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Enhancement of olefin hydroformylation related to supported bimetallic Rh–Co clusters

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The atmospheric hydroformylations of ethylene and propylene were investigated over SiO_2-supported $Rh_4(CO)_{12}$, $Co_2(CO)_8$, $Rh_2Co_2(CO)_{12}$ and $RhCo_3(CO)_{12}$-derived catalysts. The bimetal cluster-derived catalysts showed excellent activities for the formation of oxygenates. In situ IR study on partially dehydroxylated SiO_2-supported $RhCo_3(CO)_{12}$ suggested that the bimetal cluster framework may be preserved after decarbonylation under H_2 at 623 K and may be recarbonylated at room temperature. A strong physisorption of $RhCo_3(CO)_{12}$ on SiO_2 is proposed, due to a nucleophilic attack of surface oxygen on the Co atoms, which promotes a metal–support interaction and thus stabilizes the bimetal cluster framework. A subcarbonyl bimetal cluster is thought to be the actual catalytic species on the surface.

Keywords: SiO_2-supported bimetallic Rh–Co cluster; $RhCo_3(CO)_{12}$; ethylene hydroformylation; propylene hydroformylation

1. Introduction

The use of $Rh_2Co_2(CO)_{12}$ and $RhCo_3(CO)_{12}$ clusters as precursors has resulted in nice catalytic performances in a variety of homogeneously catalyzed reactions [1–3]. Nevertheless, there has been to date no example of these clusters, other than $Rh_4(CO)_{12}$, which maintain metallic structural integrity under catalytic conditions. They fragment in most cases, above all in the presence of syngas, into a mixture of coordinatively unsaturated dinuclear Rh–Co complex, Rh carbonyl and Co carbonyl [1,2,4–6]. As far as olefin hydroformylation is concerned, the prevailing active species is believed to be $RhCo(CO)_7$ [1,2,4]. Therefore, bimetallic

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Rh–Co clusters fail to become the real catalytic species with the concerted properties of multimetal centres in homogeneous catalysis.

The design of heterogenized cluster catalysts and cluster-derived metal catalysts has been attempted to preserve highly active bimetallic sites on the solid surfaces through surface organometallic chemistry since the last decade. Bimetallic Rh–Co clusters have ever been utilized as effective precursors for olefin hydroformylation and the $CO + H_2$ reaction by supporting on various inorganic carriers [7–9]. It is recognized that the presence of cobalt in bimetal cluster-derived catalysts strongly enhances catalytic activities and selectivities for syngas conversion to oxygenates [10] and olefin hydroformylation [7–9,11].

Reported herein is a study on catalysis by $RhCo_3(CO)_{12}$ and $Rh_2Co_2(CO)_{12}$ derived SiO_2-supported catalysts for the hydroformylations of ethylene and propylene. The surface active species is possibly a stabilized carbonyl Rh–Co bimetallics discussed in terms of IR data for the $RhCo_3(CO)_{12}/SiO_2$ system. We also discuss the interaction between adsorbed $RhCo_3(CO)_{12}$ and the surface groups on SiO_2.

2. Experimental

$Rh_4(CO)_{12}$, $Co_2(CO)_8$, $Rh_2Co_2(CO)_{12}$ and $RhCo_3(CO)_{12}$ were synthesized with literature methods. SiO_2 used was a silica "Aerosil" purchased from Degussa, with a surface area of 380 m^2/g. The solvent *n*-hexane was distilled over P_2O_5 and stored under Ar over activated 5 A molecular sieves. The gases used (H_2, CO, C_2H_4, C_3H_6 and Ar etc.) had a purity of 99.99%. Before admission into the reactor and IR cell, they underwent further purification via passing through 5 A molecular sieves and Mn/MnO to eliminate traces of water and oxygen.

The above four clusters were used as starting materials to prepared, by impregnation technique under atmospheric Ar, the corresponding supported catalysts on SiO_2 (60–80 mesh granule) which was predehydroxylated at 623 K in vacuum for 5 h. The atmospheric hydroformylations of ethylene and propylene were conducted in a flow reactor (with 0.1 g precursor/SiO_2 having 1% Rh loading). The supported clusters were decarbonylated in flowing H_2 at 623 K for 2 h, after which H_2 was replaced by a mixture of olefin, CO and H_2 (20 : 20 : 20 ml/min) at 423–273 K. Data were taken 7 h after the initiation of reaction. Both hydrocarbon and oxygenated products were analyzed on line with gas chromatography, using 2 m length columns and a flame ionisation detector. Ethylene, ethane and the whole of oxygenates were separated with a Porapak R column. The separation of propylene and propane was performed with a modified SiO_2 column.

