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Journal of Molecular Catalysis A: Chemical 124 (1997) 57–66

JOURNAL OF
MOLECULAR
CATALYSIS
A: CHEMICAL

Surface chemistry and catalysis of SiO_2 -supported $\text{RhCo}_3(\text{CO})_{12}$

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Received 4 June 1996; accepted 17 January 1997

Abstract

The interaction of the RhCo_3 cluster with the SiO_2 surface has been investigated via decarbonylation of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ under different atmospheres by IR spectroscopy. The bimetallic RhCo_3 framework is intactly preserved on the surface after thermal treatments of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ at 623 K under vacuum, hydrogen and oxygen (or air), which is able to regenerate the initial bimetallic carbonyl cluster under a CO atmosphere. In contrast, the $\text{RhCo}_3/\text{SiO}_2$ sample without undergoing any thermal treatment is readily disintegrated by CO to result in $\text{Rh}^+(\text{CO})_2$ and Co^{2+} with the aid of a concerted oxidation by surface OH^- . IR study also shows that $\text{RhCo}_3(\text{CO})_{12}$ is reversibly dissociated to $\text{Rh}_6(\text{CO})_{16}$ and $\text{Co}_2(\text{CO})_8$ on the surface by CO. In situ IR observations reveal that the equilibrium favoring the regeneration of $\text{RhCo}_3(\text{CO})_{12}$ is established at 423 K under atmospheric hydroformylation pressure in terms of the interconversion between the bimetallic cluster and the monometallic clusters, and that $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ is stable and responsible itself for the catalysis toward ethylene hydroformylation. Atmospheric catalytic results illustrate that $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ has high activity and stability for the formation of propanal and *n*-propanol. © 1997 Elsevier Science B.V.

Keywords: Active SiO_2 -supported $\text{RhCo}_3(\text{CO})_{12}$; Preservation of RhCo_3 ; Regeneration of $\text{RhCo}_3(\text{CO})_{12}$; High activity and stability; Hydroformylation

1. Introduction

Surface organometallic chemistry has made satisfactory progress in the molecular tailoring of metal catalysts and the mechanistic study in heterogeneous catalysis, through a better understanding of the reactivity of organometallic clusters and compounds with a diversity of solid surfaces over the past decade [1–5]. One of the principal objectives in this area is to immobilize homogeneous complex catalysts and thus pre-

serve molecular catalytic properties on the surfaces. Up to now, only a limited number of successes have been achieved regarding the true catalysis of supported organometallic clusters, on the basis of the results of spectroscopic and catalytic investigations. Moreover, they are all restricted to monometallic clusters [6–11]. To our knowledge, no convincing evidence has been provided of either homogeneous or heterogeneous catalysis by organo-bimetallic clusters themselves, although they are usually known as effective catalyst precursors for a variety of organic reactions. This is mainly because of the facile destruction of bimetallic clusters upon thermal treatment, interaction with the surfaces

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and catalytic conditions [12–19]. In particular, the breaking of M–M' bonds in organo-bimetallic clusters readily occurs in the presence of CO [18,20].

Since bimetallic Rh–Co complex systems had been reported to display excellent catalytic performances in various homogeneously catalyzed reactions [21–23], we concentrated our interest on an attempt at preparing inorganic carrier-supported Rh–Co cluster catalysts and the investigation of their catalysis for olefin hydroformylation. We found in a preliminary study that the $\text{RhCo}_3(\text{CO})_{12}$ -derived SiO_2 -grafted catalyst considerably enhances catalytic activities for the formation of oxygenates as compared with the $\text{Rh}_4(\text{CO})_{12}/\text{SiO}_2$ -derived catalyst [24]. This unusual performance spurred us to gain more insight into the chemical behavior of the bimetallic carbonyl cluster on the SiO_2 surface and the nature of supported catalytic species. In this paper, we discuss the interaction of the Rh–Co cluster framework with the surface of SiO_2 and CO following different pretreatments in terms of IR spectroscopic studies. We also show the actual catalysis by the molecular SiO_2 -supported $\text{RhCo}_3(\text{CO})_{12}$ cluster for ethylene hydroformylation at atmospheric pressure.

