IR STUDIES OF THE THERMAL DECOMPOSITION OF $[Rh_6(CO)_{16}+Co_4(CO)_{12}]/SiO_2$: EVIDENCE FOR THE FORMATION OF $RhCo_3(CO)_{12}/SiO_2$

HUANG Lin XU Yi-De

State Key Laboratory of Catalysis
Dalian Institute of Chemical Physics, The Chinese Academy of Sciences
Dalian, Liaoning 116023

Abstract Thermal decomposition of $[Rh_6(CO)_{16}+Co_4(CO)_{12}]/SiO_2$, $Ph_6(CO)_{16}/SiO_2$ and $Co_4(CO)_{12}/SiO_2$ under a static hydroformylation atmosphere (C_2H_4:CO:H_2=6.5:6.5:6.5 kPa) have been investigated by means of IR spectroscopy. $Rh_6(CO)_{16}$ is thermally more stable than $Co_4(CO)_{12}$ on the SiO_2 surface. $RhCo_3(CO)_{12}$ is formed by the direct reaction between $Rh_6(CO)_{16}$ and $Co_4(CO)_{12}$ on the SiO_2 surface at 423~473 K. Comparison of the thermal stabilities of supported $Rh_6(CO)_{16}$ and $Co_4(CO)_{12}$ suggests that the surface reaction producing $RhCo_3(CO)_{12}$ proceeds via decarbonylation of $Co_4(CO)_{12}$. Spectroscopic results under C_2H_4+CO+H_2 and under CO alone show that the formation of $RhCo_3(CO)_{12}$ from monometallic clusters is influenced by the atmosphere used.

Keywords $Rh_6(CO)_{16}$, $Co_4(CO)_{12}$, formation of $RhCo_3(CO)_{12}$, silica, thermal decomposition, hydroformylation

Introduction

The preparative approach of an effective bimetallic catalyst is always a subject of important significance in heterogeneous catalysis. In our recent studies, we found that the bimetallic carbonyl cluster $RhCo_3(CO)_{12}$ favorably gives the bimetallic $RhCo_3$ cluster on the SiO_2 surface after thermal decarbonylation under H_2 or under O_2, which brings about 20-fold enhanced rate of formation of oxygenates in ethylene hydroformylation compared to a monometallic catalyst Rh/SiO_2[1,2]. IR spectroscopic evidence has been provided that

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$RhCo_3(CO)_{12}/SiO_2$ is readily regenerated from $RhCo_3$ under catalytic conditions and is responsible for the strong catalysis[1]. The present paper describes an unexpected facile preparation of $RhCo_3(CO)_{12}$ from $Rh_4(CO)_{12}$ and $Co_2(CO)_8$ on the SiO_2 surface. We show *in situ* IR results obtained during the process of formation of $RhCo_3(CO)_{12}$ via coimpregnation of $Rh_4(CO)_{12}$ and $Co_4(CO)_8$ on the surface followed by thermal treatments under CO containing atmosphere.

Experimental

$RhCl_3\cdot nH_2O$ and $Co_2(CO)_8$ were purchased commercially. $Rh_4(CO)_{12}$ was synthesized from $RhCl_3\cdot nH_2O$ as described in Ref. 3. SiO_2 was a silica "Aerosil" supplied by Degussa with a surface area of 380 m^2/g. *n*-Hexane used as the solvent was distilled over P_2O_5. Subsequently it was stored under Ar over activated 5A molecular sieves. The gases C_2H_4, CO, H_2 and Ar had a purity of 99.99 %. Before introduction into a sample vessel and an IR cell, they were further purified by passage through traps of activated 5A molecular sieves and Mn/MnO to eliminate traces of water and oxygen.

IR experiments were carried out using a single beam cell with CaF_2 windows. SiO_2 was pressed into wafers of 20 mg each and placed in the IR cell where the wafers were subjected to the desired treatments. The SiO_2 wafers were partially dehydroxylated under vacuum (1.3×10^{-6} kPa) at 623 K for 4 h and then dripped with the carbonyl clusters in *n*-hexane under Ar in the IR cell. All IR spectra were recorded on a Bio-Rad FTS-7 spectrometer at room temperature. Surface IR spectra were measured in the presence of gas phases by subtracting the contributions of solid and gas phases.

Results and discussion

The studies were systematically performed under a hydroformylation atmosphere and under a CO atmosphere in a static IR cell. The employ of CO and hydroformylation atmospheres is to stabilize metal carbonyl clusters, avoiding their thermal decomposition at moderate temperatures and their oxidation[4]. The choice of the hydroformylation reaction is aimed at determining, as a sensitive probe, the formation of bimetallic Rh-Co clusters during the process of thermal treatments of $[Rh_6(CO)_{16} + Co_4(CO)_{12}]/SiO_2$[1].

