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# Surface behaviors of monometallic and cobalt-containing rhodium catalysts on $SiO_2$ in relation to their catalytic properties for hydroformylation

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**Summary** — The interactions of supported $Rh^0$ and cobalt-promoted $Rh^0$ with the $SiO_2$ surface have been investigated by IR spectroscopy. The supported highly-dispersed rhodium particles derived by $H_2$ decarbonylation of $Rh_6(CO)_{16}/SiO_2$ are oxidized to isolated $Rh^+$ by surface $OH^-$ via heating at 623 K under vacuum, which adsorbs CO to form $Rh^+(CO)_2$. The conventional reduction of a mixture of rhodium and cobalt compounds supported on $SiO_2$ is unlikely to give bimetallic RhCo particles and yield probably monometallic rhodium and cobalt particles. The interaction of $Co^0$ with $Rh^0$ in supported promoted catalysts suppresses the oxidation of $Rh^0$. The results show that the $Co^0$ promoter plays an electron-donating role, thus increasing the electron density of rhodium particles. The electronic effect can be correlated with the observed promotion of catalytic ethylene hydroformylation. IR study also demonstrates that the bimetallic $RhCo_3$ cluster framework is retained intact on the $SiO_2$ surface from thermal decarbonylation of $RhCo_3(CO)_{12}$ under any atmosphere and $RhCo_3(CO)_{12}/SiO_2$ readily regenerated from $RhCo_3$ under CO at room temperature. In situ IR observations indicate that supported $Rh^0$ on $Rh/SiO_2$ is an active site for hydroformylation and $RhCo_3(CO)_{12}/SiO_2$ is responsible itself for the catalysis. Moreover, such a bimetallic cluster catalyst displays an enhanced activity for ethylene hydroformylation, about 20 times that of a $Rh_4(CO)_{12}/SiO_2$-derived monometallic catalyst.

**$SiO_2$-supported rhodium / rhodium oxidation / promotion of cobalt / $SiO_2$-supported $RhCo_3(CO)_{12}$ / preservation of $RhCo_3$ / regeneration of $RhCo_3(CO)_{12}$ / hydroformylation**

**Résumé — Comportement de catalyseurs mono- et bimétalliques au rhodium et rhodium-cobalt supportés sur $SiO_2$ en relation avec leur activité catalytique dans les réactions d'hydroformylation.** *Les interactions du Rh(0) et des mélanges bimétalliques Rh(0)-Co(0) avec une surface de $SiO_2$ ont été étudiées par spectroscopie IR. La décarbonylation de $Rh_6(CO)_{16}/SiO_2$ par l'hydrogène moléculaire conduit à des particules de Rh(0) finement dispersées sur le support qui sont ensuite oxydées en Rh(I) par les $OH^-$ de surface après chauffage à 623 K. L'adsorption de CO conduit à la formation de $Rh^+(CO)_2$. La réduction d'un mélange de dérivés de Rh et de Co supportés sur $SiO_2$ forme vraisemblablement des particules monométalliques de Rh(0) et de Co(0). L'interaction des deux métaux supprime le processus d'oxydation du R(0). Les résultats montrent que le Co(0) agit comme donneur d'électron et augmente ainsi la densité électronique des particules de Rh. Ces effets électroniques peuvent être mis en corrélation avec l'activité catalytique dans l'hydroformylation de l'éthylène. Les études IR montrent également que le noyau bimétallique $RhCo_3$ est conservé lorsque $RhCo_3(CO)_{12}$ est décarbonylé par thermolyse sur la surface de $SiO_2$ et qu'il régénère le cluster de départ par traitement avec CO à température ambiante. D'après les études IR, le Rh(0) supporté sur $SiO_2$ est un site actif dans l'hydroformylation, de plus le système $RhCo_3(CO)_{12}/SiO_2$ est lui même responsable de l'activité catalytique. Ce dernier présente une activité environ 20 fois supérieure à celle du catalyseur monométallique dérivé de $Rh_4(CO)_{12}/SiO_2$ dans l'hydroformylation de l'éthylène.*

**Rh supporté sur $SiO_2$ / oxydation de Rh(0) / $RhCo_3(CO)_{12}$ supporté sur $SiO_2$ / conservation de $RhCo_3$ / régénération de $RhCo_3(CO)_{12}$ / hydroformylation**

## Introduction

The rhodium metal and rhodium compounds are very extensively studied and applied in the field of heterogeneous $C_1$ catalysis, because of their multifunctional activation toward CO and high catalytic activity. Regarding the nature of interaction of rhodium with the surfaces of oxides and CO, many investigators have described their available experimental results on the basis of spectroscopic observations. Ambiguity and debate persist concerning the formation of surface $Rh^+(CO)_2$. Based on IR studies with $Rh/Al_2O_3$, earlier investigators have proposed that the dissociative CO adsorption causes disruption of the Rh–Rh bond followed by oxidation of isolated $Rh^0$ atoms [1, 2], or that protons present as $OH^-$ on the surface oxidize $Rh^0$ atoms [3, 4].

Recently, Gelin et al communicated IR isotopic evidence for a dissociative CO adsorption over rhodium particles supported on zeolite Y, which favors the mechanism of formation of $Rh^+$ sites through CO adsorption [5]. Wong et al demonstrated that the oxidation of $Rh^0$ to $Rh^+$ in zeolite NaY occurs favorably by the combined action of $H^+$ and CO as follows [6]:

$$Rh^0 + H^+ + 2CO \longrightarrow Rh^+(CO)_2 + 1/2\ H_2 \qquad (1)$$

In addition, they suggested that the following equilibria are established between rhodium ions, rhodium metal, $H^+$ and $H_2$ [6, 7].

$$Rh^{3+} + H_2 \longrightarrow Rh^+ + 2H^+ \qquad (2)$$

$$Rh^+ + 1/2\ H_2 \longrightarrow Rh^0 + H^+ \qquad (3)$$

As a result of the surface reactions involving electron transfer, the state of supported rhodium aggregates can be expected to affect catalytic behavior. Hence, establishing the correlation of the electronic state of supported metals with catalysis is of importance. Olefin hydroformylation provides a useful molecular probe of the active sites of heterogeneous catalysts, since it virtually implies a few elementary reactions and a few olefin- and CO-based reactions. A crucial step in the sequence of elementary reactions of hydroformylation is the insertion of CO. Previous works have postulated that the electronic state of oxide-supported rhodium active for CO insertion was +1 [8–11] and the $Rh^0$ state was only responsible for CO dissociation and thus hydrocarbon formation [11]. Recent studies suggested that the linear CO adsorbed on both single $Rh^0$-atom [12, 13] and $Rh^+$-ion [12] sites can participate in CO insertion. What's more, the rhodium *gem*-dicarbonyl derived from $Rh_6(CO)_{16}/SiO_2$ was also demonstrated to be active for CO insertion and ethylene hydroformylation [14].