2. Experimental

$\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ and $\text{Co}_2(\text{CO})_8$ were purchased commercially. $\text{NaCo}(\text{CO})_4$ was synthesized from $\text{Co}_2(\text{CO})_8$ according to the report of Edgell et al. [25]. $\text{Rh}_4(\text{CO})_{12}$ and $\text{RhCo}_3(\text{CO})_{12}$ were synthesized from $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ and $\text{NaCo}(\text{CO})_4$ as described by Martinengo et al. [26,27]. SiO_2 was a silica 'Aerosil' supplied by Degussa with a surface area of $380 \text{ m}^2/\text{g}$. *n*-hexane used as the solvent was distilled over P_2O_5 and stored under Ar over activated 5 Å 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 Å molecular sieves and

Mn/MnO to eliminate traces of water and oxygen.

$\text{Rh}_4(\text{CO})_{12}$, $\text{Co}_2(\text{CO})_8$ and $\text{RhCo}_3(\text{CO})_{12}$ were employed as starting materials to prepare $\text{Rh}_6(\text{CO})_{16}/\text{SiO}_2$ (1% Rh loading) [28], $\text{Co}_4(\text{CO})_{12}/\text{SiO}_2$ (1.7% Co loading) [29] and $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ (1% Rh loading) [24]. SiO_2 (60–80 mesh granule) was dehydroxylated at 623 K under vacuum (1.3×10^{-6} kPa) for 5 h and subsequently impregnated with a dry solution of cluster in *n*-hexane under Ar. After 2 h of contact of the liquid and solid phases, the solvent was removed by evacuation at room temperature and the resulting solid sample was further treated under vacuum (1.3×10^{-3} kPa) for 1 h. The catalyst precursor thus obtained was carefully preserved under Ar prior to use.

Hydroformylation of ethylene was conducted under atmospheric pressure at 423 K in a glass tubing flow reactor (i.d. = 7 mm), to which 0.1 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) at 423–473 K. In order to make the catalytic reaction proceed possibly under a differential condition, the total conversion of C_2H_4 was governed to below 15%. Data were taken 7 h after the initiation 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 ionization detector.

IR experiments were carried out on a Bio-Rad FTS-7 spectrometer, using a double beam cell with CaF_2 windows which was depicted in detail elsewhere [30]. The catalyst precursor was pressed into wafers of 20 mg each in air and placed in the cell where the wafers were subjected to the desired treatments. In situ IR studies of the catalyst during ethylene hydroformylation were performed with this static cell to which an equimolar mixture of C_2H_4 , CO and H_2 at 78 kPa was admitted. All IR spectra were recorded at room temperature. Surface IR spectra were measured in the presence of gas phases

by subtracting SiO_2 , decarbonylated SiO_2 -supported catalyst and gaseous contributions.

The metal contents of the samples studied were determined by X-ray fluorescence spectroscopy.

3. Results and discussion

3.1. Surface chemistry of $\text{RhCo}_3(\text{CO})_{12}$ on SiO_2

In order to explain explicitly the IR spectroscopic results shown hereinafter, it should be stated that the interaction of $\text{RhCo}_3(\text{CO})_{12}$ with the SiO_2 surface prehydroxylated at 623 K by impregnation at room temperature results in a strong physisorption of $\text{RhCo}_3(\text{CO})_{12}$ on SiO_2 as has been interpreted [24,31]. Fig. 1(b) shows an in situ IR spectrum characteristic of $\text{RhCo}_3(\text{CO})_{12}$ strongly physisorbed on SiO_2 , whose shape deviates much from that of the original $\text{RhCo}_3(\text{CO})_{12}$ spectrum in solution.

Based on the catalyst precursor $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ thus obtained which contained 1% Rh, further studies were performed under different atmospheres by means of IR

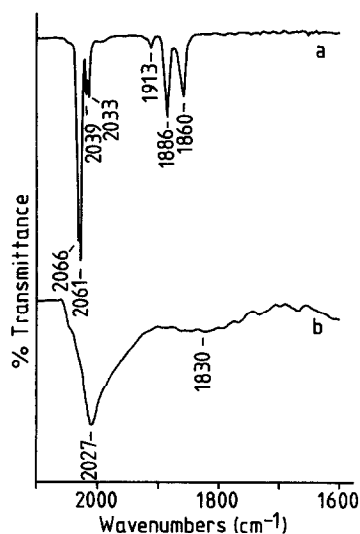


Fig. 1. IR spectra of $\text{RhCo}_3(\text{CO})_{12}$. (a) $\text{RhCo}_3(\text{CO})_{12}$ in *n*-hexane; (b) after impregnation of $\text{RhCo}_3(\text{CO})_{12}/n$ -hexane on SiO_2 prehydroxylated at 623 K, followed by 2 h of evacuation (1.3×10^{-6} kPa) at 293 K.

