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IR studies on CO insertion reaction with SiO_2-supported rhodium active site

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Summary — The reactions of Rh^0-coordinated CO and Rh^0-adsorbed CO with $C_2H_4 + H_2$ at 293 K were monitored by IR spectroscopy. The linear CO adsorbed on Rh^0/SiO_2 is consumed with formation of propanal whereas the coordinated CO in $Rh_6(CO)_{16}/SiO_2$ and its derivative do not participate in CO insertion. IR study of the thermal decomposition of $Rh_6(CO)_{16}/SiO_2$ indicates that the cluster can be stabilized on the surface up to 548 K by gaseous CO under hydroformylation conditions. Moreover the $Rh_6(CO)_{16}/SiO_2$ system exhibits increased catalytic hydroformylation activity with reducing coordinated CO. These results show that coordinative unsaturation on the Rh^0 surface is necessary for heterogeneously rhodium-catalyzed hydroformylation and that totally decarbonylated Rh^0/SiO_2 is most effective.

SiO_2-supported rhodium(0) / coordinative saturation / CO insertion / hydroformylation

Résumé — Études infrarouges sur la réactivité d'insertion de CO avec site actif de rhodium supporté sur SiO_2. *Les réactions de CO coordonné à Rh^0 et de CO adsorbé sur Rh^0 avec $C_2H_4 + H_2$ à 293 K ont été suivies par spectroscopie infrarouge. Le CO linéaire adsorbé sur Rh^0/SiO_2 est consommé avec formation du propanal, tandis que le CO coordonné dans $Rh_6(CO)_{16}/SiO_2$ et ses dérivés ne participe pas à l'insertion de CO. Une étude infrarouge de la thermodécomposition de $Rh_6(CO)_{16}/SiO_2$ indique que le cluster peut être stabilisé à la surface jusqu'à 548 K par CO gazeux dans les conditions d'hydroformylation. De plus le système $Rh_6(CO)_{16}/SiO_2$ présente une activité catalytique d'hydroformylation qui augmente à mesure de la perte de CO coordonné. Ces résultats montrent que l'insaturation coordinative au site de Rh^0 est nécessaire pour hydroformylation hétérogène en présence du rhodium et que Rh^0/SiO_2 totalement décarbonylé est le plus efficace.*

Rhodium(0) supporté sur SiO_2 / saturation coordinative / insertion de CO / hydroformylation

Introduction

The insertion of CO into an $M-C_nH_{n+1}$ bond is a key elementary step in olefin hydroformylation and Fisher-Tropsch synthesis. Much attention has been drawn to obtaining mechanistic information about it for CO site-coordinated and adsorbed on various metals [1-6]. Since rhodium catalysts are the most active for hydroformylation, more detailed studies have been performed concerning the CO insertion which might occur on different types of surface rhodium sites [3-6], with increasingly developing heterogeneity especially supporting molecular catalysis for olefin hydroformylation [7-11]. It is now generally accepted that the linear CO adsorbed at both single Rh^0 atom and Rh^+ ion sites can participate in CO insertion. Nevertheless, only single Rh^0 atom sites are of popular catalytic significance under steady heterogeneous hydroformylation conditions although Rh^+ ions are also able to serve as active sites.

It is well known that the carbonyl rhodium clusters such as $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ provide satisfactory molecular models for studying the surface chemistry and heterogeneous catalysis of Rh^0-CO. These two clusters have been tested as catalysts of olefin hydroformylation. They have proven not to serve as true catalysts themselves either in solution [12] or in supported forms [6, 13]. However, under homogeneously catalytic conditions, both $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ are converted to the coordinatively saturated rhodium complex $HRh(CO)_3$ which is the active species. Under heterogeneously catalytic conditions, the supported $Rh_6(CO)_{16}$-derived active site is likely to involve only metallic rhodium particles. However, it is not elucidated in the literature why such coordinatively-saturated rhodium carbonyls are relatively inactive compared to coordinatively-unsaturated rhodium in olefin hydroformylation.