Over the last two decades, supported second metal-containing rhodium catalysts have drawn great interest from many investigators towards the improvement of catalytic properties of monometallic rhodium for the formation of oxygenates in Fischer–Tropsch synthesis and for olefin hydroformylation. By combination with various second metal components such as Co, Fe, Zn, Mo, Mn, V and Ag as promoters, incorporated-rhodium catalysts display enhanced activities and selectivities for the formation of oxygenates [15–24]. The use of organobimetallic rhodium clusters as precursors leads to unusual catalytic performances for these reactions [25–29]. Nevertheless, the understanding of metal–metal′ and metal–support actions in those systems is still poor. The obtained catalytic results are not interpreted satisfactorily in correlation with the actual state of supported metallic species.

The current work shows the situation of valence change for supported rhodium on $SiO_2$ by CO adsorption, and provides direct IR information on the disruptive oxidation of highly dispersed $Rh_x$ crystallites to single isolated $Rh^+$ sites by surface $OH^-$ groups. Our study is extended to the influence of second metals, such as cobalt in promoted rhodium catalysts and in cobalt-containing bimetallic rhodium cluster catalysts, on the reactivity of $Rh^0$ with surface $OH^-$, from an electronic point of view. We discuss the stabilities of $Rh^0$ and bimetallic Rh–Co clusters supported on $SiO_2$ through an understanding of the interactions of metal–support and metal–metal′. We also compare monometallic and bimetallic rhodium active sites by studies of the surface chemical behaviors of $Rh/SiO_2$, $(Rh+Co)/SiO_2$ and $RhCo_3(CO)_{12}/SiO_2$ using IR spectroscopy and their catalytic properties in ethylene hydroformylation.

## Experimental section

$Rh_4(CO)_{12}$ and $RhCo_3(CO)_{12}$ were synthesized using literature methods [30, 31]. The $SiO_2$ used was a silica 'Aerosil' purchased from Degassa with a surface area of 380 $m^2/g$. *n*-Hexane for use as the solvent was distilled over $P_2O_5$ and stored under Ar over activated 5 Å molecular sieves. The gases used ($H_2$, CO, $C_2H_4$ and Ar) had a purity of 99.99%. Before admission into a reactor and an IR cell, they were passed through activated 5 Å molecular sieves and Mn/MnO to eliminate traces of water and oxygen.

The above two carbonyl clusters were employed as starting materials to prepare, by the impregnation technique under atmospheric Ar, supported rhodium catalysts on $SiO_2$ (60-80 mesh granule) which was predehydroxylated at 673 K under vacuum for 5 h. In situ IR monitoring showed that $Rh_4(CO)_{12}$ transforms to $Rh_6(CO)_{16}$, displaying carbonyl bands at 2080 s and 1802 m(br) $cm^{-1}$, on the $SiO_2$ surface, and $RhCo_3(CO)_{12}$ strongly physisorbs on $SiO_2$ [29, 32] after impregnation from *n*-hexane solution under Ar and removal of the solvent under vacuum at room temperature. The immediate formation of $Rh_6(CO)_{16}$ from $Rh_4(CO)_{12}$ on $SiO_2$ by impregnation under vacuum has been reported earlier [33]. For the preparation of promoted rhodium catalysts, $SiO_2$ was first impregnated with an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ followed by calcination in air at 673 K for 5 h. Then the resulting samples were subjected to impregnation of $RhCl_3 \cdot 3H_2O$ in water. The supported clusters as catalyst precursors were transferred to the reactor under Ar prior to catalytic tests.

The hydroformylation of ethylene was conducted under atmospheric pressure at 423 K in a dynamic reactor where 0.1 g of catalyst precursor with 1% Rh loading was charged. The chloride precursors were calcined in air at 673 K for 5 h and reduced 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) at 423–473 K. The carbonyl precursors were decarbonylated in flowing $H_2$ or $O_2$ at 623 K for 2 h. Afterwards, $H_2$ was directly replaced by the reaction gases at 423–473 K. $O_2$ was replaced by Ar and the catalysts were flushed under Ar for 1 h. Ar was finally replaced by the reaction gases at 423 K. To ensure differential conditions for the reaction, conversion of $C_2H_4$ was governed to below 10%. Data were taken 7 h after the initiation of the 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 ionization detector.

IR spectroscopy was used to determine the surface vibrational properties of supported catalysts and catalyst precursors. Each solid sample was pressed into a wafer of 20 mg ($d$ = 15 mm) in air and placed in a double beam IR cell with $CaF_2$ windows, described in detail elsewhere [34], where the wafer was subjected to the desired treatments. In situ ethylene hydroformylation reactions over supported catalysts were monitored statically in the same IR cell, to which an equimolar gas mixture of $C_2H_4$, CO and $H_2$ at 78 kPa was admitted. All IR spectra were recorded at room temperature in the presence of gas phases by subtracting $SiO_2$ and gaseous contributions, on a Bio-Rad FTS-7 spectrometer.

The metal dispersion was evaluated by $H_2$ chemisorption stoichiometry measured on a ChemiSorb 2800 apparatus. The metal contents of the samples studied were determined by X-ray fluorescence spectroscopy.