Figs.1 and 2 show the *in situ* surface IR spectra collected during thermal decomposition of $[Rh_6(CO)_{16} + Co_4(CO)_{12}]/SiO_2$ (Rh:Co=1:3 atomic ratio) under a static mixture of C_2H_4, CO and H_2 (6.5:6.5:6.5 kPa). The supported monometallic cluster

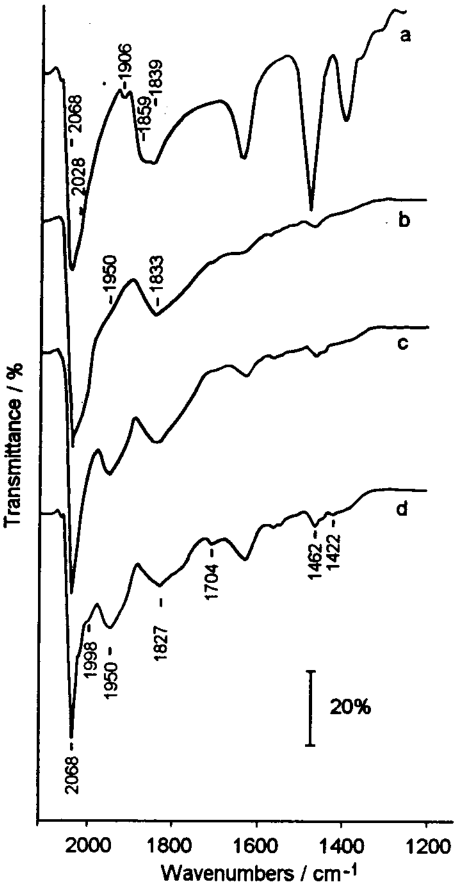

Fig.1 IR spectra of a [$Rh_4(CO)_{12}$+$Co_2(CO)_8$]-derived SiO_2-supported sample during thermal treatments under (C_2H_4+CO+H_2) (6.5:6.5:6.5 kPa) in a static IR cell

(a) After coimpregnation of $Rh_4(CO)_{12}$ and $Co_2(CO)_8$ in *n*-hexane on SiO_2 predehydroxylated at 623 K;

(b) After 50 min of evacuation (1.3×10^{-3} kPa) following (a);

(c) After exposure to (C_2H_4+CO+H_2) following (b): 16 h at 293 K;

(d) After exposure to (C_2H_4+CO+H_2) following (b): 1 h at 403 K

mixture was made by impregnating a SiO_2 wafer predehydroxylated at 623 K with an *n*-hexane solution of [$Rh_4(CO)_{12}$+$Co_2(CO)_8$] under Ar in the IR cell and removing the solvent by pumping. As soon as the mixture solution was brought in contact with the SiO_2 wafer, a superimposed spectrum of the bands for $Rh_4(CO)_{12}$ and $Co_4(CO)_{12}$ was obtained on the surface in the presence of the solvent [Fig.1(a)] since $Co_2(CO)_8$ converts promptly to $Co_4(CO)_{12}$ on SiO_2[5]. Subsequent evacuation of the solvent resulted in a spectrum containing the bands for adsorbed $Rh_6(CO)_{16}$ and $Co_4(CO)_{12}$ due to the conversion

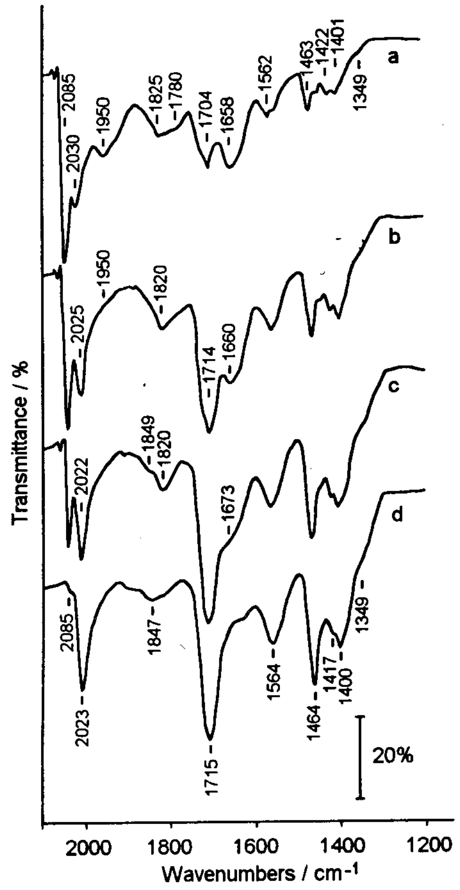

Fig.2 IR spectra of a [$Rh_4(CO)_{12}$+$Co_2(CO)_8$]-derived SiO_2-supported sample during thermal treatments under (C_2H_4+CO+H_2) (6.5:6.5:6.5 kPa) in a static IR cell [following Fig.1(d)]
(a) 1 h at 431 K; (b) 1 h at 458 K; (c) 1 h at 482 K; (d) 1 h at 508 K

of $Rh_4(CO)_{12}$ to $Rh_6(CO)_{16}$ on the surface, as demonstrated by our previous work[6]. After the wafer of [$Rh_6(CO)_{16}$+$Co_4(CO)_{12}$]/SiO_2 had been exposed to the hydroformylation atmosphere at room temperature, there was almost no spectral modification except for an intensity increase of the 1950 cm^{-1} band corresponding to the mononuclear cobalt subcarbonyl mentioned elsewhere[7], as indicated by the spectral variation from Figs.1 (b) to (c). The shape of the latter essentially had no change until 403 K, showing that the supported cluster mixture is stable till 403 K. Above this temperature, very weak bands at 1704, 1462 and 1422 cm^{-1} appeared, which are due to trace amounts of propanal adsorbed on SiO_2 resulting from ethylene hydroformylation. When the temperature was raised to 431 K, the initial band at 2068 cm^{-1} disappeared and the band at