Therefore, the present study was focused on $Rh_6(CO)_{16}$-derived SiO_2-supported Rh^0 on which the reactions of adsorbed CO and coordinated CO with $C_2H_4 + H_2$ and ethylene hydroformylation were carried out. Our work was aimed at identifying the type of CO species on surface Rh^0 that participates in the CO insertion step in ethylene hydroformylation, thus shedding light on the nature of active CO species.

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* Correspondence and reprints

Experimental section

$Rh_4(CO)_{12}$ was synthesized as described by Chini and Martinengo [14]. The SiO_2 used was a non-porous silica 'Aerosil' purchased from Degussa, with a surface area of 200 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 the IR cell, they were passed through activated 5 Å molecular sieves and Mn/MnO to eliminate traces of water and oxygen.

$Rh_4(CO)_{12}$ was employed as the starting material to prepare SiO_2-supported rhodium carbonyls and rhodium catalysts. The supporting SiO_2 (powder or wafer), after predehydroxylation under vacuum (1.3×10^{-6} kPa) at 673 K for 5 h, was impregnated with $Rh_4(CO)_{12}$ from *n*-hexane solution under atmospheric Ar using a Schlenk technique. The results of in situ IR monitoring indicate that the initial $Rh_4(CO)_{12}$ cluster transformed into $Rh_6(CO)_{16}$, displaying the bands at 2 080 s and 1 802 (m br) cm^{-1}, consistent with an earlier study [15].

IR spectra were measured in Bio-Rad FTS-7. Each solid sample was compressed into a wafer of 10 mg (d = 15 mm) and placed in a double beam IR cell with CaF_2 windows. The wafer then underwent the desired treatments. IR spectra were recorded at room temperature in the presence of the gas phase, by subtracting the SiO_2 and gaseous contributions.

Results

Study related to the catalytic active site for hydroformylation

To clarify and confirm the rhodium species active for the hydroformylation reaction in terms of their valence states and CO adsorption, the gas phase–solid phase reaction was followed by IR spectroscopy in situ under an atmosphere in the static IR cell. Figure 1 shows the results obtained when a wafer of the catalyst containing 2% Rh freshly derived by H_2 treatment from $Rh_6(CO)_{16}/SiO_2$ was exposed to a mixture of C_2H_4, CO and H_2 (1:1:1 molar ratio). In the ν(CO) region, only two bands at 2 026 and 1 896 cm^{-1} emerged on the surface at 293 K. These two bands are assigned to the adsorbed linear and bridged CO respectively. The in situ catalytic reaction was left to proceed at 448 K. During reaction for 3 h, the adsorbed CO spectrum remained unchanged. A fairly intense band at 1 706 cm^{-1} and two weak bands at 1 446 and 1 383 cm^{-1} appeared on the surface at the end of reaction. These three bands are due to the C=O vibrations of C_2H_5CHO. The results indicated the production of propanal via ethylene hydroformylation over Rh/SiO_2, which were adsorbed on the SiO_2 surface.

Studies on the thermal decomposition of $Rh_6(CO)_{16}/SiO_2$ under hydroformylation atmospheres

Based on the IR characterization of the metal catalyst, we were interested in investigating the chemical and catalytic behavior of the rhodium carbonyl cluster supported on SiO_2 under hydroformylation conditions. In order to elucidate the contribution of carbonyl species to this catalysis, $Rh_6(CO)_{16}$ was used to simulate surface carbonyl rhodium species since molecular metallic clusters are models of small metallic particles in terms of their geometric and electronic properties [16].