## Results

### *Studies on the interaction between $Rh^0$ and the $SiO_2$ surface*

Four samples of 0.3 g of $Rh_6(CO)_{16}/SiO_2$ containing 0.2, 1, 2 and 5% Rh were treated in flowing $H_2$ at 623 K for 2 h and subsequently evacuated at $1.3 \times 10^{-6}$ kPa and at 623 K for 10 min before irreversible $H_2$ adsorption measurements at 293 K. The rhodium dispersions obtained are listed in table I.

**Table I.** Rhodium metal dispersion on the surface of $SiO_2$.

| % Rh | 0.2 | 1 | 2 | 5 |
|---|---|---|---|---|
| % Dispersion | 76 | 41 | 32 | 23 |

In parallel, IR experiments were carried out using CO as a molecular probe to justify distinct metallic surface characters in relation to the amount of rhodium deposited. When $H_2$-reduced wafers of the four samples were exposed overnight to 3.9 kPa of CO after being evacuated at 293 K or treated by the same procedure as in the $H_2$ adsorption, the surfaces exhibited a set of regular IR spectra of adsorbed CO shown in figure 1. Each spectrum consisted of three types of adsorbed CO bands: geminal, linear and bridge. In the case of 0.2% Rh loading, for example, two bands at 2 090 and 2 026 $cm^{-1}$ are assigned to the rhodium *gem*-dicarbonyl, $Rh^+(CO)_2$, and a shoulder at 2 053 $cm^{-1}$ and a broad band at 1 871 $cm^{-1}$ are attributed to linear and bridged CO on $Rh^0$. It is noteworthy that the linear CO and bridged CO bands shifted toward lower wavenumbers as the rhodium loading decreased, ie, as the rhodium dispersion increased. Increasing the metal loading resulted in an enhanced intensity ratio of linear and bridged CO bands to *gem*-dicarbonyl bands.

In contrast, once the same $Rh/SiO_2$ samples underwent 3 h or more of heating under vacuum at 623 K after $H_2$ treatment at 623 K, the adsorption of CO led to another set of IR spectra shown in figure 2. Their shapes were much modified, with a systematically increased intensity of *gem*-dicarbonyl bands with respect to linear and bridged CO bands. The linear and bridged CO bands disappeared on the $Rh/SiO_2$ samples with 1% and lower Rh loadings. By contrast, the sample with 5% Rh loading still presented dominant linear and bridged CO bands at 2 036 and 1 856 $cm^{-1}$. An intermediate spectrum of adsorbed CO was obtained with the 2% Rh sample which showed all three types of bands. The intensities of linear and bridged CO bands in figure 2 (c and d) were remarkably less than those in figure 1 (c and d).

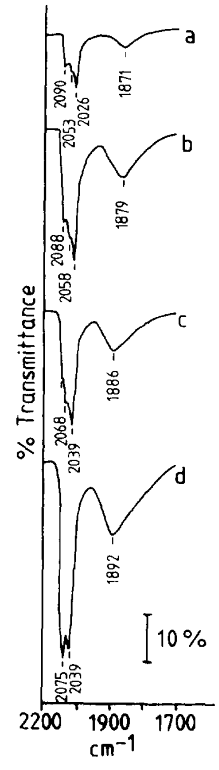

**Fig 1.** IR spectra of $Rh_4(CO)_{12}$-derived $Rh/SiO_2$ under 3.9 kPa of CO for 12 h, after $H_2$ treatment at 623 K for 2 h and evacuation ($1.3 \times 10^{-6}$ kPa) at 623 K for 10 min. (a) 0.2% Rh; (b) 1% Rh; (c) 2% Rh; (d) 5% Rh.

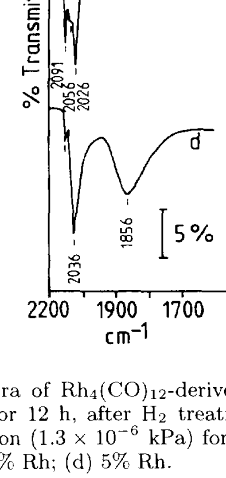

**Fig 2.** IR spectra of $Rh_4(CO)_{12}$-derived $Rh/SiO_2$ under 3.9 kPa of CO for 12 h, after $H_2$ treatment at 623 K for 2 h and evacuation ($1.3 \times 10^{-6}$ kPa) for 3 h. (a) 0.2% Rh; (b) 1% Rh; (c) 2% Rh; (d) 5% Rh.

### *IR studies pertinent to catalytic active valence on Rh/SiO$_2$*

To shed light on the nature of the rhodium active site for hydroformylation, in situ IR spectroscopy was used to monitor an ethylene hydroformylation reaction over Rh/SiO$_2$ run in a static IR cell.

Figure 3 shows the comparative IR spectra obtained on the surface before and after the reaction. A wafer of $Rh_6(CO)_{16}/SiO_2$ containing 1% Rh was first treated under $H_2$ at 623 K for 2 h followed by evacuation at room temperature for 10 min, then exposed to a CO atmosphere at 3.9 kPa. A spectrum similar to that in figure 1(b) resulted, containing the dominant bands at 2 066 and 1 879 cm$^{-1}$ due to Rh$^0$-adsorbed CO, and shoulder bands at 2 096 and 2 036 cm$^{-1}$ attributed to small amounts of $Rh^+(CO)_2$, as illustrated in figure 3(a). However, another identical wafer pretreated in the same manner did not display a pair of geminal CO bands upon exposure to 78 kPa of the reaction gases at room temperature (fig 3(b)). This indicates that the Rh$^+$ ions may be easily reduced to Rh$^0$ atoms by $H_2$. The concomitant appearance of a very weak broad band centered at 1 695 cm$^{-1}$ was noted in the spectrum. According to the literature [14, 35, 36] this band may be ascribed to adsorbed acyl species and propanal, which result from ethylene hydroformylation which might take place over Rh$^0$/SiO$_2$ at room temperature. In addition, the linear CO band shifted from 2 066 to 2 051 cm$^{-1}$. This downward shift has been interpreted by several authors; it results from a decrease in the dipole–dipole interaction of the linear CO caused by dilution from adsorbed H and $C_xH_y$ species on a neighboring rhodium atom [37], or from the coadsorption of H atoms and CO at individual exposed Rh$^0$ sites [38–41]. In the latter case, the rhodium hydride species RhH(CO) and/or $Rh(H)_2(CO)$ are formed, which leads to increased $\pi$ donation from the rhodium into the antibonding $\pi$ orbital of the CO [42, 43]. Increasing the reaction temperature led to a marked enhancement of propanal as expected, and a continuous decrease in the dipole–dipole interaction of the linear CO because of more adspecies arising from the reaction. The fact that the band center, initially observed at 1 695 cm$^{-1}$, shifted to 1 705 cm$^{-1}$ after 3 h of the reaction at 423 K is interpreted in terms of superimposition of the bands for dominant amounts of propanal and small amounts of adsorbed acyl species on the surface, since the former increased with increasing reaction time and temperature.