1950 cm^{-1} depleted. Simultaneously new bands at 2085 and 2030 cm^{-1} appeared, concomitant with the downward shift of the broad bridged band, as shown in Fig.2(a). The 2085 cm^{-1} band may be regarded as the linear carbonyl feature of $Rh_6(CO)_{16}/SiO_2$ and the 2030 cm^{-1} band may belong to the linear carbonyl feature of $RhCo_3(CO)_{12}/SiO_2$, as described before[1]. This suggests that $Co_4(CO)_{12}$ has decarbonylated in the $Rh_6(CO)_{16}$+$Co_4(CO)_{12}$ mixture and $Rh_6(CO)_{16}$ is still stable on the surface at 403 K and that $RhCo_3(CO)_{12}$ starts to form simultaneously. The appearance of the 1780 cm^{-1} shoulder may be attributed to the production of trace amounts of $Co_6(CO)_{16}$[8,9]. At this temperature, it was also noted that the bands for adsorbed propanal grew and another band at 1658 cm^{-1} emerged. We assigned this latter band to 3-pentanone adsorbed on SiO_2 as the minor product from ethylene hydroformylation over cobalt-containing catalysts[1,10,11]. As the temperature increased, the 2085 cm^{-1} band diminished in favor of the increase of the 2030 cm^{-1} band in intensity. The 1950 cm^{-1} band almost fully disappeared at 458 K. The band intensities for adsorbed propanal increased with increasing temperature, whereas that for adsorbed 3-pentanone decreased with increasing temperature, as shown in Fig.2. When the temperature reached 508 K, the typical band at 2085 cm^{-1} for $Rh_6(CO)_{16}/SiO_2$ vanished and only the bands at 2023 and 1841 cm^{-1} for $RhCo_3(CO)_{12}/SiO_2$ were present as the carbonyl features in the spectrum. At the same time, the band near 1660 cm^{-1} for adsorbed 3-pentanone disappeared and the band at 1715 cm^{-1} for adsorbed propanal became predominant. The gradual disappearance of 3-pentanone may be explained in terms of its hydrogenation to give 3-pentanol at elevated temperatures. A set of bands situated at 1464, 1417, 1400 and 1349 cm^{-1} may be ascribed to a mixture of propanal, *n*-propanol and 3-pentanol. The wavenumber diminution of the linear carbonyl band to 2023 cm^{-1} under catalytic conditions for $RhCo_3(CO)_{12}/SiO_2$ compared to the normal one at 2028 cm^{-1} [1], can be interpreted by a decrease of the dipole-dipole interaction of the linear CO due to dilution from adsorbed reaction products[12]. During this thermal decomposition, the occurrence of ethylene hydroformylation accompanied the presence of a strange band at 1564 cm^{-1}. This band developed significantly with increasing temperature but remained constant in intensity at a given temperature as the reaction proceeded[1]. This band was also present with the monometallic catalyst Co/SiO_2 but it was not with the monometallic catalyst Rh/SiO_2[13]. By comparison with some related IR data[14,15], this band and another weak band situated at 1400~1450 cm^{-1} (perhaps covered by the existing bands) may be assigned to the bidentate ethyl acetate of which the oxygen atoms attach possibly on a surface cobalt atom. The suggested bidentate species probably play the role of a hydroformylation intermediate over cobalt containing catalysts.

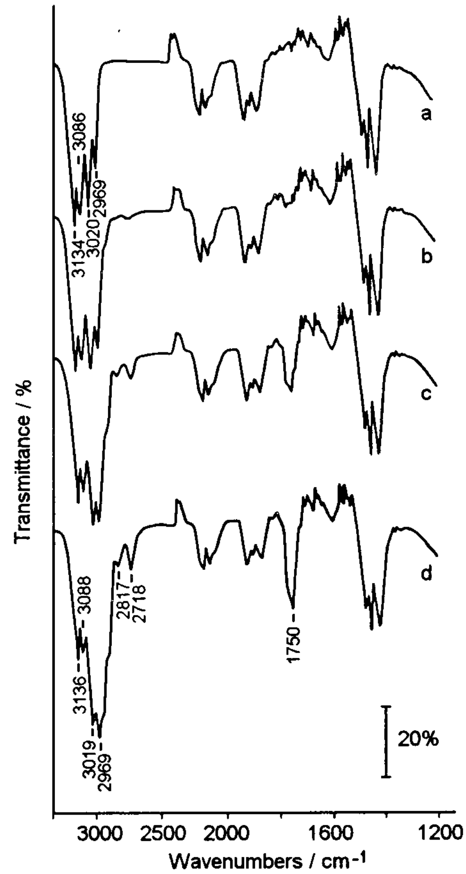

Fig.3 IR spectra in gas phase corresponding to Figs.1 and 2
(a) 16 h at 293 K; (b) 1 h at 458 K; (c) 1 h at 482 K; (d) 1 h at 508 K