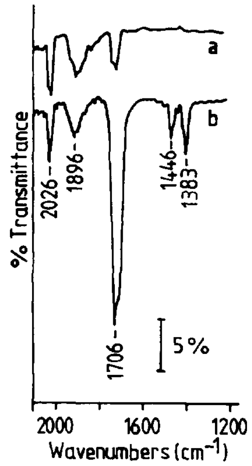

Fig 1. IR spectra in the ν(CO) region of 2% Rh loading $Rh_4(CO)_{12}$-derived Rh/SiO_2 catalyst after 2 h treatment at 623 K.
a. After 1 h exposure to an atmospheric equimolar mixture of C_2H_4, CO and H_2 at 293 K in a static IR cell;
b. after 3 h heating at 448 K following a.

An equimolar mixture (78 kPa) of C_2H_4, CO and H_2 was admitted to a wafer of $Rh_6(CO)_{16}/SiO_2$ derived from $Rh_4(CO)_{12}$ in the static IR cell. This system was successively thermally treated. Figure 2 shows the IR spectroscopic results obtained during this process. According to the spectra, there was no evolution of the cluster features after 0.5 h treatments at 378 K and 403 K. However, a band at 1 706 cm^{-1}, corresponding to propanal, appeared with very weak intensity. The intensity of this band increased progressively with temperature as shown in the following spectra. By contrast, there was no concomitant depletion of the bands characteristic of $Rh_6(CO)_{16}$ until 548 K. This indicates that the supported cluster was able to maintain its integrity under the reaction gases at this stage. At 578 K, weakening of the intensity of the $Rh_6(CO)_{16}$ bands was observed, accompanying the appearance of two small bands at 2 044 and 1 863 cm^{-1} which are due to the linear and bridged carbonyls on Rh^0. This shows that the cluster started to transform into metallic aggregates by decarbonylation. When the temperature was raised to 603 K, the decarbonylation of $Rh_6(CO)_{16}$ was nearly complete.

The evolution of the gas-phase spectrum in the 3 300–2 800 cm^{-1} region as a function of the above thermal decomposition of $Rh_6(CO)_{16}/SiO_2$ should be noticed. After a 3 h treatment at 443 K, the ethylene spectrum decreased slightly in intensity with no observable emergence of the ethane bands. This is probably due to the fairly selective hydroformylation of ethylene. At higher temperatures, the marked observation of the ethane bands at 3 012, 2 966, 2 930 and 2 889 cm^{-1} which are superimposed on the ethylene bands, is attributed to ethylene hydrogenation in competition with ethylene hydroformylation. It was estimated that the consumption of ethylene was approximately 20% by the end of the treatment at 578 K and 30% by the end of

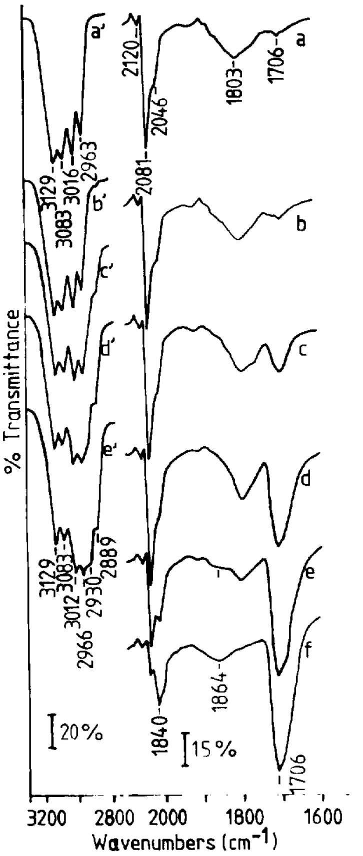

Fig 2. IR spectra after consecutive thermal treatments of $Rh_6(CO)_{16}/SiO_2$ under an equimolar mixture of C_2H_4, CO and H_2 (total pressure: 78 kPa) in a static IR cell.
Surface: a. 378 K for 0.5 h; b. 403 K for 0.5 h; c. 443 K for 3 h; d. 548 K for 3 h; e. 578 K for 3 h; f. 603 K for 3 h.
Gas phase: a'. 293 K for 2 h; b'. corresponding to c; c'. corresponding to d; d'. corresponding to e; e'. corresponding to f.

treatment at 603 K, mostly due to ethylene hydrogenation. It follows that the majority of the initial gas mixture was kept intact throughout this heat treatment of $Rh_6(CO)_{16}/SiO_2$ under C_2H_4 + CO + H_2.