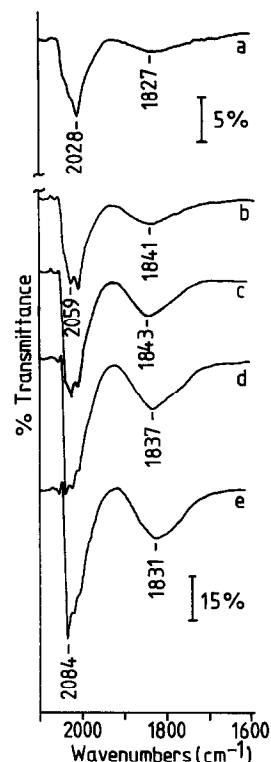


Fig. 2. IR spectra under CO of a sample derived by decarbonylation of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ (1% Rh loading) under H_2 at 623 K. (a) Under CO at 0.2 kPa for 1.5 min; after increasing CO pressure to 13 kPa: (b) 2 min; (c) 15 h; (d) 50 h; (e) 147 h.

spectroscopy using CO as a molecular probe. The precursor sample studied was first decarbonylated in air at room temperature and subsequently pressed into wafers of 20 mg each. After such a wafer had been subjected to 2 h of atmospheric H_2 treatment at 623 K, no coordinated CO remained on the surface. Admission of CO at a low pressure of 0.2 kPa immediately gave rise to two adsorbed CO bands at 2028s and 1827w(br) cm^{-1} , as shown in Fig. 2. They closely resemble those for $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$. However, the resulting spectrum varied obviously as functions of admitted CO pressure and exposure time, until the carbonyl features of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ almost disappeared with appearance and development of new carbonyl bands which may be assigned to $\text{Rh}_6(\text{CO})_{16}/\text{SiO}_2$ and $\text{Co}_2(\text{CO})_8/\text{SiO}_2$. These observations suggest that $\text{RhCo}_3(\text{CO})_{12}$ is first

regenerated from the surface by recarbonylation and then dissociated to $\text{Rh}_6(\text{CO})_{16}$ and $\text{Co}_2(\text{CO})_8$ under CO. It follows that the bimetallic RhCo_3 framework can be retained intact on the SiO_2 surface as well after decarbonylation of the precursor by oxidation in air at room temperature as also after H_2 treatment at 623 K. This part of work has been discussed in detail elsewhere [31].

Surprisingly, the identical spectroscopic results of recarbonylation were observed as in the case with H_2 treatment, when the precursor was subjected to 2 h of atmospheric O_2 treatment at 623 K, as shown in Fig. 3. This unambiguously shows that the SiO_2 -supported RhCo_3 framework is still stable in spite of such strong oxidation. In accordance with the IR spectroscopic results, the catalyst derived from $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ by oxidative processing

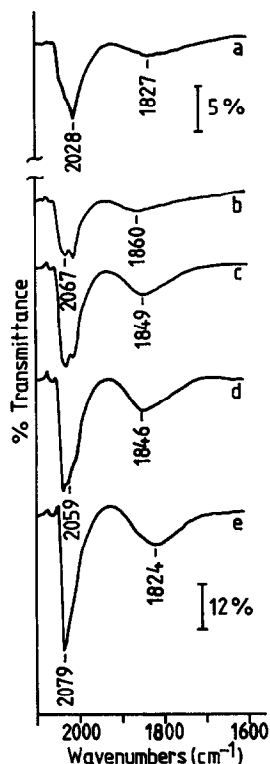


Fig. 3. IR spectra under CO of samples derived by decarbonylation of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ (1% Rh loading) under O_2 at 623 K. (a) under CO at 0.2 kPa for 1.5 min; after exposure to CO at 21 kPa: (b) 7 min; (c) 7 h; (d) 30 h; (e) 124 h.

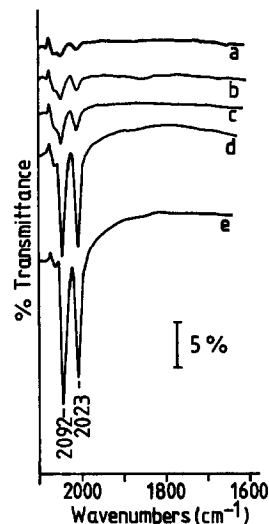


Fig. 4. IR spectra after exposure to 13 kPa of CO of a sample derived by decarbonylation of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ (1% Rh loading) in air at 293 K. (a) 1.5 min; (b) 10 min; (c) 0.5 h; (d) 12 h; (e) 35 h.

showed a much higher hydroformylation activity than the Rh/SiO_2 catalyst as in the case of the catalyst derived from $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ by reductive processing [32]. Meanwhile, the results of extended studies to the treatments in air and in vacuum confirmed this conclusion.

