

IR studies on the preservation of RhCo_3 clusters on the surface of SiO_2

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Received 30 October 1995; accepted 10 June 1996

Abstract

The adsorption of $\text{RhCo}_3(\text{CO})_{12}$ on the SiO_2 surface, and the interactions of SiO_2 -supported $\text{RhCo}_3(\text{CO})_{12}$ and SiO_2 -supported $\text{RhCo}_3(\text{CO})_{12}$ -derived catalyst with CO have been studied at room temperature by IR spectroscopy. A strong physisorption of $\text{RhCo}_3(\text{CO})_{12}$ on partially dehydroxylated SiO_2 occurs spontaneously, which results in a dramatic change of carbonyl spectral pattern and downward shifts of both linear and bridged carbonyl bands. The SiO_2 -grafted $\text{RhCo}_3(\text{CO})_{12}$ is characterized by two carbonyl bands at 2028 and 1830 cm^{-1} . These observations may be interpreted in terms of a nucleophilic attack of surface oxygen containing groups on the cobalt atoms of the bimetallic cluster. Following decarbonylation of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ under H_2 at 623 K, the resulting catalyst surface can be recarbonylated by to regenerate the starting bimetallic carbonyl cluster which is then gradually disintegrated to $\text{Rh}_6(\text{CO})_{16}$ and $\text{Co}_2(\text{CO})_8$ under CO. In parallel, the precursor $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ itself readily reacts with CO to dissociate to $\text{Rh}_6(\text{CO})_{16}$ and $\text{Co}_4(\text{CO})_{12}$. The reaction mixture is not only identified on the surface during exposure to CO but also extracted from the surface into the organic solvent. The results suggest that the RhCo_3 cluster framework is preserved on SiO_2 despite that the precursor has undergone the severe thermal decarbonylation treatment, and that $\text{RhCo}_3(\text{CO})_{12}$ is regenerated by CO adsorption. A tight SiO_2 surface-bound RhCo_3 cluster is proposed for the supported bimetallic catalyst in terms of cluster–support interaction. In addition, the discrepancy between the regenerated supported $\text{RhCo}_3(\text{CO})_{12}$ and the precursor during the dissociation processes is discussed.

Keywords: SiO_2 -physisorbed $\text{RhCo}_3(\text{CO})_{12}$; Stabilization of RhCo_3 ; Regeneration and dissociation of $\text{RhCo}_3(\text{CO})_{12}$

1. Introduction

Stabilizing successfully molecular organometallic clusters on the surfaces of inorganic materials have long been a noticeable subject in the field of surface organometallic chemistry. Unfortunately, difficulty is always encountered, particularly with most of mixed organometallic clusters which usually suffer from structural dissociation in the presence of

CO [1,2] as well as from facile thermal destruction of metallic skeleton and their oxidative decomposition by surface groups [2–9]. Preservation of the mixed metallic cluster framework on the surfaces relies to a great extent on the nature of cluster–surface interaction, the key factor to alter the strength of $\text{M–M}'$ bonds.

The cluster–support interaction may result in either enhancement of stability of the molecular supported cluster or disruption of the cluster

framework. From the point of view of bond enthalpy, it is expected that the M–M bond is always weaker than the M–CO bond in a metallic carbonyl cluster [10,11] and that the cleavage of the M–M bond must occur before that of the M–CO bond during a process of thermal decomposition for a metallic carbonyl cluster.

As a consequence of the study of the reactivity of organometallic complexes with the surfaces of inorganic supports, some fundamental concepts concerning the modes of interaction between clusters and oxides have been documented [12–14]. On the surfaces of partially dehydroxylated Al_2O_3 and MgO , zerovalent carbonyl clusters are usually strongly chemisorbed to give either anionic hydrido carbonyl clusters via nucleophilic attack of surface OH^- groups on coordinated CO followed by β -H elimination [15–19], or dianionic carbonyl clusters by surface OH^- groups [18,20]. Differing from the alkaline action of surfaces of Al_2O_3 and MgO on carbonyl clusters, the surface of SiO_2 behaves mainly as a neutral support on which almost all organometallic complexes are physisorbed without the loss of the original characteristics of molecular spectra at ambient temperature. In certain cases, the SiO_2 surface reacts with monometallic clusters to form the surface-grafted clusters through oxidative addition of the silanol group to M–M bonds of clusters at moderate temperatures [21,22]. At higher temperatures, surface OH^- groups of SiO_2 and Al_2O_3 make multiple oxidative addition with reductive elimination of H_2 at a single atom of cluster framework with disruption of metallic cluster [21,22]. Nevertheless, the approaches of formation of surface-grafted clusters previously reported seem to involve only the chemical interaction between the metal atom of cluster and the rigid ligand of support. It is seldom observed that the strong physical interaction occurs between clusters and surface groups with the change of molecular symmetry of complexes and the electron transfer.

We have recently reported a preliminary catalytic research on olefin hydroformylation re-

lated to SiO_2 -supported bimetallic Rh–Co clusters, in which the bimetallic systems were found to display appreciable catalytic performances as compared with a $\text{Rh}_4(\text{CO})_{12}/\text{SiO}_2$ -derived catalyst [23]. In order to reveal the nature of the actual SiO_2 -supported $\text{RhCo}_3(\text{CO})_{12}$ and elucidate whether or not the RhCo_3 cluster integrity can still be retained on the SiO_2 surface after decarbonylation treatment at high temperatures, we characterized in the present work the processes of the adsorption of $\text{RhCo}_3(\text{CO})_{12}$ on SiO_2 and the recarbonylation after H_2 decarbonylation at 623 K by means of IR spectroscopy. The aim of this publication is to describe a novel physical interaction which occurs between $\text{RhCo}_3(\text{CO})_{12}$ and the SiO_2 surface, probably via a nucleophilic attack of surface oxygen-containing groups on the cobalt atoms of the cluster. This interaction can be increased by thermal treatment, which is found to make it possible to stabilize the bimetallic RhCo_3 cluster framework supported on SiO_2 .

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 $\text{Co}_2(\text{CO})_8$ by the method of Edgell and Lyford [24]. $\text{Rh}_4(\text{CO})_{12}$ 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. [25,26]. SiO_2 used was a silica 'Aerosil' purchased from Degussa with a surface area of $380 \text{ m}^2/\text{g}$. *n*-hexane and tetrahydrofuran (THF) for use as the solvents were distilled over P_2O_5 and activated 4 Å molecular sieves, respectively. Subsequently they were stored under Ar over activated 5 Å molecular sieves. The gases used (H_2 , CO and Ar) had a purity of 99.99%. Before admission into a sample vessel 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.

In preparing a SiO_2 -supported $\text{RhCo}_3(\text{CO})_{12}$ sample in which 1% Rh was loaded, SiO_2 (60–

80 mesh granule) was previously dehydroxylated at 623 K under vacuum (1.3×10^{-6} kPa) for 5 h and then impregnated with a dry *n*-hexane solution of $\text{RhCo}_3(\text{CO})_{12}$ under Ar. After sufficient 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 precursor thus obtained was pressed into wafers of 20 mg each in air, and placed in a single beam IR cell. In situ IR studies during impregnation were performed, using wafers of 20 mg each made of SiO_2 which were dripped with the carbonyl clusters in dry *n*-hexane under Ar in the single beam IR cell. In the IR cell, the wafers were subjected to the desired treatments under controlled atmospheres.