For the purpose of understanding the stabilizing role of the reaction gases (H_2 (39 kPa), C_2H_4 (26 kPa) and CO (26 kPa)) on $Rh_6(CO)_{16}/SiO_2$ as described above, thermal decomposition of the supported cluster under vacuum (1.3×10^{-3} kPa) was likewise monitored by IR spectroscopy.

The supported cluster presented poor thermal stability under vacuum, H_2 and C_2H_4. Remarkably, it decomposed at around 373 K in each case to metallic rhodium particles covered with coordinated CO, which showed linear and bridged bands around 2 026 and 1 868 cm^{-1}. A similar thermal instability of $Rh_6(CO)_{16}/SiO_2$ under vacuum and H_2 was previously reported by Bilhou et al [17].

Figure 3 shows the results of IR monitoring during thermal decomposition of $Rh_6(CO)_{16}/SiO_2$ under CO. The supported cluster was stable under CO up to 545 K judging from the relative intensity of the $Rh_6(CO)_{16}$ bands with varying temperature. When the temperature reached 583 K, two bands at 2 062 and 1 882 cm^{-1}, which are assigned to the linear and bridged carbonyls on Rh^0, appeared with decreasing $Rh_6(CO)_{16}$ band intensity. This indicates that rhodium aggregates started to form at the expense of the cluster around this temperature.

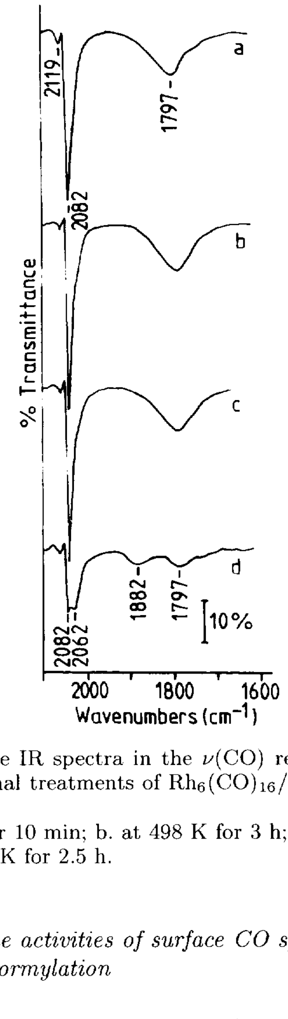

Fig 3. Surface IR spectra in the ν(CO) region after consecutive thermal treatments of $Rh_6(CO)_{16}/SiO_2$ under CO (26 kPa).
a. at 293 K for 10 min; b. at 498 K for 3 h; c. at 545 K for 3 h; d. at 583 K for 2.5 h.

Studies on the activities of surface CO species for hydroformylation

- *Reactivities of surface CO in CO insertion*

To identify the nature of CO on Rh^0 which is able to participate in hydroformylation, stoichiometric reactions of SiO_2-supported Rh^0-coordinated CO and Rh^0-adsorbed CO with an equimolar mixture of C_2H_4 and H_2 (total pressure: 52 kPa) were conducted at 293 K in a static IR cell.

Figure 4 shows IR monitoring results involving the reactions. After 1 h exposure of $Rh_6(CO)_{16}/SiO_2$ to C_2H_4 + H_2, the $Rh_6(CO)_{16}$ spectrum was almost unchanged in intensity. Meanwhile two small bands at 1 864 and 1 705 cm^{-1} appeared, corresponding to the bridged carbonyl on Rh^0 and propanal adsorbed on SiO_2. The presence of C_2H_6 bands in the gas phase (fig 4b') suggests that facile ethylene hydrogenation proceeded on a small amount of metallic rhodium particles which coexisted with the carbonyl cluster.