In parallel, the IR spectral evolution in gas phase was followed during thermal treatment of [$Rh_6(CO)_{16}$+$Co_4(CO)_{12}$]/SiO_2 under the hydroformylation atmosphere. From Fig.3, it can be seen that only the bands at 2817, 1718 and 1750 cm^{-1} characteristic of propanal were present, even at a temperature as high as 508 K, among all the oxygenated products from ethylene hydroformylation. It follows that the mixture of oxygenated products merely comprises negligible amounts of *n*-propanol, 3-pentanone and 3-pentanol in this static system, agreeing with a prevailing selectivity to propanal with respect to oxygenated products out of ethylene hydroformylation over the [$Rh_6(CO)_{16}$+$Co_4(CO)_{12}$]/SiO_2-derived catalyst found in the dynamic catalytic test[7].

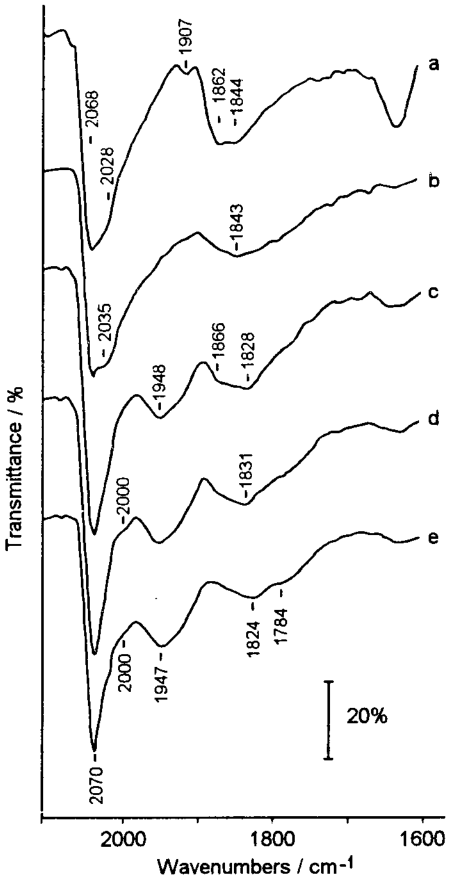

Fig.4 IR spectra of a [$Rh_4(CO)_{12}$+$Co_2(CO)_8$]-derived SiO_2-supported sample during thermal treatments under CO (6.5 kPa) in a static IR cell

(a) After coimpregnation of $Rh_4(CO)_{12}$ and $Co_2(CO)_8$ in *n*-hexane on SiO_2 predehydroxylated at 623 K;
(b) After 50 min of evacuation (1.3×10^{-3} kPa) following (a);
(c) After exposure to CO following (b): 14 h at 293 K;
(d) After exposure to CO following (b): 1 h at 369 K;
(e) After exposure to CO following (b): 1 h at 403 K

In order to further confirm the role of CO in stabilizing the $Rh_6(CO)_{16}$+$Co_4(CO)_{12}$ mixture supported on SiO_2 and understand the influence of gaseous environment on the formation of bimetallic $RhCo_3$ clusters, analysis of thermal decomposition of [$Rh_6(CO)_{16}$+$Co_4(CO)_{12}$]/SiO_2 under CO (6.5 kPa) was carried out. Figs.4 and 5 show the *in situ* surface IR spectra taken during this process. In nice agreement with the

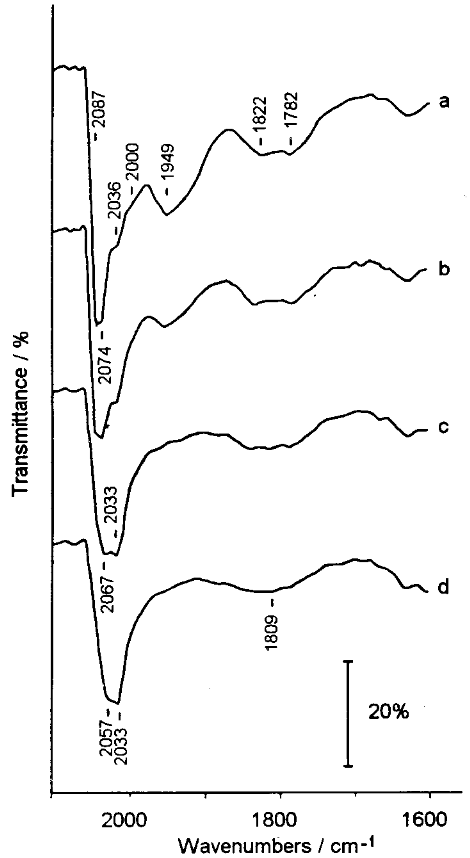

Fig.5 IR spectra of a $[Rh_4(CO)_{12}+Co_2(CO)_8]$-derived SiO_2-supported sample during thermal treatments under CO (6.5 kPa) in a static IR cell [following Fig.4(e)]
(a) 1 h at 428 K; (b) 1 h at 458 K; (c) 1 h at 483 K; (d) 1 h at 506 K