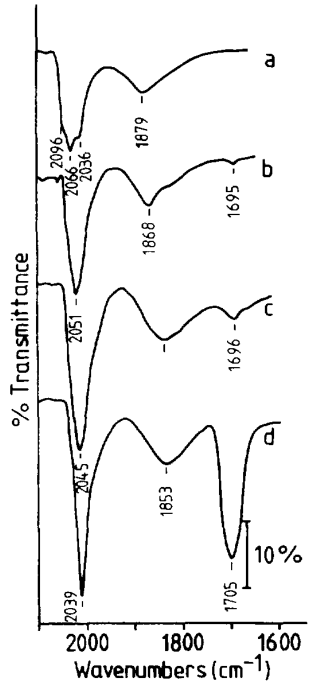

**Fig 3.** IR spectra of $Rh_4(CO)_{12}/SiO_2$-derived samples (1% Rh loading) by $H_2$ treatment at 623 K for 2 h and evacuation ($1.3 \times 10^{-6}$ kPa) at 623 K for 10 min in a static IR cell. (a) under CO at 3.9 kPa for 2 h; under an equimolar mixture (78 kPa) of $C_2H_4$, CO and $H_2$: (b) at 293 K for 1 h; (c) at 331 K for 1 h; (d) at 443 K for 3 h.

### *IR studies on the electronic effects of cobalt on rhodium catalysts and bimetallic effects of Rh–Co cluster catalysts*

In order to reveal the promotional action exerted by cobalt in promoted rhodium catalysts for the formation of oxygenates in ethylene hydroformylation, we determined the forms of adsorbed CO on the catalyst samples by IR spectroscopy. To ensure that the spectral variation caused by addition of cobalt was as striking as possible, all the samples were pretreated under $H_2$ at 623 K for 2 h and subsequently evacuated at $1.3 \times 10^{-6}$ kPa at the same temperature for 3 h, before CO adsorption at room temperature. Co/SiO$_2$ with 1% Co loading showed no adsorbed CO bands under CO. Rh/SiO$_2$ with 1% Rh loading derived from either $Rh_4(CO)_{12}$ or $RhCl_3$, exhibited just *gem*-dicarbonyl features at 2 092 and 2 028 cm$^{-1}$ under CO, as mentioned above. Comparatively, addition of cobalt to Rh/SiO$_2$ gave rise to additional linear and bridged CO bands at 2 043 and 1 858 cm$^{-1}$, in high intensity apart from the *gem*-dicarbonyl bands which appeared weak under the same conditions, as shown in figure 4. The results indicated that the zerovalent rhodium atoms were still formed in the promoted catalysts despite the samples undergoing a longer heating evacuation at 623 K after $H_2$ reduction. This is in obvious contrast with the monometallic rhodium catalysts.

When the bimetallic carbonyl cluster $RhCo_3(CO)_{12}$ was directly used to prepare a cobalt-containing bimetallic rhodium catalyst, the adsorptive behavior of CO on the resulting catalyst differed much from that in the cases with Rh/SiO$_2$ and the promoted rhodium catalysts. In fact, after the precursor $RhCo_3(CO)_{12}/SiO_2$ had been decarbonylated under $H_2$ at 623 K for 2 h, adsorption of CO at 0.2 kPa and at room temperature resulted in two bands at 2 028 and 1 827 cm$^{-1}$ as shown in figure 5(b). They closely resemble the bands characteristic of $RhCo_3(CO)_{12}$ strongly physisorbed on SiO$_2$ (fig 5(a)) which we have recently characterized [32, 44]. This suggests that the initial cluster $RhCo_3(CO)_{12}$ was basically regenerated via recarbonylation of $RhCo_3/SiO_2$. Furthermore, it was surprisingly found that there was no spectral change when $RhCo_3(CO)_{12}/SiO_2$ was subjected to oxidation under

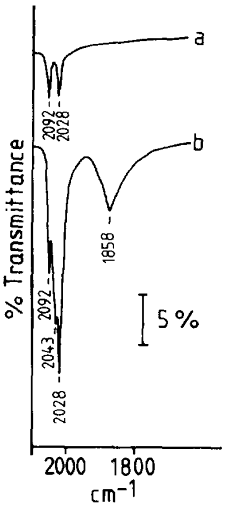

Fig 4. IR spectra after overnight exposure to 3.9 kPa of CO of the following precursor-derived samples (1% Rh loading) by $H_2$ treatment at 623 K for 2 h and evacuation ($1.3 \times 10^{-6}$ kPa) at 623 K for 3 h. (a) $Rh_4(CO)_{12}/SiO_2$ or $RhCl_3/SiO_2$; (b)[$RhCl_3$ + $Co(NO_3)_2$]/$SiO_2$ (Co/Rh = 1:1).

atmospheric oxygen at 623 K for 2 h, followed by CO adsorption, as shown in figure 5(c). This indicates that an identical result is obtained on recarbonylation of the bimetallic catalyst surface to give the starting supported cluster regardless of the atmosphere used.