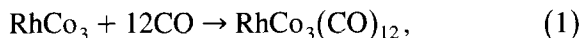
Nevertheless, if the precursor $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ was simply decarbonylated by exposure to air at room temperature without experiencing thermal treatments at higher temperatures, the resulting surface behaved differently under CO. As shown in Fig. 4, it just exhibited gem-dicarbonyl bands at 2092 and 2023 cm^{-1} , attributed to $\text{Rh}^+(\text{CO})_2$ which was formed from disintegration of $\text{RhCo}_3(\text{CO})_{12}$. This indicates that the bimetallic RhCo_3 framework is directly dissociated by the action of CO, concomitant with concerted oxidation of Rh^0 by surface OH^- in this case. Although adsorbed CO on cobalt fragments is hardly detected by IR spectroscopy, the cobalt species is probably present in the chemical state of Co^{2+} on the surface since Co^0 is more easily oxidized than Rh^0 [27]. The change of color from pale to blue on the wafer during exposure to CO was indicative of the formation of Co^{2+} . This is consistent

with the result reported by Takenchi et al. who demonstrated the transformation of Co^0 from $\text{Co}_2(\text{CO})_8$ to Co^{2+} on SiO_2 after exposure to air by EXAFS [33].

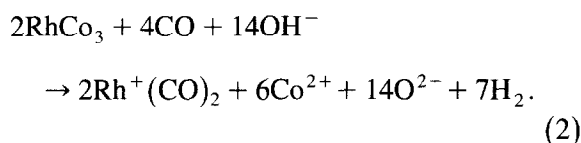
By comparison of the above IR results from different processings over $\text{RhCo}_3/\text{SiO}_2$, it is inferred that the observed difference in recarbonylation behavior is uniquely related to whether or not the sample undergoes calcination regardless of the atmosphere used. The calcination in any case may play an important role in reinforcing the interaction between RhCo_3 and SiO_2 surface and hence stabilizing the bimetallic framework. With this respect, we have proposed a kind of particular cluster–support interaction via a nucleophilic attack of surface oxygen on the cobalt atoms of RhCo_3 with a concerted action of the rhodium atom, which may prevent the Rh–Co bond from dissociation under CO [24,31]. As a matter of fact, this kind of interaction has already appeared at the moment of strong physisorption of $\text{RhCo}_3(\text{CO})_{12}$ on

SiO_2 , according to the surface IR spectrum in Fig. 1(b) where both the linear and bridged carbonyl bands shift to lower wavenumbers. However, the interaction is relatively weak at this stage, so that the RhCo_3 framework suffers from disruption upon adsorption of CO. In the case of heating at 623 K, the existing $\text{RhCo}_3\text{--SiO}_2$ interaction is believed to be enhanced to such an extent that the RhCo_3 cluster can be neither destroyed under an O_2 or a H_2 atmosphere nor dissociated by CO. The result of thermal stability of $\text{RhCo}_3/\text{SiO}_2$ under oxidative conditions also shows that oxidation of rhodium and cobalt atoms can be effectively inhibited by a surface Rh–Co bimetallic action. As a result of the stabilization of RhCo_3 on the SiO_2 surface, only the regeneration of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ is noted over $\text{RhCo}_3/\text{SiO}_2$ under a CO atmosphere. Therefore, we suggest here two types of CO adsorption on supported RhCo_3 that compete with each other in general:

(a) normal recarbonylation to regenerate $\text{RhCo}_3(\text{CO})_{12}$:



(b) dissociative adsorption to produce $\text{Rh}^+(\text{CO})_2$ and Co^{2+} with the aid of concerted oxidation by surface OH^- :



Interestingly, although the regenerated $\text{RhCo}_3(\text{CO})_{12}$ converts progressively to $\text{Rh}_6(\text{CO})_{16}$ and $\text{Co}_2(\text{CO})_8$ under CO at room temperature as mentioned hereinbefore, the reaction in the reverse direction is also feasible in this system. Fig. 5 shows the IR spectral evolution for the ultimate mixture in equilibrium with increasing temperature under 13 kPa of CO. After completion of the conversion of $\text{RhCo}_3(\text{CO})_{12}$, the 2026 cm^{-1} band developed as the temperature increased. At the same time, the 2084 cm^{-1} band decreased gradually in