In situ IR experiments were carried out by impregnating SiO_2 wafers with *n*-hexane solution of $RhCo_3(CO)_{12}$ in a double beam IR cell. The spectra were recorded in a Bio-Rad FTS-7 spectrometer at room temperature by subtracting the SiO_2 background.

3. Results and discussion

Tables 1 and 2 show catalytic results of the mon- and bi-metal carbonyl cluster-derived catalysts in the hydroformylations of ethylene and propylene, respectively. In both cases, $Co_2(CO)_8$-derived Co/SiO_2 (1.7% Co loading) was inactive. The bimetal cluster-derived catalysts gave significantly enhanced rates of oxygenate formation, compared with a $Rh_4(CO)_{12}$-derived catalyst. A concomitant enhancement of activity to alkane was observed. The presence of Co in the catalysts gave rise to the formation of alcohols. Here a $RhCo_3(CO)_{12}$-derived catalyst was the most active for both hydroformylation systems in which unusual olefin conversions were gained under the same conditions. In order for the precise comparison of catalytic selectivities of the catalysts studied, olefin conversions with this catalyst were controlled to lower levels by increasing the flow rate of reaction gases and lowering the temperature. Lowering the temperature favored the selectivity to oxygenates, while shortening the contact time seemed to lead to a decrease of selectivity to alcohols without changing the selectivity to aldehydes.

In ethylene hydroformylation, the activities of the bimetal cluster-derived catalysts were 7–13 times that of the $Rh_4(CO)_{12}$-derived catalyst for the formation of oxygenates. The selectivity to oxygenates was only slightly improved, especially that to *n*-propanol which was enhanced to a smaller extent as seen in table 1. These results indicate that Co in those two Rh catalysts promotes catalytic ethylene hydroformylation and hydrogenation almost in parallel. But for catalytic propanal hydrogenation to propanol, the promotion of Co is weak and tends to increase with increasing Co : Rh atomic ratios. In propylene hydroformylation, the activities of bimetal cluster-derived catalysts were 21–33 times that of the $Rh_4(CO)_{12}$-derived catalyst for the formation of oxygenates. The selectivity to oxygenates was appreciably enhanced and moreover the production of butanol was prevailing with a selectivity of 60% or so. These results indicate that Co in the Rh catalysts not only strongly promotes catalytic propylene hydroformylation, especially catalytic butanal hydrogenation, but also suppresses catalytic propylene hydrogenation.

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

Precursor	C_2H_4 conversion (%)	Activity (mol (Rh mol)$^{-1}$ min^{-1})		Selectivity (mol%)	
		C_2H_6	$C_2H_5CHO + n\text{-}C_3H_7OH$	$C_2H_5CHO + n\text{-}C_3H_7OH$	$n\text{-}C_3H_7OH$
$Co_2(CO)_8$	0	0	0	–	–
$Rh_4(CO)_{12}$	2.5	0.7	1.3	66	0
$Rh_2Co_2(CO)_{12}$	13.8	2.9	8.4	74	7
$RhCo_3(CO)_{12}$	26.8	4.0	16.6	80	22
	14.4[b]	8.2	19.2	70	11
	3.8[c]	0.1	2.8	97	7

[a] At 423 K, $C_2H_4 : CO : H_2 = 20 : 20 : 20$ ml/min.
[b] At 423 K, $C_2H_4 : CO : H_2 = 50 : 50 : 50$ ml/min.
[c] At 383 K, $C_2H_4 : CO : H_2 = 20 : 20 : 20$ ml/min.

Table 2
Catalytic properties of SiO_2-supported cluster-derived catalysts in atmospheric propylene hydroformylation[a]

Precursor	C_3H_6 conversion (%)	Activity (mol (Rh mol)$^{-1}$ min^{-1})		Selectivity (mol%)	
		C_3H_8	$C_3H_7CHO + C_4H_9OH$	$C_3H_7CHO + C_4H_9OH$	C_4H_9OH
$Co_2(CO)_8$	0	0	0	–	–
$Rh_4(CO)_{12}$	0.6	0.4	0.2	33	0
$Rh_2Co_2(CO)_{12}$	6.9	1.1	4.2	80	64
$RhCo_3(CO)_{12}$	12.6	3.3	6.6	67	59
	3.4[b]	0.2	1.1	85	59

[a] At 443 K, $C_3H_6 : CO : H_2 = 20 : 20 : 20$ ml/min.
[b] At 403 K, $C_3H_6 : CO : H_2 = 10 : 10 : 10$ ml/min.