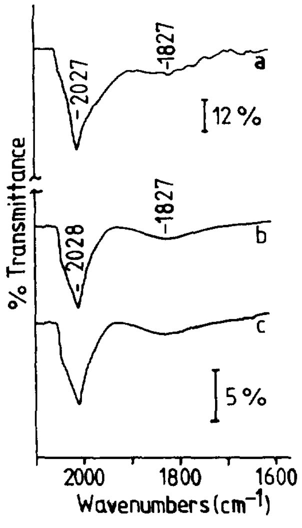

Fig 5. IR spectra of $SiO_2$-supported $RhCo_3(CO)_{12}$. (a) $RhCo_3(CO)_{12}/SiO_2$ under vacuum ($1.3 \times 10^{-6}$ kPa); (b) under 0.2 kPa of CO after 2 h of $H_2$ decarbonylation of $RhCo_3(CO)_{12}/SiO_2$ (1% Rh loading) at 623 K; (c) under 0.2 kPa of CO after 2 h of $O_2$ decarbonylation of $RhCo_3(CO)_{12}/SiO_2$ (1% Rh loading) at 623 K.

Figure 6 presents the in situ surface IR spectra obtained during an ethylene hydroformylation reaction run at 78 kPa and at 423 K over the catalyst decarbonylated from $RhCo_3(CO)_{12}/SiO_2$ by $H_2$ in a static IR cell.

The carbonyl bands corresponding to the regenerated $RhCo_3(CO)_{12}/SiO_2$ under a CO pressure, remained essentially unchanged upon exposure of $RhCo_3/SiO_2$ to the reaction atmosphere at 423 K, except that trace amounts of $Rh_6(CO)_{16}/SiO_2$ appeared, showing a shoulder band at 2 084 $cm^{-1}$. We have demonstrated that the production of $Rh_6(CO)_{16}$ in this situation is related to the dissociation of $RhCo_3(CO)_{12}$ on the $SiO_2$ surface under a higher CO pressure [32, 44].

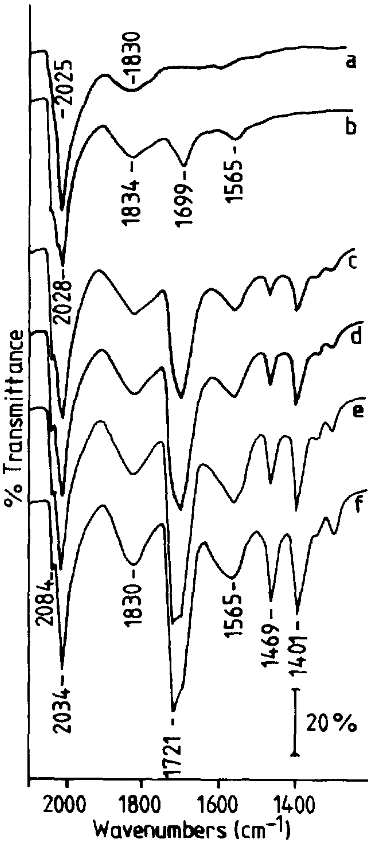

Fig 6. IR spectra of $RhCo_3(CO)_{12}/SiO_2$-derived samples in a static IR cell. (a) $RhCo_3(CO)_{12}/SiO_2$ under vacuum ($1.3 \times 10^{-6}$ kPa); after exposure of $H_2$ decarbonylated $RhCo_3(CO)_{12}/SiO_2$ to an equimolar mixture (78 kPa) of $C_2H_4$, CO and $H_2$ at 423 K for: (b) 15 min; (c) 3 h; (d) 5.5 h; (e) 15.5 h; (f) 108 h.

$Rh_6(CO)_{16}/SiO_2$ is known to be inactive for hydroformylation [13, 45, 46]. The band ascribed to $SiO_2$-adsorbed propanal and acyl species at 1 699 $cm^{-1}$ and the bands due to $SiO_2$-adsorbed propanal at 1 469 and 1 401 $cm^{-1}$ were noticed to develop with reaction time. The upward shift of the band initially situated at 1 699 $cm^{-1}$ to 1 721 $cm^{-1}$ after 108 h of the reaction, is due to the presence of prevailing amounts of propanal over adsorbed acyl species on the surface. Because the recarbonylated catalyst under catalytic conditions can be identified as $RhCo_3(CO)_{12}/SiO_2$ and was essentially accompanied by the appearance and gradual increase of the hydroformylation products throughout the prolonged reaction, it is suggested that $RhCo_3(CO)_{12}/SiO_2$

**Table II.** Catalytic properties of $SiO_2$-supported catalysts[a] in atmospheric ethylene hydroformylation[b].

| *Starting material* | *Co:Rh* *(Atomic ratio)* | *Activity*[c] *(mol/Rh mol/min)* $C_2H_6$ | *Oxygenates*[d] | *Selectivity (mol %)* *Oxygenates* | n-$C_3H_7OH$ |
|---|---|---|---|---|---|
| $Co_2(CO)_8$ | | 0 | 0 | – | – |
| $Rh_4(CO)_{12}$ | | 0.42 | 0.37 | 47 | 0 |
| $RhCl_3$ | | 0.25 | 0.20 | 44 | 0 |
| $RhCl_3$ + $Co(NO_3)_2$ | 1:2 | 0.16 | 0.46 | 74 | 3 |
| $RhCl_3$ + $Co(NO_3)_2$ | 1:1 | 0.57 | 0.91 | 61 | 1 |
| $RhCl_3$ + $Co(NO_3)_2$ | 3:1 | 0.35 | 0.96 | 74 | 9 |
| $RhCo_3(CO)_{12}$ | | 3.63 | 6.56 | 64 | 6 |
| $RhCo_3(CO)_{12}$[e] | | 5.32 | 9.95 | 65 | 8 |

[a] $Co/SiO_2$ with 1.7% Co loading, the others with 1% Rh loading, pretreated under $H_2$ at 623 K; [b] at 423 K, $C_2H_4$:CO:$H_2$ = 20:20:20 mL/min; [c] data were taken 7 h after the initiation of reaction; [d] $C_2H_5CHO$ + $n$-$C_3H_7OH$; [e] pretreated under $O_2$ at 623 K.

is actively and stably responsible for the catalysis. In addition, a strange band at 1 565 $cm^{-1}$ emerged on the surface immediately after initiation of the reaction and was concomitant with the formation of propanal. The attribution of this band remains unclear. We suspect that it might implicate a relatively stable hydroformylation intermediate adsorbed on supported bimetallic Rh–Co cluster catalyst because according to our work the use of either cobalt-containing bimetallic or cobalt-promoted rhodium catalysts in ethylene hydroformylation was always accompanied by the presence of this IR feature.