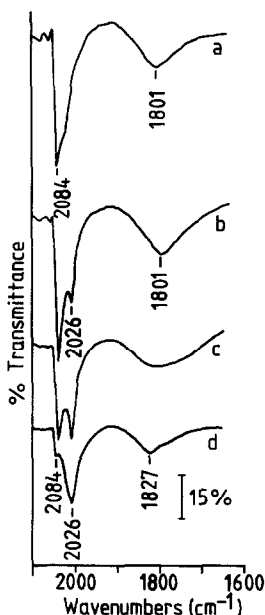


Fig. 5. IR spectra after exposure to 13 kPa of CO of a sample derived by decarbonylation of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ (1% Rh loading) under H_2 at 623 K. (a) 11 days at 293 K; (b) 2 h at 423 K following (a); (c) 2 h at 478 K following (b); (d) 2 h at 531 K following (c).

intensity and the broad bridged band centered at 1801 cm^{-1} shifted toward higher wavenumbers up to 1827 cm^{-1} . At 531 K, much the net characteristic spectrum of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ was observed again as shown in Fig. 5(d). This clearly indicates that reversal of the dissociation of $\text{RhCo}_3(\text{CO})_{12}$ occurs on the surface at elevated temperatures. Furthermore, we have observed the formation of $\text{RhCo}_3(\text{CO})_{12}$ from a combination of rhodium carbonyl and cobalt carbonyl on the SiO_2 surface [34]. Of special significance is this reversible dissociation of $\text{RhCo}_3(\text{CO})_{12}$ under CO for the study of catalytic CO-based reactions. It is via the governable interconversion between $\text{RhCo}_3(\text{CO})_{12}$ and $\text{Rh}_6(\text{CO})_{16} + \text{Co}_2(\text{CO})_8$ that the bimetallic cluster can be expected to be stabilized on the surface under catalytic hydroformylation conditions.

3.2. Catalysis of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ toward ethylene hydroformylation

In search of the contribution of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ to the catalysis for hydroformylation reactions and the true catalytic active species, a catalytic study was performed with SiO_2 -supported mono- and bi-metallic clusters as precursors. An overall comparison of catalytic results is shown in Table 1 for three supported cluster-derived catalysts in ethylene hydroformylation. The $\text{RhCo}_3(\text{CO})_{12}$ -derived catalyst obviously exhibited an incomparable superiority over the $\text{Rh}_4(\text{CO})_{12}$ -derived catalyst

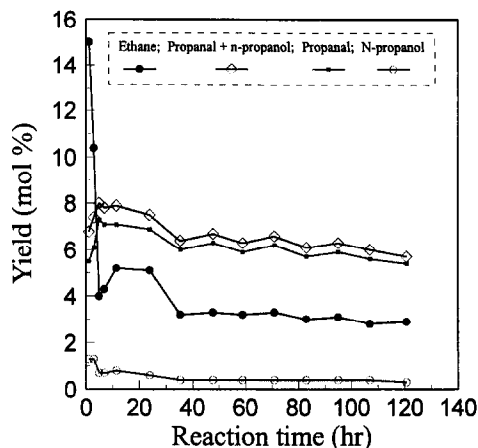


Fig. 6. Dynamic ethylene hydroformylation over a $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ (1% Rh loading)-derived catalyst at atmospheric pressure and at 423 K.

in the formation of oxygenates. The $\text{Co}_2(\text{CO})_8$ -derived catalyst showed undetectable activities for both hydroformylation and hydrogenation under the same conditions. Owing to the promotion of cobalt in the bimetallic system, the catalytic activity to oxygenates was increased by 20 times. Moreover the catalytic selectivity for the formation of oxygenates was considerably improved. This bimetallic cluster-derived catalyst also displayed a good catalytic durability as shown in Fig. 6. In fact, the reaction appeared to proceed immediately after the introduction of reaction gases without any induction period. At the initial stage, the reaction gave large amounts of C_2H_6 followed by its dramatic decline. Yields of all the products determined out of ethylene hydroformylation varied up and

Table 1
Catalytic properties of SiO_2 -supported cluster-derived catalysts^a in atmospheric ethylene hydroformylation^b

Cluster	Activity ^c		Selectivity (mol %)	
	C_2H_6	$\text{C}_2\text{H}_5\text{CHO} + n\text{-C}_3\text{H}_7\text{OH}$	$\text{C}_2\text{H}_5\text{CHO} + n\text{-C}_3\text{H}_7\text{OH}$	$n\text{-C}_3\text{H}_7\text{OH}$
$\text{Co}_2(\text{CO})_8$	0	0	—	—
$\text{Rh}_4(\text{CO})_{12}$	0.62	0.31	34	0
$\text{RhCo}_3(\text{CO})_{12}$	3.63	6.56	64	6

^a Rh/ SiO_2 and $\text{RhCo}_3/\text{SiO}_2$ with 1% Rh loading, Co/ SiO_2 with 1.7% Co loading.