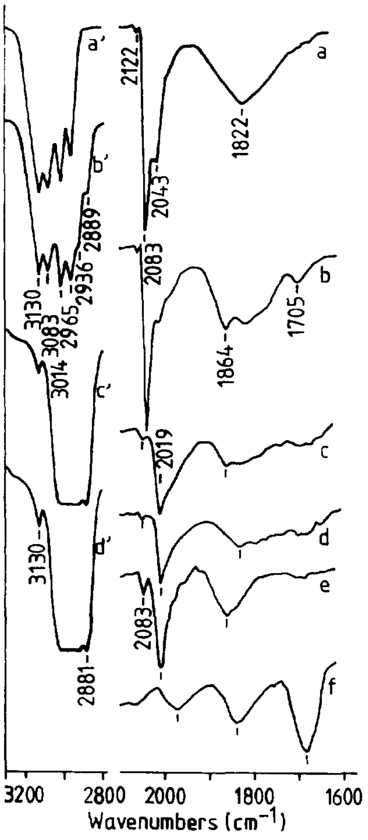

Fig 4. IR spectra before and after reactions of surface CO species with an equimolar mixture of C_2H_4 + H_2 (total pressure: 52 kPa) at 293 K in a static IR cell.
Surface: a. $Rh_6(CO)_{16}/SiO_2$ under vacuum; b. 1 h exposure to the mixture following a; c. after 0.5 h heating of $Rh_6(CO)_{16}/SiO_2$ under vacuum (1.3×10^{-3} kPa) at 383 K; d. 1 h exposure to the mixture following c; e. CO adsorbed on $Rh_4(CO)_{12}$-derived Rh/SiO_2 after H_2 treatment at 623 K; f. 1 h exposure to the mixture following e.
Gas phase: a'. the initial C_2H_4 + H_2; b'. corresponding to b; c'. corresponding to d; d'. corresponding to f.

To obtain a $Rh_6(CO)_{16}$-derived Rh^0-coordinated CO sample, a $Rh_6(CO)_{16}/SiO_2$ wafer was heated under vacuum (1.3×10^{-3} kPa) at 383 K for 0.5 h. The resulting rhodium carbonyls, whose IR bands are displayed in figure 4c, did not react noticeably with C_2H_4 + H_2 after 1 h exposure as indicated in figure 4d. However, there was a significant formation of ethane at the expense of ethylene in the gas phase as shown in figure 4c', suggesting the presence of a large number of unsaturated Rh^0 centers in this case. At this stage, approximately 20% of the initial gas mixture remained in the system.

In investigating the reactivity of Rh^0-adsorbed CO in CO insertion, the $Rh_6(CO)_{16}/SiO_2$ precursor was first decarbonylated in flowing H_2 at 623 K. Then the resulting Rh/SiO_2 was exposed to 3.9 kPa of CO at 293 K, so that the linear and bridged CO were predominantly formed. Contrary to the cases of $Rh_6(CO)_{16}/SiO_2$ and its carbonyl derivative, 1 h reaction between the adsorbed CO and C_2H_4 + H_2 resulted in a sharp band of propanal on the surface, with a strong decrease of the linear CO band intensity (fig 4f). In the meantime, ethylene hydrogenation occurred rapidly with the consumption of most of the ethylene.

- *Catalytic activities of surface CO species*

To reveal the influence of coordinative saturation on Rh^0 on hydroformylation, catalytic ethylene hydroformylations with the three CO species mentioned above were conducted in the static IR cell.