### *Catalytic investigations of $SiO_2$-supported monometallic and cobalt-containing rhodium catalysts*

To establish a general comparison of catalytic performances of mono- and bimetallic catalysts in ethylene hydroformylation, $Rh/SiO_2$, $(Rh+Co)/SiO_2$ and $RhCo_3(CO)_{12}/SiO_2$ were tested under atmospheric pressure at 423 K. The data obtained are listed in table II. As compared with a $RhCl_3$-derived monometallic $Rh/SiO_2$ catalyst, added cobalt in the promoted rhodium catalysts enhanced the hydroformylation and hydrogenation rates, and improved significantly the hydroformylation selectivity. The exhibited activities to oxygenates were 2.3–4.8 times that of that $Rh/SiO_2$ catalyst, showing the significant promoting effects of cobalt on the catalysis of monometallic rhodium. Meanwhile the slight production of $n$-propanol was detected. The $RhCo_3(CO)_{12}$-derived catalysts exhibited an incomparable superiority, with considerably higher hydroformylation activities than the others. For the $RhCo_3(CO)_{12}/SiO_2$ system, it was very surprising to note that the catalyst derived by decarbonylation under $O_2$ at 623 K displayed even higher hydroformylation activity than the catalyst derived by decarbonylation under $H_2$ at 623 K. Relative to a $Rh_4(CO)_{12}$-derived $Rh/SiO_2$ catalyst, the catalytic activities and selectivities of the $RhCo_3(CO)_{12}$-derived catalysts for the formation of oxygenates were increased respectively by 18–27 times and approximately 17%. Moreover they had a good catalytic stability during 115 h of reactions. The results indicated a probable Rh–Co bimetallic concerted role for the catalytic hydroformylation.

## Discussion

In virtue of our IR results for CO adsorption on the $Rh_4(CO)_{12}$- or $Rh_6(CO)_{16}$-derived $Rh/SiO_2$ with rhodium loadings below 5%, the rhodium surface after $H_2$ thermal treatment, even though its loading is as low as 0.2%, gives rise to a mixture of rhodium *gem*-dicarbonyl, $Rh^0$-adsorbed linear CO and $Rh^0$-adsorbed bridged CO under CO as shown in figure 1. This complex CO adsorption has also been observed on $Rh/SiO_2$ by other authors [12, 47–49]. Combining the measurements of $H_2$ chemisorption with the IR observations, it is deduced that decreasing rhodium loading results in the increase of rhodium dispersion and the enhancement of $Rh^+(CO)_2$. Therefore, the extent to which metallic rhodium particles are oxidized to $Rh^+$ ions on a partially dehydroxylated $SiO_2$ surface is associated with rhodium dispersion. More dispersed metal atoms are more easily oxidized, according to the intensity ratios of *gem*-dicarbonyl bands to $Rh^0$-adsorbed CO bands in figure 1. Combining the present results with the work of Basu et al [4], the proportion of oxidized $Rh^0$ on $SiO_2$ is lower than that on $Al_2O_3$. Nevertheless, it is unclear whether CO, serving as an IR probe, is instrumental in the oxidation. Our IR data provide direct evidence in favor of the oxidative pathway of highly-dispersed rhodium by surface $OH^-$ or $H^+$. After the freshly $H_2$-reduced $Rh/SiO_2$ samples have been treated under vacuum ($1.3 \times 10^{-6}$ kPa) at 623 K for 3 h. $Rh^0$ atoms actually undergo strong interaction with the acidic $OH^-$ groups on the $SiO_2$ surface, which can effectively form $Rh^+$ sites:

$$2\,Rh^0 + 2H^+ \longrightarrow 2\,Rh^+ + H_2 \qquad (4)$$

This produces much more atomically-dispersed $Rh^+$ sites than with a temperature of 293 K. As a consequence, a greatly enhanced intensity of *gem*-dicarbonyl bands relative to linear and bridged CO bands was observed in figure 2. Especially on the surface of less than 1% Rh loading, $Rh^0$ atoms seemed to convert completely to $Rh^+$ ions after having interacted with $OH^-$ groups, the spectra showing only doublet features under CO. The small proportion of $Rh^+(CO)_2$ with the *gem*-dicarbonyl shoulder bands observed in figure 1 may also result from $Rh^0$ oxidation after 10 min of evacuation at 623 K. Comparing the two sets of IR spectra in figures 2 and 3, we infer that the direct oxidation of $Rh^0$ by surface $OH^-$ play a key role in the formation of $Rh^+(CO)_2$, since the proportion of the latter increases with increasing oxidizability of $OH^-$ at a given Rh loading. Here it is worth recalling that only $Rh^+(CO)_2$ is formed under CO on reduced $Rh/Al_2O_3$ at 2.2% Rh loading [4]. That means that the surface $OH^-$ of $Al_2O_3$ is a stronger oxidant than that of $SiO_2$. In contrast, the interaction of CO with highly dispersed $SiO_2$-supported rhodium fails to lead to appreciable formation of $Rh^+(CO)_2$ within a reasonable time as seen in figure 1(a). Moreover, the amount of $Rh^+(CO)_2$ on $Rh/SiO_2$ develops to just a small extent with increasing CO pressure [4, 12]. Hence, the $Rh^0 \rightarrow Rh^+$ transition is highly dependent on the oxidizability of surface $OH^-$, and appears independent of the adsorption of CO in the presence of both surface $OH^-$ and gaseous CO. We suggest that the interaction mechanism of $Rh^0$ with surface $OH^-$ and CO involves the oxidation of $Rh^0$ to $Rh^+$ by surface $OH^-$ before CO coordination to form $Rh^+(CO)_2$.