^b At 423 K, $\text{C}_2\text{H}_4:\text{CO}:\text{H}_2 = 20:20:20$ ml/min.

^c Expressed by (mol/Co mol/min) for Co/ SiO_2 and (mol/Rh mol/min) for Rh/ SiO_2 and $\text{RhCo}_3/\text{SiO}_2$. Data were taken 7 h after the initiation of reaction.

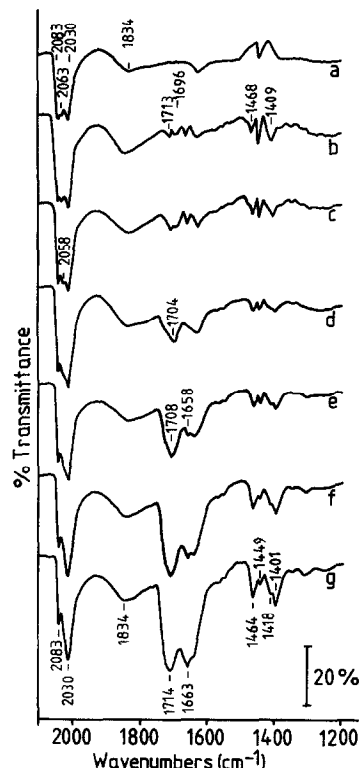


Fig. 7. IR spectra of a $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ (1% Rh loading)-derived catalyst under a hydroformylation atmosphere ($\text{C}_2\text{H}_4:\text{CO}:\text{H}_2 = 26:26:26$ kPa) in a static IR cell. (a) 20 min at 293 K; after increasing temperature to 423 K: (b) 1 min; (c) 6 min; (d) 12 min; (e) 25 min; (f) 1 h; (g) 2 h.

down along with time on stream till approximately 35 h. Afterward, they remained almost constant up to 120 h.

Insomuch as the $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ -derived catalyst possesses those superior catalytic performances toward ethylene hydroformylation as mentioned above, we attempted to shed light on the nature of active species in the catalytic system by IR monitoring. The in situ reaction was run in a static IR cell. Figs. 7 and 8 present the surface IR spectra of the catalyst taken during the reaction and Fig. 9 shows the corresponding IR spectral evolution in gas phase. When a wafer of $\text{RhCo}_3/\text{SiO}_2$, which was derived by decarbonylation of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ under H_2 at 623 K, was exposed to the reaction gases ($\text{C}_2\text{H}_4:\text{CO}:\text{H}_2 = 26:26:26$ kPa) at room temperature, it displayed a complex spectrum

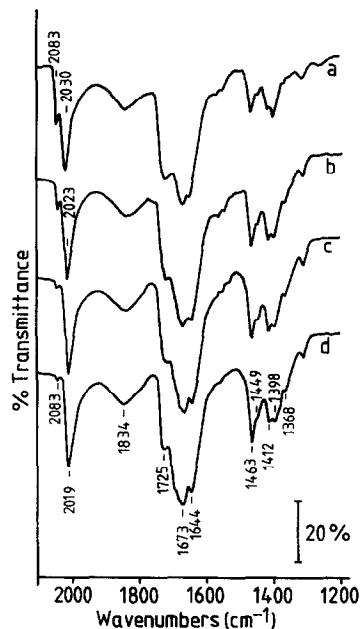


Fig. 8. IR spectra of a $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ (1% Rh loading)-derived catalyst under hydroformylation conditions (423 K, $\text{C}_2\text{H}_4:\text{CO}:\text{H}_2 = 26:26:26$ kPa) in a static IR cell (following Fig. 7(g)). (a) 5 h; (b) 16 h; (c) 40 h; (d) 110 h.