Figure 5 shows surface IR information about the catalytic system at 378 K after 0.5 h. As stated above, a wafer of $Rh_6(CO)_{16}/SiO_2$ was only weakly active. This wafer was then treated under vacuum (1.3×10^{-3} kPa) at 368 K for 20 min to produce the zerovalent rhodium carbonyls which were characterized by the 2 046 and 1 840 cm^{-1} bands. The latter led to an obvious propanal band under catalytic conditions. After the same wafer had been completely decarbonylated under H_2 at 623 K, it exhibited a more intense propanal band under catalytic conditions.

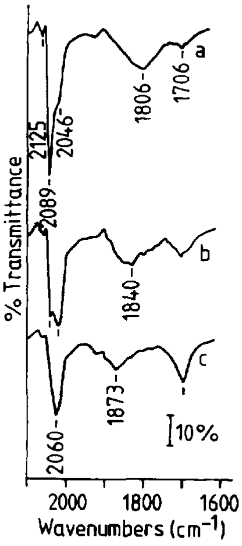

Fig 5. Surface IR spectra in the ν(CO) region after 0.5 h ethylene hydroformylation with surface CO species under an equimolar mixture of C_2H_4, CO and H_2 (total pressure: 78 kPa) at 378 K in a static IR cell.
a. $Rh_6(CO)_{16}/SiO_2$; b. a carbonyl rhodium catalyst obtained from 20 min treatment of the above precursor wafer under vacuum at 368 K; c. Rh/SiO_2 obtained from 2 h H_2 treatment of the same wafer following b.

Figure 6 shows the similar IR results obtained with another wafer of $Rh_6(CO)_{16}/SiO_2$ for hydroformylation at 418 K. A marked difference in catalytic formation of propanal was observed between the three CO species. Since the catalytic activity increased with decreasing amounts of coordinated CO, it was suggested that the production of propanal on the $Rh_6(CO)_{16}/SiO_2$ wafer is ascribed to a small number of rhodium particles coexisting from decomposition of $Rh_6(CO)_{16}$, and that the saturated rhodium carbonyls are inactive for hydroformylation.

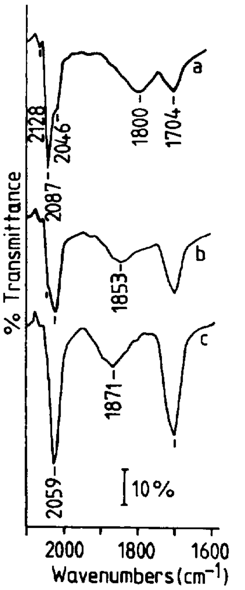

Fig 6. Surface IR spectra in the ν(CO) region after 0.5 h ethylene hydroformylation with surface CO species under an equimolar mixture of C_2H_4, CO and H_2 (total pressure: 78 kPa) at 418 K in a static IR cell.

a. $Rh_6(CO)_{16}/SiO_2$; b. a carbonyl rhodium catalyst obtained from 0.5 h treatment of the above precursor wafer under vacuum at 368 K; c. Rh/SiO_2 obtained from 2 h H_2 treatment of the same wafer following b.

Discussion

The surface organometallic chemistry of $Rh_6(CO)_{16}$ on SiO_2 is well understood in terms of IR spectroscopy as described by previous studies [17, 18]. At room temperature no chemical reaction occurs, under vacuum or under inert atmospheres, between $Rh_6(CO)_{16}$ and the partially dehydroxylated SiO_2 surface. Above a temperature of 323 K, $Rh_6(CO)_{16}$ progressively decarbonylates in favor of the formation of metallic rhodium particles. At higher temperatures rhodium atoms are more or less oxidized to Rh^+ by surface OH^-, depending on the rhodium dispersion on SiO_2. Under an atmosphere of H_2, both $Rh_6(CO)_{16}$ and Rh^+ supported on SiO_2 are virtually transformed into metallic rhodium particles at temperatures above 393 K, despite the fact that the precursor $Rh_6(CO)_{16}/SiO_2$ is easily oxidized to Rh^+/SiO_2 after exposure to air or O_2. Equally, in the presence of CO + H_2, several groups have demonstrated that the formation of $Rh^+(CO)_2$ on Rh/SiO_2 is suppressed and the observed IR spectra exhibit only linear and bridged CO bands [18-22].