observations in the case under C_2H_4 + CO + H_2, the supported cluster mixture was stable with the formation of the mononuclear cobalt subcarbonyl in less amounts displaying the 1948 cm^{-1} band below 403 K under CO, as indicated by a set of analogous spectra from Figs.4 (c) to (e). Above 403 K, the initial carbonyl bands decreased progressively in intensity and the shoulder at 1784 cm^{-1} presumably related to $Co_6(CO)_{16}$ was clearly observed. At 428 K, the depletion of the 2070 cm^{-1} band led to the emergence of two bands at 2087 and 2074 cm^{-1}. As in the case under C_2H_4+CO+H_2, the 2087 cm^{-1} band may be attributed to the linear carbonyl feature of $Rh_6(CO)_{16}/SiO_2$. $Co_4(CO)_{12}$ is assumed to have been more or less decarbonylated at this stage. The simultaneous appearance of a shoulder at 2036 cm^{-1} suggests the beginning of formation of $RhCo_3(CO)_{12}/SiO_2$. However, as the temperature continued to increase, the 2036 cm^{-1} band developed no longer although the 2087 and 1949 cm^{-1} bands disappeared gradually.

After thorough decarbonylation of the initial monometallic clusters at 506 K, the spectrum displayed another linear band at 2057 cm^{-1} as well as the 2033 cm^{-1} band. The 2057 cm^{-1} band was still fairly present at higher temperatures. It is highly likely to correspond to linear CO adsorbed on metallic rhodium particles resulting from the decomposition of $Rh_6(CO)_{16}$ on SiO_2. This result slightly differs from that obtained under the hydroformylation atmosphere. Under CO alone, $RhCo_3(CO)_{12}$ appears likely to be only partly produced from rhodium and cobalt monometallic clusters on SiO_2.

For the purpose of gaining more insight into the nature of the surface reaction between the two monometallic clusters which results in $RhCo_3(CO)_{12}$, thermal stabilities of $Rh_6(CO)_{16}/SiO_2$ and $Co_4(CO)_{12}/SiO_2$ under the same hydroformylation atmosphere were examined.

Figs.6 and 7 present the *in situ* surface IR spectra obtained during thermal decomposition of $Rh_6(CO)_{16}/SiO_2$ under a static mixture of C_2H_4, CO and H_2 (6.5:6.5:6.5 kPa). $Rh_6(CO)_{16}/SiO_2$ was derived by impregnating a SiO_2 wafer predehydroxylated at 623 K with $Rh_4(CO)_{12}$/*n*-hexane under Ar and removing the solvent under vacuum [Fig.6 (a and b)]. After exposure of $Rh_6(CO)_{16}/SiO_2$ to the hydroformylation atmosphere, there was no spectral modification until at least 451 K, as shown in Fig.7(b). At 475 K, the carbonyl spectrum of $Rh_6(CO)_{16}/SiO_2$ decreased slightly in intensity in favor of the appearance of shoulder bands near 2054 and 1887 cm^{-1} [Fig.7(c)], indicative of the partial transformation of $Rh_6(CO)_{16}$ to metallic rhodium particles on the surface[4,16]. Increasing the temperature to 493 K resulted in the almost thorough disappearance of $Rh_6(CO)_{16}$ and the obvious appearance of the bands at 2053 and 1906 cm^{-1} due to adsorbed CO on metallic rhodium particles. The results indicate that $Rh_6(CO)_{16}$ is stable up to at least 451 K and decarbonylates to give metallic particles at higher temperatures on SiO_2 under operating hydroformylation atmosphere. During this thermal decomposition, the formation of propanal as the only oxygenated product from ethylene hydroformylation was obviously noted on the surface. At a temperature lower than 451 K, *e.g.* at 425 K, the spectrum exhibited the weak features at 1706, 1466, 1417 and 1399 cm^{-1} for adsorbed propanal together with the very intense carbonyl bands at 2083 and 1805 cm^{-1} for $Rh_6(CO)_{16}/SiO_2$. At higher temperatures, the bands for adsorbed propanal developed considerably as the decarbonylation of $Rh_6(CO)_{16}/SiO_2$ proceeded. Based on our and other previous investigations, $Rh_6(CO)_{16}$ is inactive itself for hydroformylation in either homogeneous or heterogeneous catalysis[4,17~19]. The observed activity for the formation of propanal before the decomposition of $Rh_6(CO)_{16}/SiO_2$ may be assumed to be related to trace amounts of metallic rhodium particles or rhodium subcarbonyls which might rise from the cluster decarbonylation during the $Rh_4(CO)_{12}$

⟶ $Rh_6(CO)_{16}$ conversion on the surface by evacuation or/and during exposure of $Rh_6(CO)_{16}/SiO_2$ to the C_2H_4 + CO + H_2 atmosphere[4,18]. It is noteworthy that there were neither pentanone formed nor additional band at 1564 cm^{-1} observed in the rhodium-catalyzed hydroformylation system.