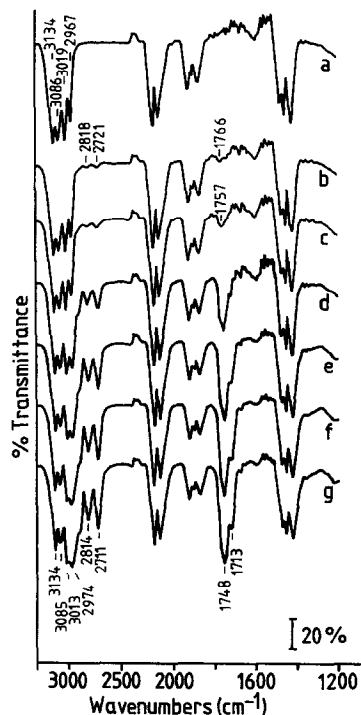
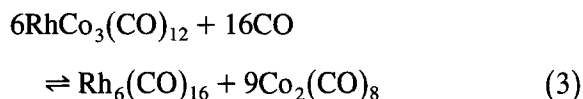


Fig. 9. IR spectra in gas phase corresponding to Figs. 7 and 8. (a) 0 h; (b) 2 h; (c) 5 h; (d) 16 h; (e) 40 h; (f) 75 h; (g) 110 h.

consisting of the carbonyl bands at 2083, 2063, 2030 and 1834 cm^{-1} , belonging to a mixture of surface-grafted $\text{RhCo}_3(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$ and $\text{Co}_2(\text{CO})_8$ (Fig. 7(a)), as expected. This further confirms the regeneration of the initial bimetallic cluster from $\text{RhCo}_3/\text{SiO}_2$ and the subsequent dissociation to the monometallic rhodium and cobalt carbonyl clusters under a CO-containing atmosphere. After the temperature had been raised to 423 K, the bands corresponding to $\text{Rh}_6(\text{CO})_{16}$ and $\text{Co}_2(\text{CO})_8$ depleted quite rapidly in favor of restoration of the features for $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$, as shown in Fig. 7(b). This accounts for shift of the following surface chemical equilibrium



to the left upon heating treatment under a hydroformylation atmosphere, in agreement with what has been observed under a CO atmosphere. Upon heating at 423 K, the wafer presented the small band at 1696 cm^{-1} corresponding to acyl species adsorbed on SiO_2 and the weak bands at 1713, 1468 and 1409 cm^{-1} due to $\text{C}_2\text{H}_5\text{CHO}$ adsorbed on SiO_2 , both of which resulted from ethylene hydroformylation. As noted in the spectral intensity, $\text{Rh}_6(\text{CO})_{16}$ and $\text{Co}_2(\text{CO})_8$ converted nearly completely to $\text{RhCo}_3(\text{CO})_{12}$ with increasing reaction time. The features of adsorbed $\text{C}_2\text{H}_5\text{CHO}$ developed progressively, concomitant with appearance of a new band at 1658 cm^{-1} , as shown in Fig. 7(e). This latter band grew more rapidly than those of adsorbed $\text{C}_2\text{H}_5\text{CHO}$ on the surface. After saturated adsorption of $\text{C}_2\text{H}_5\text{CHO}$ on the surface, there started to appear its IR bands at 2818, 2721 and 1766 cm^{-1} in gas phase (Fig. 9(b)) and these bands increased in intensity with reaction time. The reaction ceased after 110 h. The band initially emerging at 1658 cm^{-1} became quite intense and was finally observed at 1673 cm^{-1} , as shown in Fig. 8(d). In parallel, the IR spectrum in gas phase at this stage gave an extra shoulder band at 1713 cm^{-1} as well as the

features at 2814, 2711 and 1748 cm^{-1} characteristic of $\text{C}_2\text{H}_5\text{CHO}$ as the main hydroformylation product, as presented in Fig. 9(g). The 1713 cm^{-1} band exactly matches the principal band for $(\text{C}_2\text{H}_5)_2\text{CO}$. Taking into account the pronounced production of ketone from ethylene hydroformylation over cobalt catalysts [35,36], this band can be assigned to $(\text{C}_2\text{H}_5)_2\text{CO}$. Thus, the observed 1673 cm^{-1} band on the surface which fully corresponds to the 1713 cm^{-1} band in gas phase as evidenced in our experiments, can logically be attributed to adsorbed $(\text{C}_2\text{H}_5)_2\text{CO}$ on the catalyst surface. However, supported metal catalysts apparently disfavor the formation of $(\text{C}_2\text{H}_5)_2\text{CO}$ in ethylene hydroformylation in contrast to homogeneous catalysts, because of the strong steric factor hindering the elimination step which occurs between acyl species and adsorbed ethyl. Although the weak band at 1713 cm^{-1} in the gas phase and the intense band at 1673 cm^{-1} on the surface were observed in the static IR cell, which probably indicated a small cumulative amount of $(\text{C}_2\text{H}_5)_2\text{CO}$ formed after 110 h of reaction, a significant amount of $(\text{C}_2\text{H}_5)_2\text{CO}$ was not detected in the dynamic ethylene hydroformylation reaction under operating conditions. The complex bands situated at 1463, 1412, 1398 and 1368 cm^{-1} can plausibly be ascribed to a mixture of $\text{C}_2\text{H}_5\text{CHO}$, $n\text{-C}_3\text{H}_7\text{OH}$ and $(\text{C}_2\text{H}_5)_2\text{CO}$. The shoulder observed at 1644 cm^{-1} is attributed to H_2O adsorbed on SiO_2 .