With regards to the catalytic active site, the present IR results under in situ conditions clearly demonstrate that Rh^0 is the unique active site for steady hydroformylation on the Rh/SiO_2 catalysts, consistent with previous studies concerning supported rhodium valence states in the presence of H_2. Although the Rh^+ site can become active once linear CO is adsorbed on it [5], it is readily reduced under an H_2-containing atmosphere.

The behavior of $Rh_6(CO)_{16}/SiO_2$ and its carbonyl derivative under ethylene hydroformylation conditions were investigated in terms of IR data in this study. First, $Rh_6(CO)_{16}$ can be well stabilized on SiO_2 (till 548 K) under a hydroformylation atmosphere. This stabilization is explicitly ascribed to CO in the gas mixture, because $Rh_6(CO)_{16}/SiO_2$ displays as good a thermal stability only under CO as under the gas mixture. Subsequently, the cluster starts to decompose to metallic rhodium particles covered with CO from 548 K. Since no *gem*-dicarbonyl bands appear in figure 2, the original zerovalent state of rhodium in the $Rh_6(CO)_{16}$ cluster remains unchanged throughout the thermal decomposition. This observation is further evidence that the oxidation of Rh^0 by surface OH^- is inhibited in the presence of H_2 and that Rh^0 is uniquely responsible for hydroformylation. Consequently, it is evident that the (CO + H_2)-containing gas mixture is able to stabilize supported rhodium carbonyl clusters on the one hand, and prevent the oxidation of Rh^0 on the surface on the other hand.

At the same time, it is highly likely that $Rh_6(CO)_{16}/SiO_2$ is itself inactive for hydroformylation. As a matter of fact, no propanal band was present together with those of $Rh_6(CO)_{16}$ under catalytic conditions at temperatures lower than 378 K. However, at 378 K the carbonyl and non-carbonyl metallic rhodium particles derived from $Rh_6(CO)_{16}$ clearly give rise to propanal as evidenced by the IR spectra in figure 5. A further decarbonylated species is more active (figs 5 and 6). These results seem to show that the active site Rh^0 must be coordinatively unsaturated and the catalytic activity increases with increasing unsaturation, and that the Rh^0-coordinated CO does not act in the CO insertion step. Indeed, different unsaturations on Rh^0 can be detected in that ethylene hydrogenation results in a small amount of ethane on the $Rh_6(CO)_{16}/SiO_2$ sample, and an appreciable amount of ethane on the carbonyl and non-carbonyl Rh^0 sites derived from $Rh_6(CO)_{16}$, as shown in figure 4. The study of reactivities of rhodium carbonyls with C_2H_4 + H_2 proves that coordinated CO in $Rh_6(CO)_{16}/SiO_2$ and its carbonyl derivative only participates with difficulty in CO insertion as compared with the Rh^0-adsorbed CO. The inactivity of $Rh_6(CO)_{16}$ for hydroformylation has been reported on zeolite Y by Rode et al [13] and Takahashi et al [6].

As for the observation of the propanal band at 1 706 cm^{-1} appearing together with the $Rh_6(CO)_{16}$ spectrum under the ethylene hydroformylation atmosphere above 378 K, we assume that this may be due to a small minority of metallic rhodium particles and/or unsaturated rhodium carbonyls arising from decomposition of the cluster. They might be formed during exposure of $Rh_6(CO)_{16}/SiO_2$ to the reaction gas mixture [6]. The reproducible results of the C_2H_4 + H_2 reaction over the $Rh_6(CO)_{16}/SiO_2$ sample indicate that the surface is somewhat catalytically active at 293 K as shown in figure 4b′. Meanwhile the surface has a 1 864 cm^{-1} band upon exposure to C_2H_4 + H_2, which is assigned to the rhodium bridged carbonyl. In addition, the formation of ethane in the gas phase was also observed under hydroformylation conditions with $Rh_6(CO)_{16}/SiO_2$ (fig 2), which is indicative of ethylene hydrogenation competing with ethylene hydroformylation over active species. A comparison of the catalytic activities of the three rhodium surfaces with different saturations in figures 5 and 6 support the above interpretation.