In this work, although the $Rh/SiO_2$ catalyst with 1% Rh loading prepared from $Rh_4(CO)_{12}$ by $H_2$ treatment and 10 min of evacuation at 623 K, yielded some $Rh^+(CO)_2$ under a CO atmosphere as shown in figure 3(a), it instead produced only linear and bridged CO adsorbed on $Rh^0/SiO_2$ under a mixture of $C_2H_4$, CO and $H_2$. This shows that small amounts of $Rh^+$ ions formed probably via the oxidation of $Rh^0$ atoms by surface $OH^-$ during the short evacuation treatment at 623 K, are rereduced by $H_2$ at a temperature as low as 293 K. On the other hand, it appears to further demonstrate that surface $OH^-$ is responsible for the oxidation of $Rh^0$ independently of the dissociative CO adsorption. We speculate that $Rh/SiO_2$ catalysts resulting from rhodium compounds by $H_2$ decarbonylation or reduction normally contain only $Rh^0$ atoms on the surface if the ultimate evacuation process is not involved prior to CO adsorption. The result is consistent with that of Basu et al who have assumed not only the involvement of surface $OH^-$ in the disruptive oxidation of $Rh_x$ crystallites to give $Rh^+(CO)_2$ in equation 5, but also its inverse reaction [4].

$$1/x Rh_x^0 + OH^- + 2\,CO \rightarrow Rh^+(CO)_2 + 1/2\,H_2 + O^{2-} \qquad (5)$$

Also in agreement with the involvement of $H^+$ in the oxidation and the interconversion between $Rh^0$ and $Rh^+$ on zeolite Y [7], the introduction of $H_2$ enables equilibrium 3 to shift to the right on $SiO_2$. It is logical to assess that the reduction of $Rh^+$ proceeds more easily on $SiO_2$ than on zeolite Y and $Al_2O_3$. At the same time, several groups have demonstrated that in the presence of CO + $H_2$, the formation of $Rh^+(CO)_2$ on $Rh/SiO_2$ and $Rh/Al_2O_3$ is suppressed and the observed IR spectra exhibit only linear and bridged CO bands [39–41, 50]. In our case, since the observed $Rh^0$-adsorbed CO species were obviously concomitant with the formation of propanal on the surface, and no trace of $Rh^+(CO)_2$ was invoked with the increase of reaction temperature up to 423 K, the catalytic hydroformylation active site is likely to be $Rh^0/SiO_2$.

Insomuch as $H_2$ is capable of preventing the oxidation of metallic rhodium particles on the surface, $Rh/SiO_2$ catalysts pretreated with $H_2$ should present all their surface rhodium atoms available as active sites under a hydroformylation atmosphere.

The view of zerovalent rhodium as the heterogeneous hydroformylation active site has also been claimed by other groups. Takahashi et al, who studied the zeolite Y-supported rhodium system by means of IR and XPS, indicated that the catalytic activity for ethylene hydroformylation can be considerably enhanced only when $Rh^+(CO)_2$ is reduced with $H_2$ to metallic rhodium particles [13]. Detailed research by Chuang and Pien on $Rh/SiO_2$ catalysts treated in different conditions showed using IR spectroscopy that the linear CO adsorbed on both $Rh^0$ and $Rh^+$ sites participates in CO insertion, leading to the formation of propanal from $C_2H_4$ and $H_2$ [12]. Although certain $Rh^+$ sites on which specific CO groups are adsorbed and coordinated can become active for hydroformylation [12, 14], reduced $Rh/SiO_2$ catalysts cannot give $Rh^+$ species under steady catalytic hydroformylation conditions and $Rh^+$ species, if any, are readily reduced under a $H_2$-containing atmosphere. Moreover, supported $Rh^+$ species display much lower hydroformylation activity than supported $Rh^0$ under atmospheric pressure [12, 14]. Accordingly, only the $Rh^0$ active site is of popular catalytic significance.

With regard to the promotional roles of second metals on the catalysis, addition of cobalt to $Rh/SiO_2$ does indeed influence the electronic state of rhodium according to the IR observations. Under oxidation conditions, namely through surface evacuation treatment at $1.3 \times 10^{-6}$ kPa and 623 K, $Rh^0$ completely converts to $Rh^+$ on $SiO_2$, exhibiting just the geminal CO bands under CO, whereas the oxidation of $Rh^0$ in the presence of cobalt is strongly inhibited, for the intense adsorbed linear and bridged CO bands appear under CO, as shown in figure 4(b). Thus, cobalt atoms in the promoted catalysts can be viewed as electron donors to interact effectively with rhodium atoms and thus to increase the electron density of rhodium metal ensembles. In this manner the scission of the Rh–Rh bond due to oxidative addition of surface $OH^-$, resulting in isolated $Rh^+$ ions, can be prevented. In order to explain the promotion of catalytic formation of oxygenates in ethylene hydroformylation, we suggest that $Co^0$ atoms exert an electron-donating action on $Rh^0$ atoms in the promoted catalysts. A similar promoting effect of cobalt on various noble metal catalysts for the formation of oxygenates in the CO + $H_2$ reaction and for hydroformylation, has been observed by other authors [15, 16]. As for the oxidation state of the metals in the actual promoted catalysts and the nature of such supported catalysts, it is necessary to cite the pertinent work of van't Blik et al concerning the temperature-programmed reduction (TPR) and temperature-programmed oxidation (TPO) of $SiO_2$-supported (Rh + Co) systems [51]. During a TPR process up to 623 K, the reduction of cobalt ions such as $Co_3O_4$ and CoO is facilitated by the presence of rhodium. Both rhodium and cobalt metallic particles are readily formed in cobalt-promoted rhodium catalysts after reduction at 623 K. They are not isolated from each other but are in close contact on the surface.