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 SiO_2 and gaseous contributions. The metal contents of the samples studied were determined by X-ray fluorescence (XRF) and atomic emission (AE) spectroscopies.

3. Results and discussion

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

A wafer of SiO_2 predehydroxylated at 623 K was impregnated with a *n*-hexane solution of $\text{RhCo}_3(\text{CO})_{12}$ under Ar. 0.7% Rh loading was charged in this solid sample according to the analytical result by AE spectroscopy. Figs. 1 and 2 present the IR spectral evolution in the $\nu(\text{CO})$ region during the adsorption of $\text{RhCo}_3(\text{CO})_{12}$ on the SiO_2 surface. Upon contact with the surface, the carbonyl spectrum changed from the initial shape in solution shown in Fig. 1(a) to a new one on the surface shown in Fig. 1(b), the wafer turned deep brown. The latter displayed an apparent degeneration and a

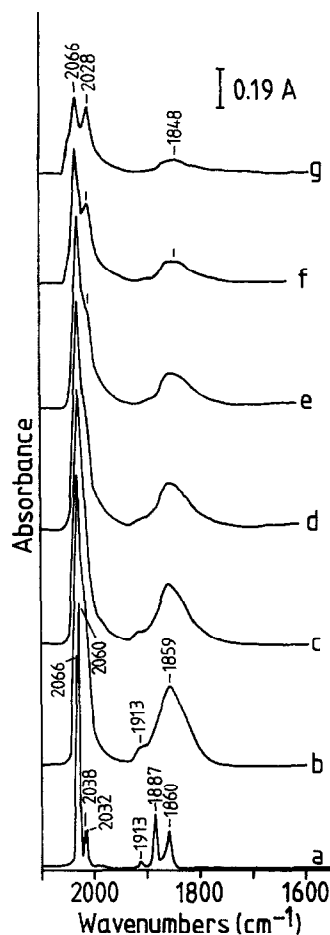


Fig. 1. IR spectral evolution of $\text{RhCo}_3(\text{CO})_{12}$ adsorbed on SiO_2 (0.7% Rh loading) under atmospheric Ar in the presence of *n*-hexane. (a) $\text{RhCo}_3(\text{CO})_{12}$ in *n*-hexane; after impregnation: (b) immediately; (c) 15 min; (d) 35 min; (e) 1 h; (f) 3 h; (g) 6 h.

significant downward shift of bridged carbonyl bands with respect to the spectrum of $\text{RhCo}_3(\text{CO})_{12}$ in *n*-hexane. This is interpreted by the fact that surface oxygen containing groups of SiO_2 interact sensitively as electron-donors with the cobalt atoms of the cluster, thereby modifying the normal spectral symmetry of $\text{RhCo}_3(\text{CO})_{12}$, as has been described in Ref. [23].

Following impregnation, it was clearly observed that the resulting spectrum (Fig. 1(b)) varied progressively with contact time in the presence of the solvent. Systematically, the linear band at 2066 cm^{-1} and the bridged band at

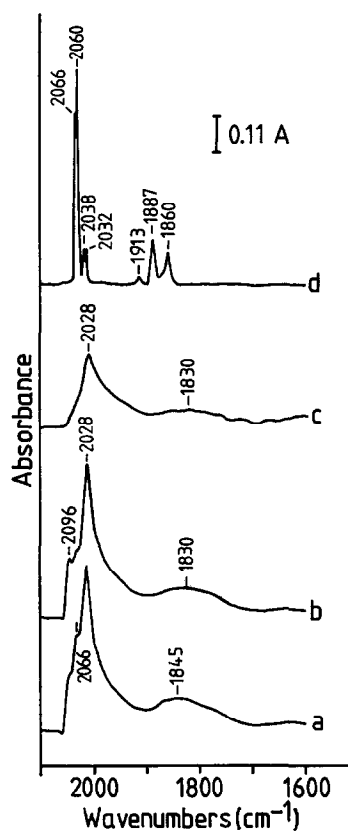


Fig. 2. IR spectral evolution of $\text{RhCo}_3(\text{CO})_{12}$ adsorbed on SiO_2 following Fig. 1(g), under vacuum (1.3×10^{-6} kPa): (a) 15 min; (b) 25 min; (c) $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ (0.3% Rh loading) under vacuum (1.3×10^{-6} kPa); (d) extract in *n*-hexane from $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ (0.5% Rh loading) treated under vacuum (1.3×10^{-6} kPa).

1859 cm^{-1} progressively decreased in intensity. The terminal absorption band width gradually enlarged. 3 h later, a linear band at 2028 cm^{-1} appeared concomitant with depletion of the 2066 cm^{-1} band, and the bridged band center shifted from 1859 to 1848 cm^{-1} . After 6 h of contact of $\text{RhCo}_3(\text{CO})_{12}$ with the surface in the presence of *n*-hexane, the 2028 cm^{-1} band was comparable to the 2066 cm^{-1} band in intensity. The observations on the carbonyl features at this stage doubtless indicated that the starting cluster continued interacting with the SiO_2 surface. The strong diminution of carbonyl band intensity seemed indicative of decarbonylation of the starting cluster. However, no CO evolved in gas phase during this process according to careful

examinations by IR spectroscopy and gas chromatography. The linear band at 2028 cm^{-1} and the broad band at 1848 cm^{-1} do not resemble the bands of CO adsorbed on Rh^0/SiO_2 with less than 1% Rh loading on the basis of our recent study [27]. Also, the carbonyl vibrations on Co/SiO_2 derived from $\text{Co}_2(\text{CO})_8$ give rise to a different spectral pattern, as shown in Fig. 6(b). At the same time, in a separate experiment, after impregnation of $\text{RhCo}_3(\text{CO})_{12}$ in *n*-hexane on SiO_2 in granule followed by a long contact, the initial color (deep brown) in solution was still observed in both solid phase and liquid phase and there was no decolorization in liquid phase. This was plausibly indicative of the physisorption of $\text{RhCo}_3(\text{CO})_{12}$ on the surface of SiO_2 , as observed systematically in the cases of all the SiO_2 -supported organometallic clusters studied. Accordingly, the presence of the two bands at 2028 and 1848 cm^{-1} was suggested to be related to alternative form of $\text{RhCo}_3(\text{CO})_{12}$ in abnormal interaction with the surface of SiO_2 .