Throughout 110 h of reaction, it was noticed that there was no substantial change in the carbonyl spectral pattern of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$. The slight downward shift of the linear band from 2030 to 2019 cm^{-1} can be explained in terms of a continuous decrease of the dipole–dipole interaction of the linear CO caused by dilution from gradually increased adsorbed products from the reaction [37]. This shows that $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ is fairly stable under the working hydroformylation conditions. From the spectra collected in the gas phase during the static reaction (Fig. 9), it can be seen that $\text{C}_2\text{H}_5\text{CHO}$ is the predominant product from

ethylene hydroformylation over $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ and the amounts of C_2H_6 and other products are incomparable. The IR results are supportive of the catalytic observation of high selectivity to propanal. During the in situ reaction, $\text{Rh}_6(\text{CO})_{16}/\text{SiO}_2$ coexisted more or less with $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$, the former is identified by the linear carbonyl band at 2083 cm^{-1} . But supported $\text{Rh}_6(\text{CO})_{16}$ has been demonstrated to be inactive for hydroformylation [38–40] as is the case of $\text{Rh}_6(\text{CO})_{16}$ in solution [41]. In this catalytic system, it is unlikely that besides those mentioned above there were other mono- and bi-metallic species on the surface in significant amounts arising from $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ by H_2 decarbonylation at 623 K, according to the in situ IR observations. Although trace amounts of metallic fragments could not be fully excluded under catalytic conditions, our recent studies have suggested that RhCo_3 clusters are favorably produced under reducing conditions at elevated temperatures from the binary monometallic system $(\text{Rh} + \text{Co})/\text{SiO}_2$ derived from $\text{Rh}_4(\text{CO})_{12}$ and $\text{Co}_2(\text{CO})_8$ [34,42]. Therefore, it is well believed that the regenerated $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ is catalytically responsible itself for the observed strong catalysis in ethylene hydroformylation. Its good stability in the prolonged reaction evidenced by in situ IR spectroscopy is coherent with the data of catalytic durability test.

The present paper has reported, to our knowledge, the first example of mixed organometallic cluster catalyzed reaction, at least for hydroformylation reaction. The preservation of the bimetallic RhCo_3 cluster framework following treatments under drastic conditions entirely lies in the specific stabilizing effect by the supporting SiO_2 surface, that guarantees the special advantage of a mixed metallic cluster in catalysis. This is in contrast with unsupported bimetallic Rh–Co clusters which cannot maintain their structural integrity under hydroformylation conditions [22,23,43,44]. They fragment into a mixture of $\text{RhCo}(\text{CO})_7$, rhodium carbonyl and cobalt carbonyl. Extensive studies of het-

erogenized homogeneous catalysis are undoubtedly of important interest for a variety of reactions.

4. Conclusions

The results obtained by IR spectroscopy demonstrate that the bimetallic RhCo_3 cluster framework can be preserved on the surface by decarbonylation of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ under any atmosphere at elevated temperatures. Two types of competitive CO adsorption are suggested on SiO_2 -supported RhCo_3 : (a) recarbonylation to regenerate $\text{RhCo}_3(\text{CO})_{12}$; (b) dissociative adsorption to yield $\text{Rh}^+(\text{CO})_2$ and Co^{2+} in terms of the coincident oxidation by surface OH^- . The dominant adsorption form depends on the extent to which RhCo_3 interacts with the support. IR study also suggests that the dissociation of $\text{RhCo}_3(\text{CO})_{12}$ under CO to form $\text{Rh}_6(\text{CO})_{16}$ and $\text{Co}_2(\text{CO})_8$ proceeds reversibly on the SiO_2 surface. The catalytic and in situ IR studies show that $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ is actually responsible for the observed high catalytic activity and stability.

Acknowledgements

The authors acknowledge the support from the Chinese Academy of Sciences.

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