Based on the above performances of the bimetal cluster-derived catalysts, we sought to understand the behavior of such bimetal carbonyl clusters on the surface of SiO_2 and the nature of supported catalytic species thus derived. We focused our IR investigation on the $RhCo_3(CO)_{12}/SiO_2$ system.

Under Ar, when $RhCo_3(CO)_{12}$ was dripped from a deep brown *n*-hexane solution (ν(CO) bands in fig. 1 (a)) onto a SiO_2 wafer which had experienced dehydroxylation at 623 K, the surface IR spectrum in the presence of the solvent exhibited two broad bands at 2067s and 1857m cm^{-1} and a shoulder at 1913 cm^{-1} as shown in fig. 1 (b). It seems that a significant downward shift of the bridged carbonyl bands for the original cluster occurs on the surface as well as the apparent degeneration of the 1893m and 1866m cm^{-1} bands. A subsequent 2 h treatment under vacuum (1.3×10^{-6} kPa) at room temperature led to a strong downward shift and broadening of both linear carbonyl and bridged carbonyl bands with considerable weakening in their intensities. Meanwhile the wafer remained deep brown. Wondering whether the starting cluster $RhCo_3(CO)_{12}$ is still intactly retained on SiO_2 with only electron transfer from surface groups, we carried out a type experiment for extracting the adspecies in the following.

Under in situ conditions, 0.2 g SiO_2 was impregnated with 5.8 mg $RhCo_3(CO)_{12}$ in *n*-hexane solution in a Schlenk vessel to give a deep brown solid coexisting with the $RhCo_3(CO)_{12}$ solution. After 2 h contact only part of $RhCo_3(CO)_{12}$ was adsorbed on the surface. The solution was separated from the solid and the latter was washed carefully with 1 ml *n*-hexane. Then the solid was subjected to treatment under vacuum at room temperature for 2 h. The resulting sample was transferred to a clean Schlenk tube and 1 ml *n*-hexane was added onto it. After a little stirring, the liquid turned deep brown and showed a spectrum characteristic of $RhCo_3(CO)_{12}$ (fig. 1 (d)). This extraction result demonstrates that the starting cluster which interacted with the surface is strongly physisorbed on SiO_2 dehydroxylated at 623 K. Since the initial carbonyl bands systematically shift to lower wavenumbers upon treatment under vacuum, it is suggested that there exists a nucleophilic attack by electron-donating groups on the surface of SiO_2 on the metal centres of $RhCo_3(CO)_{12}$. Although it is documented that cobalt-containing clusters are sensitive to basic solvents possibly due to a higher affinity of cobalt

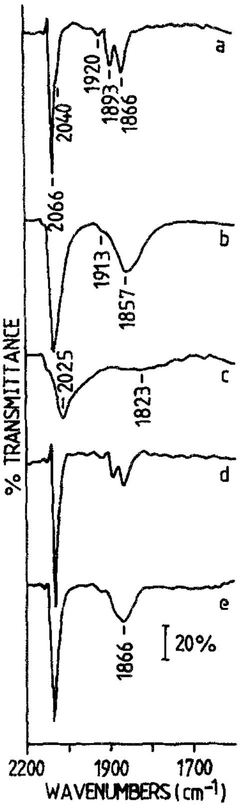

Fig. 1. IR spectra in ν(CO) region of $RhCo_3(CO)_{12}$ and SiO_2-supported $RhCo_3(CO)_{12}$. (a) $RhCo_3(CO)_{12}$ in *n*-hexane; (b) upon contact with SiO_2 predehydroxylated at 623 K by the above solution under Ar; (c) after 2 h evacuation (1.3×10^{-6} kPa) at 293 K following (b); (d) extract in *n*-hexane from the solid surface after (c); (e) $RhCo_3(CO)_{12}$ in $CHCl_3$.

towards oxygen [12], no significant downward shift of IR bands for $Co_4(CO)_{12}$ was observed on the surface of SiO_2 [13] as was the case with $Rh_6(CO)_{16}/SiO_2$ [14]. We have also confirmed these IR results via treating $Co_4(CO)_{12}/SiO_2$ and $Rh_6(CO)_{16}/SiO_2$ under vacuum for 2 h. Apparently, there is no electron-deficiency phenomenon for the metal atoms in the $RhCo_3(CO)_{12}$ cluster: nucleophilic attack rarely takes place. But in such a bimetallic Rh–Co system, it was proposed that Co atoms play the role of an electron donor to Rh atoms on the surfaces of certain oxides [8]. Probably due to the concerted action of electron transfer from surface donor groups, we infer the Co atoms in a $RhCo_3(CO)_{12}$ cluster become real electron withdrawing centres resulting in the observed downward shift of the carbonyl bands.