To accelerate the interaction of $\text{RhCo}_3(\text{CO})_{12}$ with the surface, the solvent was removed by evacuation and the wafer was treated under vacuum at 1.3×10^{-6} kPa. The initial band at 2066 cm^{-1} was found to deplete rapidly in favor of development of the band at 2028 cm^{-1} . Meanwhile the bridged band became more broad and continued shifting toward lower wavenumbers, as shown in Fig. 2(a, b). After disappearance of the initial carbonyl bands, the surface spectrum obviously exhibited a linear band at 2028 cm^{-1} and a very broad bridged band centered at 2030 cm^{-1} (Fig. 2(b)). The coexisting shoulder near 2096 cm^{-1} could be regarded as one of doublet features. It may be ascribed to a trace amount of subcarbonyl bimetallic cluster $\text{RhCo}_3(\text{CO})_{12-x}$ which probably resulted from partial decarbonylation of the initial cluster on the surface, as described in Ref. [20]. If a lower amount of $\text{RhCo}_3(\text{CO})_{12}$ is introduced onto the surface, the 2096 cm^{-1} band is not visible. The spectrum in Fig. 2(c) displays only the two bands at 2028 and 1830 cm^{-1} for

$\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ containing 0.3% Rh under vacuum. Throughout the above process of adsorption, the wafer remained deep brown.

In order to advance the assumption that the starting cluster is well retained on the SiO_2 surface without decomposition under the above conditions, extraction of adspecies on the surface after evacuation treatment was conducted with *n*-hexane under Ar. The experimentation detail was described in Ref. [20]. As a result, the starting cluster $\text{RhCo}_3(\text{CO})_{12}$ could be successfully extracted from the surface into *n*-hexane. The solvent extract exhibited the carbonyl features characteristic of $\text{RhCo}_3(\text{CO})_{12}$ as shown in Fig. 2(d). When a $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ sample with 0.5% Rh loading following removal of the solvent was treated under vacuum at 1.3×10^{-3} kPa for 2 h, the percent of extracted cluster was 60. If the same sample was treated under vacuum at 1.3×10^{-6} kPa for 2 h, the percent of extracted cluster was only 28.

It is quite interesting to note that the carbonyl spectrum of $\text{RhCo}_3(\text{CO})_{12}$ adsorbed on SiO_2 following treatment under vacuum (Fig. 2(b or c)) is incompatible with that of $\text{RhCo}_3(\text{CO})_{12}$ in solution and that of $\text{RhCo}_3(\text{CO})_{12}$ adsorbed on SiO_2 in the presence of *n*-hexane at the initial stage (Fig. 1(b)). The fact that the starting cluster can be extracted from such a surface by a non-polar solvent is surprising. The result reasonably accounts for a strong physisorption rather than a chemisorption of $\text{RhCo}_3(\text{CO})_{12}$ on SiO_2 that causes a dramatic change in the carbonyl vibrational frequency. In the light of the results of spectral evolution for the surface carbonyls, the interaction between $\text{RhCo}_3(\text{CO})_{12}$ and partially dehydroxylated SiO_2 takes place upon impregnation and increases with contact time. It is well embodied in the fact that the initial carbonyl bands progressively disappear in favor of emergence of new carbonyl bands in weaker intensity at lower wavenumbers. The resulting both linear and bridged carbonyl bands attributed to $\text{RhCo}_3(\text{CO})_{12}$ adsorbed on SiO_2 under vacuum have striking downward shift. Hence, the $\text{RhCo}_3(\text{CO})_{12}\text{-SiO}_2$ interaction is

likely to involve a nucleophilic attack of surface groups on the metal centers of the cluster, thus lowering regularly carbonyl vibrational frequency and changing the original spectral symmetry of $\text{RhCo}_3(\text{CO})_{12}$. Since the surface of dehydroxylated SiO_2 at 623 K is rich in OH^- and O^{2-} groups [28], the electron-donating group is believed to be OH^- or O^{2-} . With regards to the corresponding electron-acceptor, the cobalt atoms in the RhCo_3 cluster are preferentially accessible to the oxygen containing group because of a higher affinity of cobalt toward oxygen [26,29]. This coordination may be favored by treatment under vacuum as seen in Fig. 2(a and b). In this way $\text{RhCo}_3(\text{CO})_{12}$ not only can be tightly grafted on the SiO_2 surface but also can stay almost intact without decomposition. The $\text{RhCo}_3(\text{CO})_{12}$ strongly physisorbed on SiO_2 is characterized by the two carbonyl bands at 2028 and 1830 cm^{-1} . The strength of this kind of cluster–support interaction actually depends on the intimacy of cluster and support and the treatment conditions for a supported cluster. This is clearly demonstrated by the different values of extracted cluster from $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ following evacuation treatments under different vacua at room temperature as mentioned above.

3.2. Studies of the stability of SiO_2 -supported RhCo_3 cluster

To investigate the stability of a SiO_2 -grafted RhCo_3 framework and its structural evolution under the action of CO, wafers made of the precursor $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ with 1% Rh loading underwent decarbonylation before CO adsorption. The wafers were fully decarbonylated after 2 h of treatment in flowing H_2 at 623 K. As soon as 0.2 kPa of CO was admitted onto such a decarbonylated wafer, the surface spectrum presented a linear band at 2028 cm^{-1} and a broad bridged band centered at 1827 cm^{-1} as shown in Fig. 3(a). This spectrum closely resembles that of $\text{RhCo}_3(\text{CO})_{12}$ strongly physisorbed on SiO_2 . It appeared that the RhCo_3

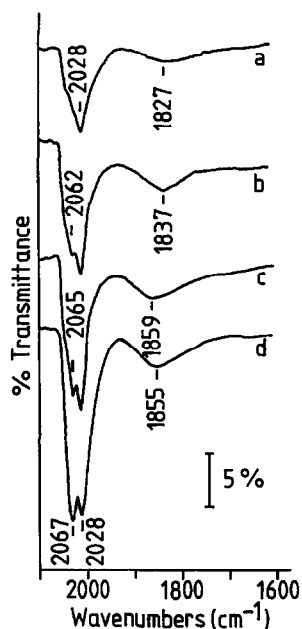


Fig. 3. IR spectra of samples derived by decarbonylation of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ (1% Rh loading) under H_2 at 623 K. (a) Under 0.2 kPa of CO for 1.5 min; (b) under 3.5 kPa of CO for 1.5 min; (c) under 10.7 kPa of CO for 3 min; (d) under 26.4 kPa of CO for 3 min.

framework is readily recarbonylated to $\text{RhCo}_3(\text{CO})_{12}$ on the surface. However, the spectral pattern varied obviously as a function of admitted CO pressure (Fig. 3). Increasing CO pressure led to appearance of another linear band between 2060 and 2070 cm^{-1} and increase of the bridged band in wavenumber, as well as systematic increase of the bands in intensity. With increasing CO pressure, that linear band increased from 2062 to 2067 cm^{-1} in both wavenumber and intensity. Such a set of IR spectra for CO adsorbed are indeed rarely observed on a given metallic surface. Therefore, the initial CO adspecies could have undergone certain chemical change under CO to give partially rise to new adspecies in this case.