Finally, it is of interest to discuss the contribution of coordinated CO to catalysis for hydroformylation. The carbonyls from both $Rh_6(CO)_{16}$ and its derivative are not reactive with $C_2H_4 + H_2$ at 293 K to result in propanal, whereas this reaction is extremely facile for the linear CO adsorbed on Rh^0. This difference shows the weak ability of coordinated CO to insert with respect to adsorbed CO from the gas phase, which can be interpreted from the viewpoint of Rh–CO bond strength. For the $Rh_6(CO)_{16}$ compound, the enthalpy of the Rh–CO bond is estimated to be 182 $kJ.mol^{-1}$ from the study of Housecroft et al [23]. However the corresponding energy of CO adsorption on a metallic rhodium surface is about 132 $kJ.mol^{-1}$ [24, 25]. Hence, in any case the CO adsorbed on rhodium desorbs more easily than the coordinated CO in the rhodium complex dissociates.

In principle, the reactivities of coordinated and adsorbed CO with $C_2H_4 + H_2$ at 293 K cannot represent their abilities to insert at catalytic reaction temperatures. At a catalytic reaction temperature of 373 K, both kinds of CO are totally and rapidly transformed into the hydroformylation products, and hence a comparison of their stoichiometric reactivities is meaningless. But the Rh–CO bond in $Rh_6(CO)_{16}$ can be stabilized by gaseous CO at higher temperatures, so that the carbonyl ligand does not dissociate under hydroformylation conditions. The catalytic inactivity of $Rh_6(CO)_{16}$ and the increase in catalytic activity with increasing unsaturation on the metallic rhodium surface confirm this. This inertness of carbonyl ligands coordinated to rhodium metallic clusters is embodied in the difficult dissociation to give surface Rh^0 sites to which ethylene and H_2 are coordinated on the one hand, and in the difficult migratory insertion to lead to the formation of oxygenates on the other. In contrast, the Rh^0-adsorbed CO desorbs easily since catalytic ethylene hydroformylation proceeds fastest on the totally decarbonylated rhodium catalysts. In this study, the results of stoichiometric and catalytic ethylene hydroformylation with surface Rh–CO species appear significant to account for the role of coordinated CO in the heterogeneous catalysis. Coordinatively saturated rhodium carbonyls can yield active sites only when decarbonylated. The thoroughly decarbonylated rhodium catalysts are most effective.

Conclusion

The linear CO adsorbed on Rh^0/SiO_2 is very reactive in CO insertion, leading to the formation of propanal from $C_2H_4 + H_2$ at 293 K, whereas the coordinated CO in $Rh_6(CO)_{16}/SiO_2$ and its carbonyl derivative is not reactive. $Rh_6(CO)_{16}/SiO_2$ can be thermally stabilized by CO under hydroformylation conditions. $Rh_6(CO)_{16}/SiO_2$ is catalytically inactive. The $Rh_6(CO)_{16}$ system exhibits an increased catalytic activity with increasing coordinative unsaturation on the rhodium surface by decarbonylation. The Rh–CO bond is proposed to have a similar stability and to be inactive for CO insertion. By combining the reactivities of surface CO species with $C_2H_4 + H_2$ with the catalytic activities of these species, it is suggested that rhodium-catalyzed heterogeneous hydroformylation requires the Rh^0 surface to be as coordinatively unsaturated as possible.

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