It appears much more interesting to discuss the surface chemical behavior of $SiO_2$-supported $RhCo_3(CO)_{12}$

and the promotional role of cobalt in the bimetallic cluster in relation to the catalytic results in ethylene hydroformylation. In virtue of our IR observations, the production of surface carbonyls having the bands at 2 028 and 1 827 $cm^{-1}$, after $RhCo_3(CO)_{12}/SiO_2$ has been decarbonylated under either $H_2$ or $O_2$, can be interpreted by the regeneration of $RhCo_3(CO)_{12}$ present in the strongly physisorbed form from $RhCo_3/SiO_2$. The $RhCo_3$ framework is hence suggested to be well-retained on the surface in spite of the drastic calcination treatments. This is contrary to the case of $Rh_6(CO)_{16}/SiO_2$ where the $Rh_6$ framework is not retainable on the surface but instead agglomerates into metallic rhodium particles upon decarbonylation under the same conditions [52]. It is worth pointing out that bimetallic particles are generally readily oxidized to monometallic components. Many examples have been shown of segregation of supported bimetallic catalysts and concomitant oxidation of metallic particles after thermal treatments under oxygen atmospheres [51, 53–55], among which a bimetallic Rh–Co catalyst was nearly completely converted to $Rh_2O_3$ and $Co_3O_4$ on $SiO_2$ after TPO in 5% $O_2$/He up to 623 K [51]. However, the $RhCo_3$ cluster was found to remain very stable on $SiO_2$ after 2 h of treatment at 623 K under atmospheric oxygen in our case. This surprising result seems to indicate particular strong $RhCo_3$-support and Rh–Co interactions that are able to preserve the $RhCo_3$ framework and prevent the bimetallic cluster from $O_2$ oxidation. In fact, no $Rh^+$ or $Rh^{3+}$ fragment was detected over $RhCo_3/SiO_2$ under CO following the oxidation treatment. In contrast, $Rh^+(CO)_2$ was more or less discerned over cobalt-promoted $Rh/SiO_2$ under CO after reduction followed by oxidation under vacuum. In order to understand the cause of stabilization of $RhCo_3$ on $SiO_2$, we have recently advanced a hypothesis concerning a particular strong cluster–support interaction, via nucleophilic attack of surface oxygen on the cobalt atoms of $RhCo_3$ with the synergetic electron-donating action of cobalt atoms to rhodium atom [29, 32]. This kind of interaction may prevent the Rh–Co bond from thermal destruction and oxidative addition by surface $OH^-$ as well as dissociation by CO. Furthermore, increasing the temperature results in an enhancement of the $RhCo_3$–$SiO_2$ interaction so as to further stabilize the $RhCo_3$ cluster [44]. Yokoyama and Ichikawa et al previously reported the interactions of carbonyl Rh–Co clusters with carbon and $Al_2O_3$ by an EXAFS study [56, 57]. They suggested that the $RhCo_3$ and $Rh_2Co_2$ cluster frameworks could be preserved on both kinds of surfaces, concomitant with the metal–oxygen bonding, after $H_2$ treatment at 673 K. This is consistent with the present observations with $RhCo_3(CO)_{12}/SiO_2$.

The above interpretation of surface chemistry gains support from the results of the catalytic investigation. The enormous difference in hydroformylation activity between the $RhCo_3(CO)_{12}$-derived catalysts and the cobalt-promoted catalysts would arise from the different natures of the two categories of metallic surfaces. The fact that the former display much higher catalytic activities than the $Rh_4(CO)_{12}$-derived catalyst seems to result reasonably from the preservation of the bimetallic $RhCo_3$ cluster on the surface, in agreement with the IR characterization results. Although the promotion of added cobalt to $Rh/SiO_2$ results in a significant increase in catalytic activity, on the basis of our IR results and the literature the surface species characterized do not involve bimetallic Rh–Co particles or $RhCo_3$ clusters. In contrast, $RhCo_3(CO)_{12}/SiO_2$ is not only regenerable by exposure to CO after decarbonylation, but also stable under catalytic hydroformylation conditions, as evidenced by in situ IR study. The convincing results of in situ IR monitoring demonstrate that the molecular $SiO_2$-supported $RhCo_3(CO)_{12}$ is itself catalytically-active for ethylene hydroformylation. The observed high activity and stability are believed to be attributed to the supported bimetallic cluster. The reason why thermal decarbonylation under $O_2$ results in an increased hydroformylation activity, with respect to thermal decarbonylation under $H_2$ at the same temperature, for $RhCo_3(CO)_{12}/SiO_2$, remains unknown. It might be related to the increase in the $RhCo_3$ cluster dispersion on the surface after $O_2$ treatment.

## Conclusions

1. The oxidation chemistry of $Rh^0$ on $SiO_2$ under CO can be translated by the oxidation of highly-dispersed metallic rhodium particles to isolated $Rh^+$ by surface $OH^-$, which converts to $Rh^+(CO)_2$ after adsorbing CO, irrespective of dissociative CO adsorption on $Rh^0$. It is suggested that $SiO_2$-supported rhodium catalysts derived from $Rh_4(CO)_{12}$ or $Rh_6(CO)_{16}$ by $H_2$ decarbonylation, contain only $Rh^0$ on the surface, which is an active site for hydroformylation.

2. In cobalt-promoted rhodium catalysts, $Co^0$ behaves as an electron donor to $Rh^0$ to increase the electron density of metallic rhodium particles. The interaction of the second metal with $Rh^0$ significantly promotes $Rh^0/SiO_2$ catalysis for ethylene hydroformylation. However, the conventional preparative technique cannot lead to the formation of bimetallic Rh–Co catalysts from two different metal compounds.

3. By use of $RhCo_3(CO)_{12}$, the bimetallic $RhCo_3$ framework has been found to be preserved intact on the $SiO_2$ surface, even if $RhCo_3(CO)_{12}/SiO_2$ is decarbonylated under $O_2$ at 623 K. $RhCo_3/SiO_2$ is readily recarbonylated to $RhCo_3(CO)_{12}/SiO_2$. Under catalytic conditions, $RhCo_3(CO)_{12}/SiO_2$ has been characterized to be active and stable for ethylene hydroformylation. $RhCo_3(CO)_{12}/SiO_2$ exhibits considerably enhanced hydroformylation activity as compared with $Rh/SiO_2$.

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