The above spectra continued varying with exposure time at a given CO pressure. Fig. 4 shows further IR observations on a wafer during exposure to CO. The spectrum corresponding to the initial adspecies in Fig. 4(a) varied progressively, even under 0.2 kPa of CO pressure, with appearance of the 2058 cm^{-1} band and upward

shift of the bridged band, besides systematic increase of band intensity. To accelerate the spectral variation, the pressure of CO was increased from 0.2 to 13 kPa. In the resulting spectra (Fig. 4(c and d)), the 2058 cm^{-1} band developed markedly and the broad bridged band shifted upward to 1843 cm^{-1} , concomitant with emergence of a shoulder toward 2084 cm^{-1} . Based on these surface IR bands, although they are ill resolved, we tried to compare the bands at 2084 and 2058 cm^{-1} with the bands of rhodium carbonyls and cobalt carbonyls adsorbed on SiO_2 .

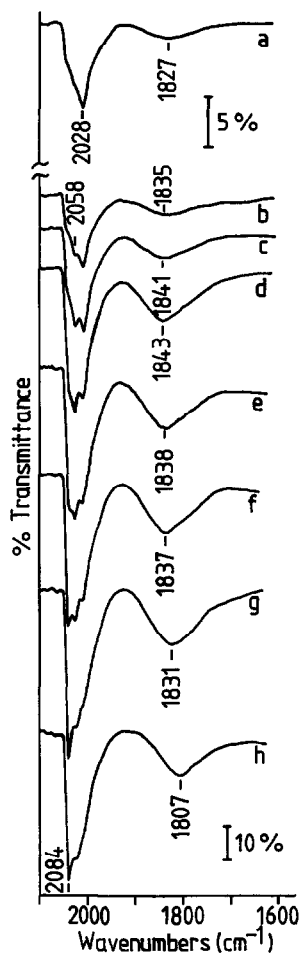


Fig. 4. IR spectra under CO of a sample derived by decarbonylation of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ (1% Rh loading) under H_2 at 623 K. (a) Under 0.2 kPa of CO for 1.5 min; (b) under 0.2 kPa of CO for 1 h; after increasing CO pressure to 13 kPa: (c) 1.5 min; (d) 15 h; (e) 27.5 h; (f) 50.5 h; (g) 147 h; (h) 196 h.

When $\text{Co}_2(\text{CO})_8$ is adsorbed on the SiO_2 surface, there exists a spontaneous and prompt conversion of $\text{Co}_2(\text{CO})_8$ to $\text{Co}_4(\text{CO})_{12}$ due to facile loss of CO [30–32]. But the reaction is completely inhibited by a pressure of CO, as indicated by an earlier work of Schneider et al. [30]. The observed linear band centered at 2058 cm^{-1} may be attributed to $\text{Co}_2(\text{CO})_8$ on SiO_2 under 13 kPa of CO. Simultaneously, the obvious shoulder toward 2083 cm^{-1} may involve the simultaneous presence of $\text{Rh}_6(\text{CO})_{16}$ adsorbed on SiO_2 . But their bridged bands cannot be defined because of the very broad band centered at 1843 cm^{-1} which covered almost the bridged $\text{T}(\text{CO})$ region. On the basis of the carbonyl features and the spectral evolution, these ulterior bands appear related to the transformation of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ to new carbonyl species. On the other hand, the bands of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ ascended in intensity as well with increases of CO pressure and exposure time. Hence we suggest that the bimetallic RhCo_3 framework is first recarbonylated to the starting cluster $\text{RhCo}_3(\text{CO})_{12}$ and then the latter dissociated to the monometallic clusters $\text{Rh}_6(\text{CO})_{16}$ and $\text{Co}_2(\text{CO})_8$ under CO. This seems to show that the bimetallic framework can still be well retained on the SiO_2 surface, despite that the precursor has been exposed to air during compression into a wafer, followed by H_2 treatment at a high temperature.

To confirm this hypothesis, we have studied the reactivity of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ against CO using the precursor with 0.7% Rh loading. As shown in Fig. 5(a), as soon as the wafer of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ was exposed to 13 kPa of CO, an obvious surface spectral change occurred with appearance of new bands at 2068, 1951 and 1850 cm^{-1} at the expense of the band intensity at 2027 cm^{-1} . This indicates a conversion of supported $\text{RhCo}_3(\text{CO})_{12}$ to new carbonyl species upon contact with CO. Apparently, the linear band at 2068 cm^{-1} and the broad bridged band at 1850 cm^{-1} are assignable to $\text{Co}_4(\text{CO})_{12}$ adsorbed on SiO_2 [30], and the shoulder band at 1951 cm^{-1} presumably is related to a cobalt

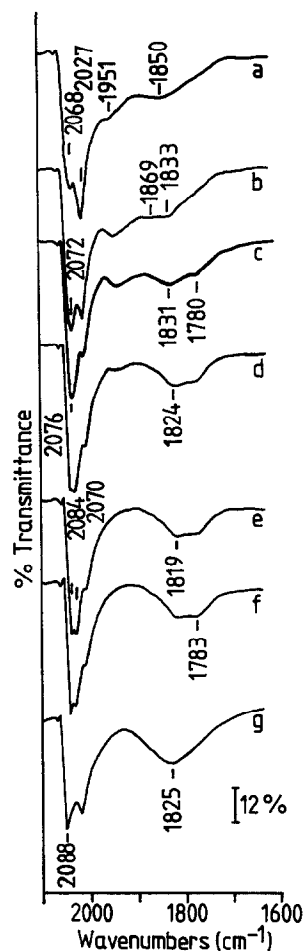


Fig. 5. IR spectra of derivatives from $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ (1% Rh loading) under CO at 13 kPa and at 293 K. (a) 1.5 min; (b) 1 h; (c) 9 h; (d) 14 h; (e) 19 h; (f) 24 h; (g) under vacuum (1.3×10^{-3} kPa) for 1.5 h, following (f).

subcarbonyl complex not identified [30,33] in small amounts. The presence of these features of monometallic cobalt carbonyls coincide with the case of $\text{Co}_4(\text{CO})_{12}/\text{SiO}_2$ obtained from $\text{Co}_2(\text{CO})_8$ by impregnation with a *n*-hexane solution. As presented in Fig. 6(a), the conversion of $\text{Co}_2(\text{CO})_8$ to $\text{Co}_4(\text{CO})_{12}$ on SiO_2 gave not only the bands at 2066s, 2028sh, 1996sh, 1906sh and $1850(\text{br})\text{m cm}^{-1}$ for $\text{Co}_4(\text{CO})_{12}/\text{SiO}_2$, but also a strange broad band at 1950 cm^{-1} . The latter resembles much the 1951 cm^{-1} band shown in Fig. 5. After such a sample wafer had been treated under vacuum at 1.3×10^{-6} kPa and at room temperature for

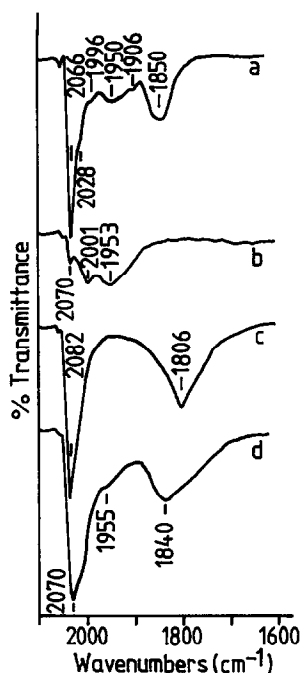
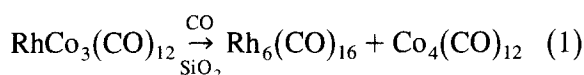