Furthermore, if $RhCo_3(CO)_{12}$ was dissolved in weakly basic solvents such as methyl phenyl ether and chloroform, the solutions exhibited similar spectra to curve b of fig. 1 with a convergence of the two bridged bands as well. Curve e of fig. 1 can convert to curve a after removal of chloroform and addition of *n*-hexane.

This confirms that appropriate Lewis bases do behave as electron-donors to interact with the metal centres of $RhCo_3(CO)_{12}$ to such an extent that $RhCo_3(CO)_{12}$ only loses its normal spectral symmetry presented in *n*-hexane but without decomposition. The corresponding Lewis base on the surface of SiO_2 is likely to be OH^- or/and O^{2-} groups.

Probably as a result of the coordinative attack of surface oxygen on the Co atoms of the cluster, the supported cluster was quite unstable. It transformed into a gem-dicarbonyl-like species presenting doublet features upon slight heating under vacuum as shown in fig. 2. After heating at 348 K the wafer did not change the initial color.

After $RhCo_3(CO)_{12}/SiO_2$ was decarbonylated under H_2 at 623 K, the resultant sample gave a complex spectrum shown in fig. 3 (a) under the mixed gases of C_2H_4, CO and H_2. However, after this catalytic system was treated at 443 K for 2.5 h, a surface carbonyl spectrum resembling curve b of fig. 2 was obtained. Meanwhile a very intense band at 1720 cm^{-1} appeared, which is assigned to propanal, indicating that ethylene hydroformylation proceeded probably on the observed gem-dicarbonyl-like species. To identify this catalytic species, we undertook an IR study on $Rh_4(CO)_{12}$-derived Rh/SiO_2 in parallel.

When a freshly reduced Rh/SiO_2 (1% Rh loading) was exposed to a CO atmosphere alone, the surface Rh consisted of a mixture of geminal CO, linear CO and bridged CO species as shown in fig. 3 (c). Once the gaseous CO was replaced by the reaction gases, only Rh^0-adsorbed CO appeared (fig. 3 (d)) because the oxidation of Rh^0 to Rh^+ on the surface is suppressed by H_2 [15]. Moreover, the adsorbed linear CO band increased in intensity after 2.5 h reaction at 443 K. Accordingly, no

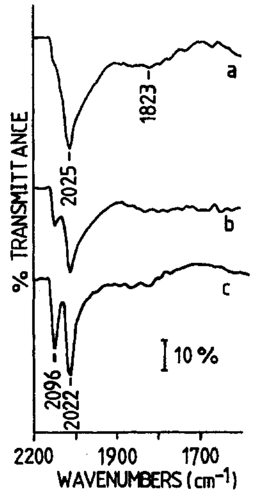

Fig. 2. IR spectra in ν(CO) region of SiO_2-supported $RhCo_3(CO)_{12}$ and its derivatives. (a) The same sample as in curve c of fig. 1; (b) after 0.5 h heating of the above sample under vacuum (1.3×10^{-3} kPa) at 321 K; (c) after 0.5 h heating under vacuum (1.3×10^{-3} kPa) at 348 K following (b).

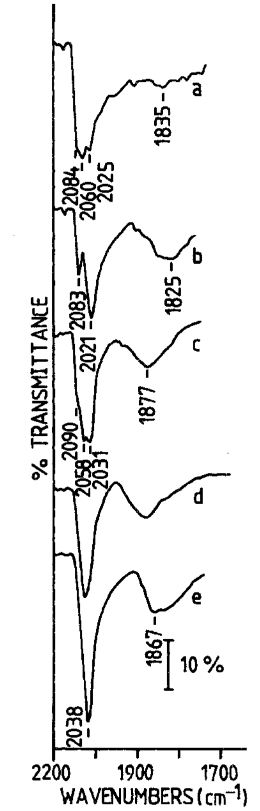

Fig. 3. IR spectra in ν(CO) region of SiO_2-supported samples. (a) After 1 h exposure to an equimolar mixture of C_2H_4, CO and H_2 (total pressure: 39 kPa) at 293 K of $RhCo_3(CO)_{12}/SiO_2$ treated with H_2 at 623 K for 2 h; (b) after 2.5 h heating at 443 K in a close IR cell following (a); (c) after 1 h exposure to CO at 3.9 kPa and 293 K of $Rh_4(CO)_{12}/SiO_2$ treated with H_2 at 623 K for 2 h; (d) after 1 h exposure of the same catalyst as in (c), to an equimolar mixture of C_2H_4, CO and H_2 (total pressure: 78 kPa) at 293 K; (e) after 2.5 h heating at 443 K in a close IR cell following (d).