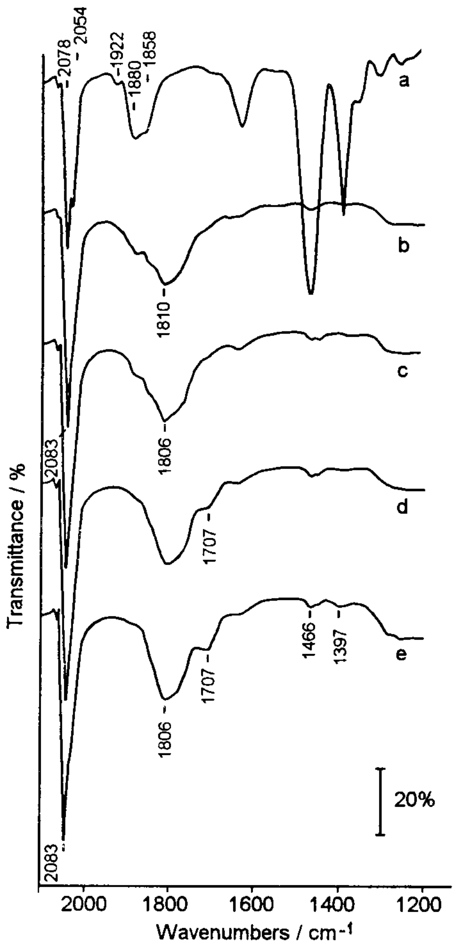

Fig.6 IR spectra of a $Rh_4(CO)_{12}$-derived SiO_2-supported sample during thermal treatments under (C_2H_4+CO+H_2) (6.5:6.5:6.5 kPa) in a static IR cell

(a) After impregnation of $Rh_4(CO)_{12}$/*n*-hexane on SiO_2 predehydroxylated at 623 K;

(b) After 50 min of evacuation (1.3×10^{-3} kPa) following (a);

(c) After exposure to (C_2H_4+CO+H_2) following (b): 2 h at 293 K;

(d) After exposure to (C_2H_4+CO+H_2) following (b): 1 h at 373 K;

(e) After exposure to (C_2H_4+CO+H_2) following (b): 1 h at 401K

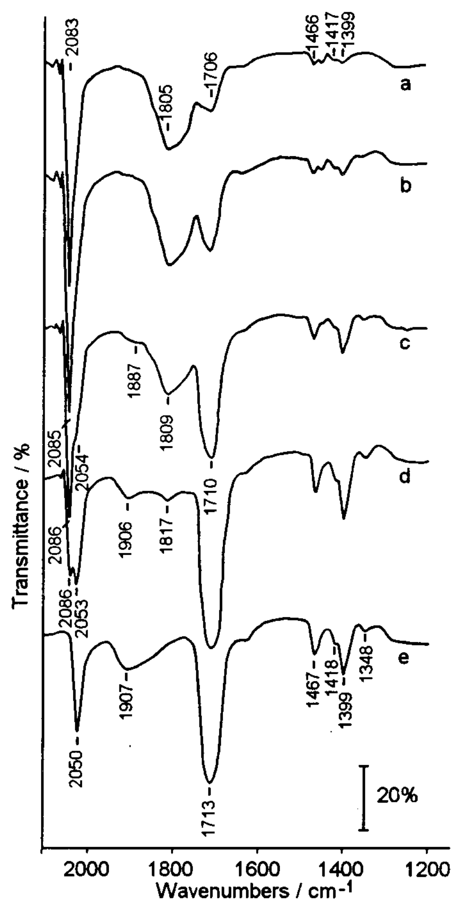

Fig.7 IR spectra of a $Rh_4(CO)_{12}$-derived SiO_2-supported sample during thermal treatments under (C_2H_4+CO+H_2) (6.5:6.5:6. 5 kPa) in a static IR cell [following Fig.6(e)]
(a) 1 h at 425 K; (b) 1 h at 451 K; (c) 1 h at 475 K; (d) 1 h at 493 K; (e) 1 h at 526 K

Figs.8 and 9 show the *in situ* surface IR spectra collected during thermal decomposition of $Co_4(CO)_{12}/SiO_2$ under a static mixture of C_2H_4, CO and H_2 (6.5:6.5:6.5 kPa). $Co_4(CO)_{12}/SiO_2$ was derived by impregnating a SiO_2 wafer predehydroxylated at 623 K with $Co_2(CO)_8$/*n*-hexane under Ar. As shown in Fig.8(a), $Co_2(CO)_8$ converted promptly to $Co_4(CO)_{12}$ upon contact of $Co_2(CO)_8$/*n*-hexane with the SiO_2 wafer, concomitant with the production of a small amount of the presumed mononuclear cobalt subcarbonyl. The latter species increased slightly after removal of the solvent under vacuum. After exposure of the resulting supported cobalt carbonyls to the hydroformylation atmosphere, $Co_4(CO)_{12}$ was stable till 428 K only whereas the