Fig. 6. IR spectra of SiO₂-supported metal carbonyls. (a) 1 h after impregnation of Co₂(CO)₈ / *n*-hexane on SiO₂ predehydroxylated at 623 K; (b) under vacuum (1.3 × 10⁻⁶ kPa) for 4.5 h, following (a); (c) Rh₆(CO)₁₆ adsorbed on SiO₂ under vacuum; (d) after coimpregnation of Rh₄(CO)₁₂ and Co₂(CO)₈ in *n*-hexane (Rh:Co = 1:3 atomic ratio) on SiO₂ predehydroxylated at 623 K, followed by 2 h of evacuation (1.3 × 10⁻³ kPa).

hours, Co₄(CO)₁₂/SiO₂ was completely decarbonylated whereas the presumed subcarbonyl band did not decrease at all in intensity. Meanwhile, two new bands at 2070 and 2001 cm⁻¹ were disclosed in the spectrum because of disappearance of the bands for Co₄(CO)₁₂/SiO₂, as shown in Fig. 6(b). These three bands with relatively weak intensity may be suggested to be due to cobalt subcarbonyls supported on SiO₂, which were found to be more stable than Co₄(CO)₁₂/SiO₂ and to vary synchronously in intensity during thermal decarbonylation. If they arise from a single polycarbonyl species, we can assign this spectrum (Fig. 6(b)) to complexes such as Co^{*n*+}(CO)₃ · S (*n* = 0 or 1, S represents a surface site) based on the similarity of the spectra of complexes like RCo(CO)₃ (R = cyclopentadienyl, allyl or NO) [34,35].

As a result of the dissociation of RhCo₃(CO)₁₂, the production of Co₄(CO)₁₂ must have accompanied the presence of rhodium fragments on the surface. Since the total content of rhodium is actually rather weak in the sample at an atomic ratio of Rh:Co = 1:3, monometallic rhodium carbonyls even if formed from the bimetallic cluster exhibit observable and resolvable bands with difficulty in the presence of cobalt carbonyls plus RhCo₃(CO)₁₂. This is clearly demonstrated by a mixed spectrum for [Rh₆(CO)₁₆ + Co₄(CO)₁₂]/SiO₂ derived from Rh₄(CO)₁₂ and Co₂(CO)₈ by coimpregnation with Rh:Co = 1:3 atomic ratio (Fig. 6(d)). The displayed bands are dominantly attributed to Co₄(CO)₁₂/SiO₂. Addition of the minority of Rh₆(CO)₁₆ seemingly only makes the bands of Co₄(CO)₁₂/SiO₂ shift and broaden in the complex spectrum. In order to elucidate the outcome of this surface reaction out of RhCo₃(CO)₁₂/SiO₂, we further followed the *in situ* transformation of RhCo₃(CO)₁₂ under CO. From Fig. 5(b), the 2027 cm⁻¹ band depleted progressively in favor of development of the 2068 cm⁻¹ band with exposure time. A new shoulder near 1780 cm⁻¹ emerged in Fig. 5(c), which could be assigned to a small amount of Co₆(CO)₁₆ [31,36,37] referring to the spectral data of cobalt carbonyls available. Meanwhile the developing band position at 2068 cm⁻¹ shifted toward higher wavenumbers as the transformation proceeded. After the large consumption of RhCo₃(CO)₁₂ which left only a small linear shoulder, the band center at 2076 cm⁻¹ was diverged into two sharp bands at 2084 and 2070 cm⁻¹, together with downward shift of the broad bridged band at 1869 cm⁻¹ to 1819 cm⁻¹. At this stage, the broad band at 1951 cm⁻¹ due to a possible cobalt carbonyl disappeared. The presence of the 2084 cm⁻¹ band and the downward shift of the bridged band center are probably due to the production of Rh₆(CO)₁₆ from the dissociation of RhCo₃(CO)₁₂. Why did Rh₆(CO)₁₆ become increasingly prevailing over Co₄(CO)₁₂ which tended to decrease in view of spectral intensity

during extended period of the surface reaction? This may be because cobalt carbonyls are extremely sensitive to some environments like OH^- and O^{2-} containing surfaces, toward which they have strong tendency to decompose [30]. Indeed, SiO_2 -supported cobalt carbonyls derived from $\text{Co}_2(\text{CO})_8$ by solution impregnation spontaneously gradually decarbonylated under the same CO pressure, showing gradually decreased carbonyl bands in intensity in Fig. 7. After the ultimate mixture in chemical equilibrium had been treated under vacuum at 1.3×10^{-3} kPa for 1.5 h, the loss of the carbonyl bands for the suggested $\text{Co}_4(\text{CO})_{12}$ led to a satisfactory resolution of the 2088 cm^{-1} band, as shown in Fig. 5(g). This favors the explanation for the formations of $\text{Rh}_6(\text{CO})_{16}$ and $\text{Co}_4(\text{CO})_{12}$ from $\text{RhCo}_3(\text{CO})_{12}$ by dissociation under CO on the SiO_2 surface:



Interestingly, although the dissociative property under CO is documented systematically with many mixed metal clusters in organometallic chemistry [1,2], this reaction did not take place in solution. The initial IR spectrum for $\text{RhCo}_3(\text{CO})_{12}$ remained unchanged and no other bands appeared, after 24 h of stirring of a *n*-hexane solution of $\text{RhCo}_3(\text{CO})_{12}$ under atmospheric CO at room temperature. Therefore, this is a surface-mediated and -promoted dissociation reaction.

With the aid of the results regarding the dissociative behavior of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ under CO, we refocus our attention on the spectra in Fig. 4 to understand the detailed process of recarbonylation on the catalyst surface. Substantially consistent with what has been examined in the case of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$, the 2028 cm^{-1} band gradually decreased from Fig. 4(d) with exposure time in favor of enhancement of the 2084 cm^{-1} shoulder in intensity until a sharp band emerged at 2084 cm^{-1} in equilibrium. At the same time, the band inten-

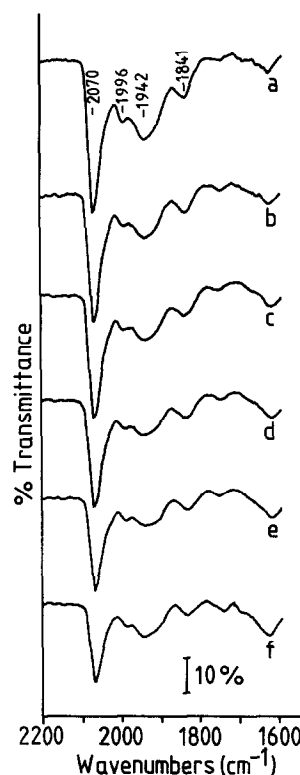
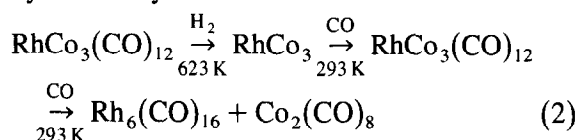


