydroformylation by combination of noble metals with cobalt with respect to monometallic catalysts may be attributed to the synergistic effect of two heteronuclear monometallic sites.[19—25] For this reason, we recently did another study on the formation of bimetallic Rh–Co clusters or particles from monometallic compounds.[11] We suggested that the increase of hydroformylation activity over a binary rhodium and cobalt catalyst compared to that over a monometallic rhodium catalyst is due to the bimetallic catalysis of Rh–Co_3 clusters or particles regardless of the synergistic catalysis by monometallic rhodium and cobalt sites. In this case, the possible formation of bimetallic $RhCo_3$ clusters may be attributed to the effective interaction between highly dispersed rhodium and cobalt atoms derived from carbonyl complexes under reducing conditions. The combination of rhodium and cobalt carbonyl complexes appears to yield preferentially the bimetallic $RhCo_3$ cluster on the SiO_2 surface.[10,11] Therefore, despite that $Co_4(CO)_{12}$ cannot react with $[Rh(CO)_2Cl]_2$ to form directly $RhCo_3(CO)_{12}$ on the surface as compared to $Co_2(CO)_8$, an equivalent bimetallic SiO_2-supported Rh–Co catalyst may be obtained from $[Rh(CO)_2Cl]_2$ and $Co_4(CO)_{12}$ by thermal treatment under a reducing atmosphere.

Conclusions

This paper illustrates the chemistry of preparation of bimetallic Rh–Co catalysts from $[Rh(CO)_2Cl]_2+Co_2(CO)_8$ and $[Rh(CO)_2Cl]_2+Co_4(CO)_{12}$. $Co_2(CO)_8$ is able to react with $[Rh(CO)_2Cl]_2$ at room temperature both in *n*-hexane solution and on a SiO_2 surface to give $RhCo_3(CO)_{12}$. The reaction proceeds much faster on the surface than in solution. The solid surface of SiO_2 therefore plays a strong promotional role toward this organometallic synthesis. $RhCo_3(CO)_{12}$ produced on SiO_2 is comfirmed by extraction from the surface into *n*-hexane. By contrast, $Co_4(CO)_{12}$ is not reactive with $[Rh(CO)_2Cl]_2$ either in *n*-hexane solution or on the SiO_2 surface. However, thermal decarbonylation of $([Rh(CO)_2Cl]_2+Co_4(CO)_{12})/SiO_2$ under H_2 or under an ethylene hydroformylation atmosphere may effectively result in a bimetallic supported Rh–Co catalyst. Even if $([Rh(CO)_2Cl]_2+Co_4(CO)_{12})/SiO_2$ is oxidized to $(Rh^{+}+Co^{2+})/SiO_2$ in air, bimetallic Rh–Co catalysts may still be efficiently obtained under an ethylene hydroformylation atmosphere at 423 K. Catalytic study indicates that the SiO_2-supported catalysts derived from $[Rh(CO)_2Cl]_2$ and cobalt carbonyls ($Co_2(CO)_8$ and $Co_4(CO)_{12}$) had comparable catalytic properties to those of $RhCo_3(CO)_{12}/SiO_2$ in ethylene hydroformylation. Nevertheless, the exact natures of these binary rhodium and cobalt catalysts are not identified in this work and remain to be systematically investigated by multiple techniques.

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