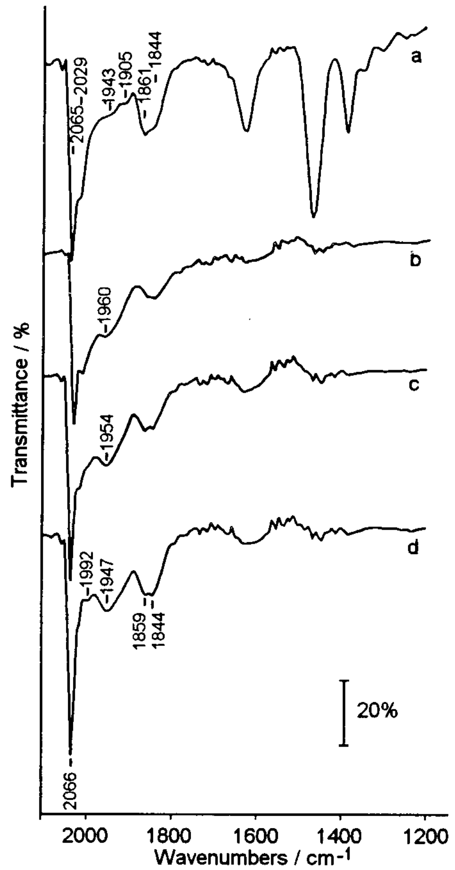

Fig.8 IR spectra of a $Co_2(CO)_8$-derived SiO_2-supported sample during thermal treatments under (C_2H_4+CO+H_2) (6.5:6.5:6.5 kPa) in a static IR cell

(a) After impregnation of $Co_2(CO)_8$/*n*-hexane on SiO_2 predehydroxylated at 623 K;

(b) After 50 min of evacuation (1.3×10^{-3} kPa) following (a);

(c) After exposure to (C_2H_4+CO+H_2) following (b): 2 h at 293 K;

(d) After exposure to (C_2H_4+CO+H_2) following (b): 1 h at 367 K

cobalt subcarbonyl was stable up to 428 K, judging from the carbonyl spectral intensity. A considerable decarbonylation of $Co_4(CO)_{12}/SiO_2$ occurred when the temperature reached 399 K. A further heating at 428 K led to full disappearance of its carbonyl bands. At this stage, the spectrum displayed two other weak bands at 2064 and 1992 cm^{-1} and a shoulder at 2024 cm^{-1} as well as the 1946 cm^{-1} band, as shown in Fig.9(b). We presumably attributed the bands at 2064, 1992 and 1946 cm^{-1} to surface complexes such as $Co^{n+}(CO)_3$·*S* (*n*= 0 or 1, *S* represents a surface site)[13]. At 482 K, this set of bands were replaced by a very weak band at 2028 cm^{-1} corresponding to linear adsorbed CO on metallic cobalt particles[20,21]. During this thermal decomposition, ethylene hydroformylation was noted to occur above 428 K, probably over metallic cobalt particles[20]. The catalytic reaction gave rise to propanal as the predominant oxygenated product identified by the bands at 1713, 1466, 1414, 1400 and 1348 cm^{-1}, and pentanone as the minor oxygenated product identified by the very weak band at 1666 cm^{-1}. The band toward 1564 cm^{-1} could not clearly be detected, probably because of much lower activity of the cobalt catalyst.

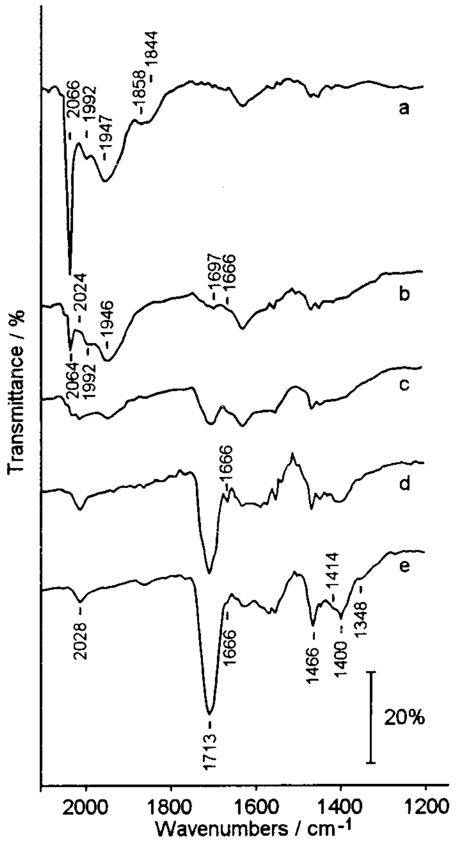

Fig.9 IR spectra of a $Co_2(CO)_8$-derived SiO_2-supported sample during thermal treatments under (C_2H_4+CO+H_2) (6.5:6.5:6.5 kPa) in a static IR cell [following Fig. 8(d)]
(a) 1 h at 399 K; (b) 1 h at 428 K; (c) 1 h at 453 K; (d) 1 h at 482 K; (e) 1 h at 507 K