Fig. 7. IR spectra under 13 kPa of CO of SiO_2 -supported cobalt carbonyls derived from $\text{Co}_2(\text{CO})_8$ by impregnation. (a) 2 min; (b) 13 h; (c) 24 h; (d) 2 days; (e) 4 days; (f) 9 days.

sity at 2058 cm^{-1} gradually diminished with concomitant downward shift of the broad band center at 1843 cm^{-1} up to 1807 cm^{-1} . The two bands at 2084 and 1807 cm^{-1} shown in Fig. 4(h) can be assigned to $\text{Rh}_6(\text{CO})_{16}/\text{SiO}_2$. At the final stage, the spectral shape mostly resembles that of $\text{Rh}_6(\text{CO})_{16}/\text{SiO}_2$ presented in Fig. 6(c). As the observed both linear and bridged bands are quite broad throughout the recarbonylation, the presence of a small amount of $\text{Co}_6(\text{CO})_{16}$, having bands at 2115w , 2063vs , 2042sh , 2022w , 1808w and $1791\text{vs} \text{ cm}^{-1}$ [37] cannot be excluded. As a result of the spectral evolution similar to that of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ under CO, it is reasonably believed that the monometallic clusters suggested as $\text{Rh}_6(\text{CO})_{16}$ and $\text{Co}_2(\text{CO})_8$ were yielded from the dissociation of $\text{RhCo}_3(\text{CO})_{12}$ and the latter was initially

regenerated from supported RhCo_3 framework by recarbonylation:



In addition to the in situ surface investigation, extraction of those neutral carbonyl clusters which were produced during the course of interaction of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ with CO from the surface was undertaken. 0.4 g of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ containing 0.5% Rh after pretreated under vacuum at 1.3×10^{-6} kPa for 3 h was exposed to 3.3 kPa of CO and 78 kPa of CO, respectively. 15 h later, it was observed that addition of *n*-hexane was capable of extracting deep brown adspecies from both solid samples under Ar. By comparison with the IR spectra of $\text{RhCo}_3(\text{CO})_{12}$ and $\text{Co}_4(\text{CO})_{12}$ in *n*-hexane (Fig. 8(a and b)), each IR carbonyl spectrum of the solvent extracts consists of the bands of both $\text{RhCo}_3(\text{CO})_{12}$ and $\text{Co}_4(\text{CO})_{12}$ (Fig. 8(c and d)). As shown in Fig. 8(d), aside from the remaining $\text{RhCo}_3(\text{CO})_{12}$ characterized by bands at 2066, 2062, 2042, 2031, 1914, 1886 and 1860 cm^{-1} , other bands situated at 2056, 2025 and 1866 cm^{-1} match those of $\text{Co}_4(\text{CO})_{12}$ formed, by a spectral superimposition of these two clusters. It is also noteworthy that the relative band intensity of $\text{Co}_4(\text{CO})_{12}$ to that of $\text{RhCo}_3(\text{CO})_{12}$ increased with increasing CO pressure. This indicates that the formation of $\text{Co}_4(\text{CO})_{12}$ from $\text{RhCo}_3(\text{CO})_{12}$ is favored at a higher CO pressure. Since $\text{Rh}_6(\text{CO})_{16}$ which was suggested to result simultaneously on the surface, is insoluble in *n*-hexane, we carried out further extraction using THF as the solvent as follows. After the sample treated under 78 kPa of CO had been washed several times with *n*-hexane, until the solution became colorless, the solvent was removed by evacuation and the solid sample was treated under vacuum at 1.3×10^{-6} kPa for 3 h. Afterward, onto the sample was added 2 ml of THF under Ar, which resulted in a light red solution immediately. The latter displayed the only carbonyl spectrum of

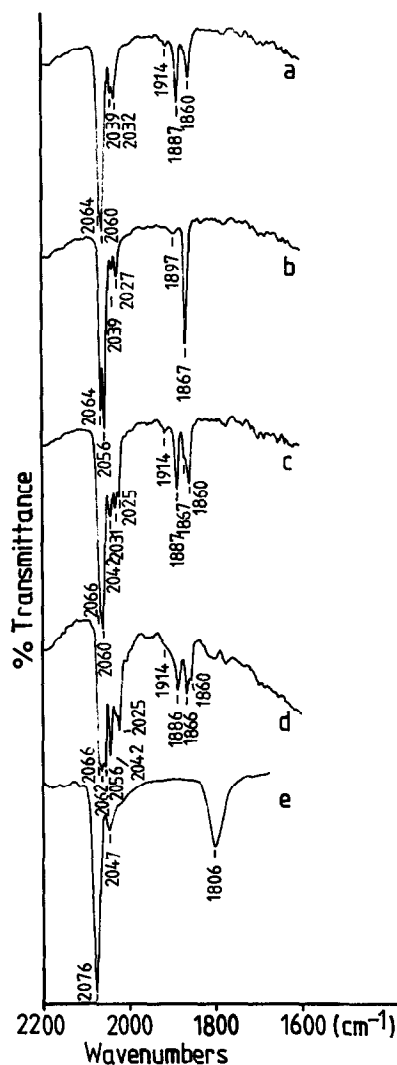


Fig. 8. IR spectra of metal carbonyls in solution. (a) $\text{RhCo}_3(\text{CO})_{12}$ in *n*-hexane; (b) $\text{Co}_4(\text{CO})_{12}$ in *n*-hexane; (c) extracts in *n*-hexane from $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ (0.5% Rh loading) after 15 h of exposure to 3.3 kPa of CO; (d) extracts in *n*-hexane from $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ (0.5% Rh loading) after 15 h of exposure to 78 kPa CO; (e) extract in THF from the surface following (d) which was washed several times with *n*-hexane followed by 3 h of evacuation (1.3×10^{-6} kPa).

$\text{Rh}_6(\text{CO})_{16}$ as shown in Fig. 8(e). The above results confirm the occurrence of dissociation of adsorbed $\text{RhCo}_3(\text{CO})_{12}$ by CO on the SiO_2 surface, breeding the cobalt carbonyl $\text{Co}_4(\text{CO})_{12}$ and the rhodium carbonyl $\text{Rh}_6(\text{CO})_{16}$ as suggested by surface IR study.

In contrast, the attempt to extract carbonyl adspecies which were formed in the course of

recarbonylation of $\text{RhCo}_3/\text{SiO}_2$ was unsuccessful. None of the carbonyl extracts was observed, although the preceding in situ IR results indicate the recarbonylation of supported RhCo_3 and the subsequent formation of $\text{Rh}_6(\text{CO})_{16}$ and $\text{Co}_2(\text{CO})_8$. This inconsistency may be highly related to the strong interaction between RhCo_3 and the SiO_2 surface. As discussed herein before, increasing the cluster–support interaction leads to a decrease in the amount of extracted cluster from a $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ precursor. Once $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ undergoes a heating treatment, the interaction can be further enhanced as proposed by us [38], so that the regenerated supported $\text{RhCo}_3(\text{CO})_{12}$ cannot be extracted by the solvent.