$Rh^+(CO)_2$ was formed on Rh/SiO_2 under these catalytic conditions. It has been documented that Rh^0 is an active site for heterogeneous hydroformylation [16].

However, on the $RhCo_3(CO)_{12}$-derived catalyst, terminal CO species evolved in favor of the gem-dicarbonyl-like species under the catalytic conditions. This change is similar to that in fig. 2. Although the choice of $RhCo_3(CO)_{12}$ is conducive for the production of atomically dispersed Rh sites on the surface, such Rh sites appear not to be isolated in the form of Rh^+. We have communicated [17] that the oxidation of Rh^0 by surface OH^- can be inhibited by the electron-donating effect of the Co additive. In addition, only Rh^0 carbonyls and Co^0 carbonyls were discerned by IR spectroscopy during thermal decompositions of $Rh_6(CO)_{16}/SiO_2$ [15] and $Co_4(CO)_{12}/SiO_2$ [18] under vacuum. These observations lead us to speculate that CO is not simply adsorbed on isolated Rh ensembles but on bimetallic Rh–Co clusters so as to regenerate, in part, the starting carbonyl cluster. The latter may decarbonylate to a pseudo-gem-dicarbonyl species by heating under vacuum or under the catalytic conditions, keeping its bimetallic structural integrity.

Further information is obtained by IR study as shown in fig. 4. When $RhCo_3(CO)_{12}/SiO_2$ was directly treated under an ethylene hydroformylation atmosphere at 491 K, the gem-dicarbonyl-like species was also detected. After heating to 526 K, a linear CO band at 2028 cm^{-1} appeared in place of the 2084 and 2024 cm^{-1} bands in the terminal ν(CO) region. This seems to indicate that the bimetal cluster is destroyed due to the M–M′ bond dissociation by CO [19,20] at higher temperatures.

It is worth emphasizing that the formation of supported bimetal particles from the organotransition bimetal clusters with the same composition has become a successful example of the preparative approach to bimetal catalysts [21]. Regarding the Rh–Co system, Ichikawa reported an interaction between Rh–Co carbonyl clusters and carbon and Al_2O_3 by an EXAFS study [8]. He suggested that $RhCo_3$ and Rh_2Co_2 cluster frameworks could be kept on both kinds of surfaces after H_2 treatment at 673 K in spite of the metal–oxygen bonding on the surface. In our case with $RhCo_3(CO)_{12}/SiO_2$, combining the unusual catalytic performances for hydroformylation with the IR characterization results, we reckon that the Rh–Co cluster framework may be preserved, at least in part, after H_2 treatment at 623 K

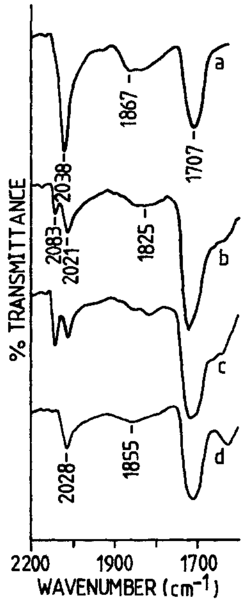

Fig. 4. IR spectra in ν(CO) region of SiO_2-supported catalysts after ethylene hydroformylation under an equimolar mixture of C_2H_4, CO and H_2 in a close IR cell. (a) Rh/SiO_2 under 78 kPa at 443 K for 2.5 h, which was derived from $Rh_4(CO)_{12}$ by 2 h H_2 treatment at 623 K; (b) a catalyst under 39 kPa at 443 K for 2.5 K, which was derived from $RhCo_3(CO)_{12}$ by 2 h H_2 treatment at 623 K; (c) $RhCo_3(CO)_{12}/SiO_2$ under 39 kPa at 491 K for 0.5 h; (d) under 39 kPa at 526 K for 0.5 h following (c).

and may be recarbonylated at room temperature. The actual catalyst with the pseudo-gem-dicarbonyl bands is suggested to be a subcarbonyl cluster $RhCo_3(CO)_{12-x}$. It is possible that a nucleophilic attack of surface oxygen on the Co atoms of $RhCo_3(CO)_{12}$ facilitates the decarbonylation of the cluster according to the IR evolution in fig. 2. Such a direct attack favors the formation of metal–oxygen bonds, thus stabilizing the $RhCo_3$ framework as well as dispersing the bimetal catalysts on the surface. This kind of cluster–support interaction may play an important role of preventing the dissociation of M–M′ bonds in the cluster by CO under catalytic hydroformylation conditions.

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