In the light of the IR results of thermal decompositions of the above four systems, it may be possible to understand the synthesis of $RhCo_3(CO)_{12}$ from $Rh_6(CO)_{16}$ and

$Co_4(CO)_{12}$ on the SiO_2 surface. Under a hydroformylation atmosphere, the carbonyl clusters can indeed be stabilized by CO, since $[Rh_6(CO)_{16}+Co_4(CO)_{12}]/SiO_2$ displays as good thermal stability under $C_2H_4+CO+H_2$ as under CO alone. This is in good accordance with the result in the case of $Rh_6(CO)_{16}/SiO_2$[4]. Comparatively, $Rh_6(CO)_{16}/SiO_2$ is thermally more stable than $Co_4(CO)_{12}/SiO_2$. It is interesting to point out that $RhCo_3(CO)_{12}/SiO_2$ is apparently formed at the temperature (431 K) between the decarbonylation temperatures of $Rh_6(CO)_{16}/SiO_2$ and $Co_4(CO)_{12}/SiO_2$. In the meantime, a comparable band intensity of adsorbed pentanone to that of adsorbed propanal was observed, which seems to be able to support the formation of $RhCo_3(CO)_{12}/SiO_2$[1]. We have demonstrated that SiO_2 supported molecular $RhCo_3(CO)_{12}$ itself is actively responsible for catalysis for ethylene hydroformylation[1]. Below 451 K, $Rh_6(CO)_{16}/SiO_2$ is fairly stable and the rhodium cluster is coordinatively saturated. In contrast, $Co_4(CO)_{12}/SiO_2$ starts to decarbonylate above 367 K. Thus, to initiate the reaction between $Rh_6(CO)_{16}$ and $Co_4(CO)_{12}$ to produce $RhCo_3(CO)_{12}$ on the surface, it is very likely that the coordinatively unsaturated metal center requires to be created. Once the unsaturated cobalt center is produced via decarbonylation, the combination of cobalt and rhodium atoms could be induced to favor the selective formation of $RhCo_3(CO)_{12}$. This is evidenced by the reaction of the coordinatively unsaturated rhodium complex $Rh_2(CO)_4Cl_2$ with $Co_2(CO)_8$. This reaction was reported to take place in solution at room temperature to give $Rh_2Co_2(CO)_{12}$[22]. There has been no report on reactions between coordinatively saturated rhodium and cobalt complexes toward the synthesis of bimetallic Rh-Co clusters in solution. From the current work, it is expected that at least either of $Co_4(CO)_{12}$ and $Rh_6(CO)_{16}$ should be decarbonylated in order to cause the Rh-Co interaction resulting in $RhCo_3(CO)_{12}$ on the surface. In such a case, the surface of SiO_2 plays an important role in dispersing rhodium and cobalt atoms, thus guaranteeing the formation of the Rh-Co bond. It is noteworthy that the atmosphere used influences the occurrence of the surface reaction. Under a hydroformylation atmosphere, $RhCo_3(CO)_{12}$ can be efficiently obtained. In contrast, under an atmosphere of CO alone, $PhCo_3(CO)_{12}$ can be formed only to a limited extent.

The results of IR studies on the formation of $RhCo_3(CO)_{12}/SiO_2$ from $Rh_4(CO)_{12}$ and $Co_2(CO)_8$ by coimpregnation can gain support from the catalytic results. In a parallel work, we have shown that an SiO_2-supported catalyst thus derived and a $RhCo_3/SiO_2$ catalyst derived from $RhCo_3(CO)_{12}$ have equivalent catalytic performances in ethylene hydroformylation and that the high hydroformylation activity is probably ascribed to the bimetallic catalysis rather than to the synergistic catalysis by monometallic rhodium and cobalt sites[7].

The present work has shown the formation of $RhCo_3(CO)_{12}$ from monometallic rhodium and cobalt clusters on SiO_2 in terms of *in situ* IR spectroscopic evidence. The effective formation of bimetallic Rh-Co clusters essentially depends on the choice of monometallic precursors and media. Inorganic rhodium and cobalt salts cannot efficiently give rise to bimetallic Rh-Co clusters on SiO_2 under equivalent conditions[13]. It is impossible to realize the synthesis of bimetallic Rh-Co clusters from coordinatively saturated metal complexes such as $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Co_2(CO)_8$ and $Co_4(CO)_{12}$ in solution[22]. The coimpregnation of monometallic rhodium and cobalt clusters on inorganic supports may provide a promising way for the preparation of bimetallic Rh-Co catalysts in place of the way with bimetallic Rh-Co clusters as precursors.

Conclusions

In this paper, we have shown the IR results of thermal decompositions of $[Rh_6(CO)_{16}+Co_4(CO)_{12}]/SiO_2$, $Rh_6(CO)_{16}/SiO_2$ and $Co_4(CO)_{12}/SiO_2$ under a hydroformylation atmosphere. $RhCo_3(CO)_{12}$ is indeed formed by the surface reaction between $Rh_6(CO)_{16}$ and $Co_4(CO)_{12}$ on SiO_2. The formation of $RhCo_3(CO)_{12}$ is more efficient under $C_2H_4+CO+H_2$ than under CO.

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