In the present studies, an important conclusion can be reached that prior to recarbonylation the bimetallic RhCo_3 cluster skeleton is comfortably retained on SiO_2 possibly via a strong interaction with surface oxygen containing groups despite severe thermal decarbonylation under H_2 .

From the reaction models between the organometallic complex and the oxide surface described in the literature, the nucleophilic attack seems to occur only between surface OH^- and coordinated CO [12]. In this work, the proposed nucleophilic attack of surface oxygen on the metal atoms of $\text{RhCo}_3(\text{CO})_{12}$ may be regarded as a complementary concept in surface organometallic chemistry. It is indeed difficult to imagine that an electronically saturated metal center in $\text{RhCo}_3(\text{CO})_{12}$ can accept additional ligands from the surface without disruption or decarbonylation of the cluster. However, the observed IR spectrum during adsorption of the cluster on SiO_2 shows the downward shifts of both linear and bridged carbonyl bands compared to the spectrum of $\text{RhCo}_3(\text{CO})_{12}/n$ -hexane, indicating an increase of electron density on the metal centers which causes weakening of all the C–O bonds. Furthermore, $\text{RhCo}_3(\text{CO})_{12}$ can be extracted from the surface into n -hexane after adsorption. Thus we reckon that this adsorption belongs to a strong ph-

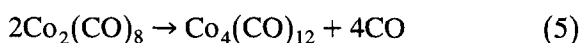
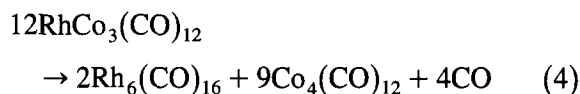
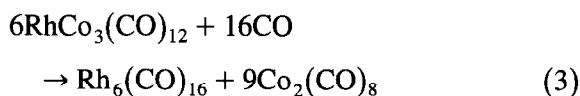
ysisorption. On the other hand, surface chemistry of $\text{Co}_2(\text{CO})_8$ and adsorption of $[\text{Co}(\text{CO})_4][\text{PPN}]$ on MgO have provided a typical model of electronic interaction between the metal center of complexes and the surface group [31,39]. The surface-linked $[\text{Co}(\text{CO})_4]^-$ exhibits a greatly changed spectral symmetry. The difference from the present case is that the electron transfer goes from $[\text{Co}(\text{CO})_4]^-$ to the surface with coordination of Co^- in $[\text{Co}(\text{CO})_4]^-$ to surface Mg^{2+} . $[\text{Co}(\text{CO})_4]^-$ can also be extracted from the surface by ion exchange. An electronic interaction between the organometallic cluster and support with the spectral change of carbonyl vibrations is not necessarily related to the chemical interaction with decomposition or decarbonylation of clusters. For example, anionic clusters such as $[\text{HM}_3(\text{CO})_{11}]^-$ ($\text{M} = \text{Fe}, \text{Ru}$), $[\text{HFeM}_3(\text{CO})_{13}]^-$ ($\text{M} = \text{Os}, \text{Ru}$), $[\text{FeCo}_3(\text{CO})_{12}]^-$ and $[\text{HRuOs}_3(\text{CO})_{12}]^-$ are tightly linked to the surface of MgO or Al_2O_3 via ion pairing between the bridged carbonyl group and the surface Lewis acid sites Mg^{2+} and Al^{3+} [15,16,40,41]. Although this kind of coordination also result in deviation of $\mathcal{T}(\text{CO})$ patterns from those of the anionic clusters in solution, these clusters still maintain their integrity and can be extracted into the organic solvent by ion exchange.

Although the mechanism of interaction of $\text{RhCo}_3(\text{CO})_{12}$ with the SiO_2 surface is not understood yet, it may be possible that coordination of surface oxygen to the cobalt atoms implicates a concerted action of the rhodium and cobalt atoms in the bimetallic cluster, since such an interaction does not take place in the cases of $\text{Rh}_6(\text{CO})_{16}/\text{SiO}_2$ and $\text{Co}_4(\text{CO})_{12}/\text{SiO}_2$ alone [30,42]. This RhCo_3 – SiO_2 interaction may play an important role in grafting and preserving effectively RhCo_3 clusters on the surface at elevated temperatures. The interaction is assumed to be reinforced with increasing temperature. The fact that $\text{RhCo}_3(\text{CO})_{12}$ is regenerated under CO after decarbonylation of $\text{RhCo}_3(\text{CO})_2/\text{SiO}_2$ under H_2 at 623 K clearly demonstrates that disruption of the RhCo_3

framework can be suppressed during the process of breaking of M–CO bonds and thereby RhCo_3 can be stabilized on the surface by the strong $\text{RhCo}_3\text{--SiO}_2$ interaction. After thermal decarbonylation, the surface oxygen containing groups are believed to be strongly coordinated to RhCo_3 . Moreover the exogenous ligand binding may be reversible [14] for the recarbonylation of RhCo_3 to regenerate $\text{RhCo}_3(\text{CO})_{12}$. According to the observed IR band intensity of adsorbed CO species on the catalyst and the result of extraction, reversible opening of the O–M bond is realized only to a small extent by coordination of CO at room temperature. Meanwhile our recent work has illustrated that increasing temperature favors the formation of RhCo_3 clusters in the $(\text{Rh}_6 + \text{Co}_4)/\text{SiO}_2$ system under reducing conditions [43]. The majority of bimetallic clusters may therefore remain in the form of RhCo_3 bound to the SiO_2 surface. This is also suggested by the considerably enhanced hydroformylation activity over this catalyst compared to that over Rh/SiO_2 [23,38]. From the IR data obtained in both the present work and an in situ catalytic reaction study [38], no other visible adsorbed CO species appear on the catalyst surface. In addition, studies of temperature program reduction on Rh/SiO_2 , Co/SiO_2 and $(\text{Rh} + \text{Co})/\text{SiO}_2$ have shown that rhodium and cobalt oxides are readily fully reduced to metallic particles at temperatures below 423 K and 623 K, respectively [44–47].

Concerning the cobalt carbonyl species issued out of fragmentation of the bimetallic cluster, we found by reproducible experiments that the cobalt carbonyls present in our two systems studied are indeed different. They regularly displayed the linear bands at 2058 cm^{-1} in Fig. 5 and at 2068 cm^{-1} in Fig. 6 under an equal CO pressure. This difference in wavenumber is of significance. The linear carbonyl bands centered at 2058 and 2068 cm^{-1} are attributed to $\text{Co}_2(\text{CO})_8/\text{SiO}_2$ and $\text{Co}_4(\text{CO})_{12}/\text{SiO}_2$ respectively, according to the work of Schneider et al. [30]. The reason why the cobalt carbonyls of different nuclearities are obtained in the same

type of reaction which occurs on the SiO_2 surface, remains unclear. There might be different mechanisms involved in the formation of these two carbonyl compounds on the surface. In general, addition of a CO pressure ought to favor the production of $\text{Co}_2(\text{CO})_8$, in terms of both dissociation of $\text{RhCo}_3(\text{CO})_{12}$ and interconversion between $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ in the following:



Practically, the observations of recarbonylation for the catalyst sample with $\text{Co}_2(\text{CO})_8$ produced are consistent with this common argument. Nevertheless, it is worth pointing out that reaction (4) which is on principle inhibited under 13 kPa of CO, is also feasible on SiO_2 by exposure of a $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ sample to CO. This is probably due to an unusual role of surface sites and hence the dissociation of $\text{RhCo}_3(\text{CO})_{12}$ is promoted and proceeds in the direction resulting in $\text{Rh}_6(\text{CO})_{16}$ and $\text{Co}_4(\text{CO})_{12}$. In this case, the surface reaction also gives a small amount of so-called mononuclear cobalt subcarbonyl species not known, and a small amount of presumed $\text{Co}_6(\text{CO})_{16}$. Interestingly, the subcarbonyl species appears simultaneously when $\text{Co}_4(\text{CO})_{12}$ is produced, especially from $\text{Co}_2(\text{CO})_8$ on SiO_2 by impregnation as mentioned hereinbefore. Adsorption of $\text{Co}_4(\text{CO})_{12}$ on SiO_2 by the same impregnation gives no rise to this subcarbonyl species. The latter can also be yielded by direct decarbonylation of $\text{Co}_4(\text{CO})_{12}/\text{SiO}_2$ as shown in Fig. 9. By contrast, the surface of catalyst sample on which $\text{Co}_2(\text{CO})_8$ is yielded does not display any feature of the cobalt subcarbonyl under CO. This comparison allows us to speculate that such a supported subcarbonyl species may play the role of surface intermediate in converting cobalt

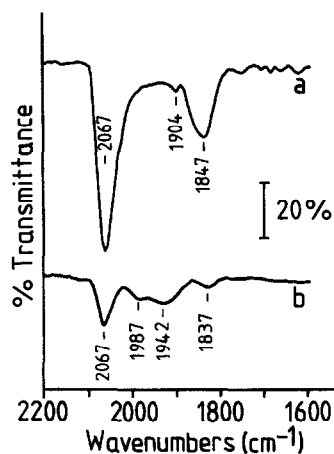


Fig. 9. IR spectra of (a) $\text{Co}_4(\text{CO})_{12}$ adsorbed on SiO_2 under vacuum and (b) surface carbonyl species derived by decarbonylation of $\text{Co}_4(\text{CO})_{12}/\text{SiO}_2$ under $\text{CO} + \text{H}_2$ (13:13 kPa) at 423 K.

fragments to $\text{Co}_4(\text{CO})_{12}$ upon dissociation of $\text{RhCo}_3(\text{CO})_{12}$. The lack of such a supported subcarbonyl species on the surface might preferably lead to conversion of cobalt fragments to $\text{Co}_2(\text{CO})_8$ under CO. Regardless, the cause of production of different cobalt carbonyls may be associated with different concentrations of $\text{RhCo}_3(\text{CO})_{12}$ on the surface. When the precursor $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ is directly exposed to 13 kPa of CO, the amounts of $\text{RhCo}_3(\text{CO})_{12}$ and the resulting cobalt subcarbonyl fragments are relatively abundant so as to favor the formation of cobalt clusters of higher nuclearities. In contrast, the catalyst sample, although derived from $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$, must undergo recarbonylation to give $\text{RhCo}_3(\text{CO})_{12}$ before the dissociation reaction. In the latter case, $\text{RhCo}_3(\text{CO})_{12}$ fragments to monometallic clusters immediately after formed by recarbonylation. The transient amount of the cobalt subcarbonyl thus obtained may be small enough on the surface to beneficially give rise to $\text{Co}_2(\text{CO})_8$ under the identical CO pressure.

It should be emphasized that the monometallic clusters $\text{Rh}_6(\text{CO})_{16}$, $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ cannot result from direct recarbonylation of Rh/SiO_2 and Co/SiO_2 , as demonstrated by previous studies [27,42,48,49]. Other monometallic fragments during thermal treat-

ment under H_2 , if any, would be mainly present as rhodium and cobalt metallic particles. However, there was no detected IR band between 1870 and 1880 cm^{-1} throughout the recarbonylation. A band situated in this region might be attributed to bridged CO adsorbed on Rh^0/SiO_2 with less than 1% Rh loading [27]. In a separate experiment, adsorption of CO on Co/SiO_2 (less than 5% Co loading) derived from $\text{Co}_2(\text{CO})_8$ by H_2 treatment at 623 K, resulted in no IR signal.

SiO_2 -supported $\text{RhCo}_3(\text{CO})_{12}$ is, to our knowledge, the first mixed organometallic cluster found to be able to retain its cluster framework and to be regenerable after thermal decarbonylation. The stabilization of the RhCo_3 cluster essentially resides in its particular strong interaction with the surface of supporting SiO_2 . This is in marked contrast with unsupported mixed organometallic clusters and most of supported mixed organometallic clusters which usually cannot maintain metallic structural integrity under CO and under catalytic conditions. Such surface-stabilized mixed metallic clusters are of special advantage and may find important application in catalysis.

4. Conclusions

In the present paper, the nature of adsorption of $\text{RhCo}_3(\text{CO})_{12}$ on the surface of partially dehydroxylated SiO_2 is revealed in terms of a detailed IR study. $\text{RhCo}_3(\text{CO})_{12}$ is intactly grafted on the SiO_2 surface, possibly via a nucleophilic attack of surface oxygen containing groups on the cobalt atoms. This interaction makes the IR carbonyl spectrum of $\text{RhCo}_3(\text{CO})_{12}/\text{SiO}_2$ deviate greatly from that of $\text{RhCo}_3(\text{CO})_{12}$ in solution. IR studies of CO adsorption on a $\text{RhCo}_3(\text{CO})_{12}$ -derived SiO_2 -supported catalyst suggest that the RhCo_3 cluster framework can be successfully retained on SiO_2 via thermal treatment of the catalyst precursor under H_2 at 623 K. The supported RhCo_3 is characterized through recarbonylation to reform the initial carbonyl cluster at a lower CO pres-

sure, as well as through dissociation of the regenerated $\text{RhCo}_3(\text{CO})_{12}$ to produce $\text{Rh}_6(\text{CO})_{16}$ and $\text{Co}_2(\text{CO})_8$ at a higher CO pressure. A similar dissociative behavior of the catalyst precursor under CO, which is definitely demonstrated by extraction of carbonyl adspecies from the surface into the organic solvent, agrees with the regeneration of $\text{RhCo}_3(\text{CO})_{12}$ from $\text{RhCo}_3/\text{SiO}_2$ and the subsequent dissociation. Due to the specific interaction between RhCo_3 and the SiO_2 surface which is reinforced by thermal treatment at high temperatures, RhCo_3 is considered to be tightly grafted on the support so that a mixture of $\text{RhCo}_3(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$ and $\text{Co}_2(\text{CO})_8$ formed on the surface during recarbonylation, which is observed by in situ IR spectroscopy, cannot be extracted into the organic solvent.

Acknowledgements

The author thanks the support from the Chinese Academy of Sciences.

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