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SURFACE-SUPPORTED METAL CLUSTER CARBONYLS. CHEMISORPTION, DECOMPOSITION AND REACTIVITY OF $\text{Rh}_6(\text{CO})_{16}$ SUPPORTED ON SILICA

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Summary

A partially decarbonylated metal cluster is quickly formed on the surface of silica by oxidation at room temperature; it is possible to regenerate the initial cluster compound under a carbon monoxide atmosphere at 200°C. Decarbonylation of $\text{Rh}_6(\text{CO})_{16}$ at higher temperature produces a new metallic material on the surface, characterized by two $\nu(\text{CO})$ vibration bands at $2048 \pm 7 \text{ cm}^{-1}$ and $1893 \pm 10 \text{ cm}^{-1}$. These two bands have been respectively assigned to a terminal carbonyl group and a bridged carbonyl group bonded to two rhodium atoms. Oxidation of this compound occurs very easily under oxygen at room temperature and gives an oxidized material presumably of the same nuclearity; adsorption of carbon monoxide produces two intense sharp bands at 2093 and 2038 cm^{-1} which have been assigned to the symmetric and asymmetric stretching modes of two CO molecules bonded to a single oxidized Rh site as $\text{Rh}^{\text{I}}(\text{CO})_2$. The conversion from the oxidized surface species to the metallic one can be performed under mild conditions, but attempts to regenerate the initial cluster compound were unsuccessful.

For some years, there has been a growing interest in the field of the characterisation, the behaviour and the reactivity of molecular clusters deposited on surfaces [1–3]. Cluster complexes, which generally have a well defined “molecular character”, may be regarded as being very close to the metallic state characterized by very small particles of transition metals used as supported heterogeneous catalysts [3].

Some attempts concerning the possibility of going from the molecular state to the metallic state and conversely have been reported. A favorable approach to this problem seems to be the study of ligand dissociation with molecular clusters supported on inorganic oxides. Immobilization of the organometallic compound on a support might prevent fragmentation as well as intermolecular reactions leading to aggregation [3-5]. Starting from platinum or nickel cluster compounds, different studies have shown that very small particles, probably of the same size as in the original clusters, can be obtained after decoordination of the ligands [6-7]. Moreover a certain reversibility to reform a carbonyl cluster by reaction with CO has been proved [7]. In the same way, previous work seems to indicate the possibility for $\text{Rh}_6(\text{CO})_{16}$ to be reversibly decarbonylated on a surface of alumina while keeping the initial Rh_6 cluster frame [8]; however the results appear to be affected by the manner by which adsorption of the cluster onto the surface is achieved as well as by the nature of the support.

We have therefore undertaken an infrared investigation of the behaviour of $\text{Rh}_6(\text{CO})_{16}$ on silica in order to determine to what extent carbonyl ligands are reversibly removed from the Rh_6 cluster frame and to determine the nature as well as the reactivity under oxygen and hydrogen of the remaining surface species.

Experimental

$\text{Rh}_6(\text{CO})_{16}$ was purchased from STREAM Chemicals. $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ was purchased from Engelhard Industries. The silica is a non-porous silica "Aerosil O", with a specific area of 200 m^2 per gram. The solvents used (benzene, chloroform) were supplied by CANLAB and had a purity of at least 99.8%. They were distilled under argon on sodium or molecular sieve (5A) to remove all traces of water. They were stored under argon on sodium or molecular sieve. Carbon monoxide was obtained from Matheson and had a purity of at least 99.99%. Hydrogen and oxygen (Matheson) had a purity of 99.95% and were passed through a molecular sieve trap before use.

IR spectra

For IR spectra, a pellet made of 25 mg of silica is fitted to a pyrex support which can slide inside a pyrex tube of 30 mm outside diameter. At one end of this tube, two CaF_2 windows are fastened in such a way that IR spectra of the pellet can be recorded. The other extremity is sealed to allow for thermal treatment of the sample. This infrared cell can work under vacuum or any controlled atmosphere.

A system consisting of two stopcocks and a rubber septum is connected to the body of the cell in order to allow the introduction of the cluster compound onto the pellet. All the solid spectra were obtained using a Beckman IR-9 spectrophotometer. To eliminate all the absorptions of the silica in the $\nu(\text{CO})$ region, an identical pellet of silica is used in the reference beam. The base line is adjusted with a reference beam attenuator. In most of the cases, the automatic slit control system is used to obtain a sufficient signal level thus giving a resolution of $3-5 \text{ cm}^{-1}$.

Results

1. Behaviour of $\text{Rh}_6(\text{CO})_{16}$ on a silica surface

In all cases, silica samples were treated for 16 h under vacuum at 300°C . A

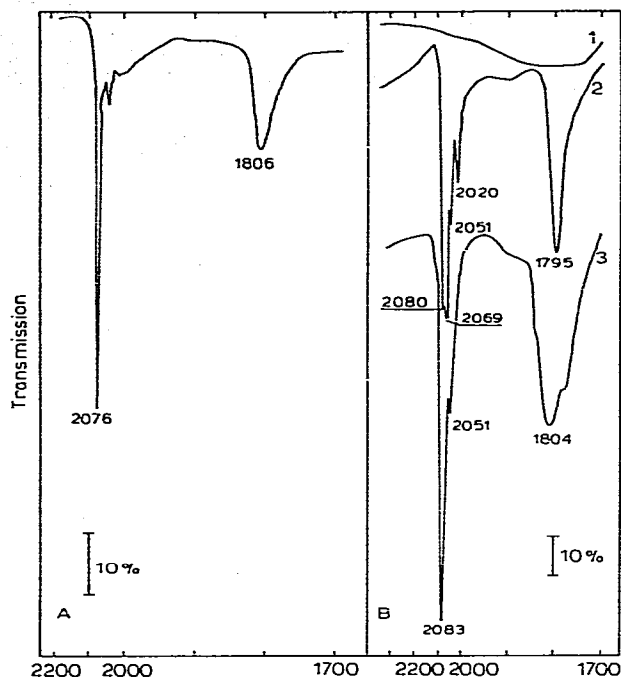


Fig. 1. IR spectra in the $\nu(\text{CO})$ region. A: $\text{Rh}_6(\text{CO})_{16}$ in solution (CCl_4). B-1: Silica sample pretreated at 300°C for 16 h under vacuum. B-2: $\text{Rh}_6(\text{CO})_{16}$ on silica after 45 min at 25°C under vacuum. B-3: Same sample after 30 min of exposure to 1 atm of CO at 200°C .

known amount of $\text{Rh}_6(\text{CO})_{16}$ is dissolved in 5 ml of chloroform under argon. A known volume of the solution is introduced with a syringe inside the infrared cell, onto the silica pellet. The solvent is removed at room temperature by treating the sample for 45 minutes under vacuum and the spectra recorded. The amounts of rhodium on silica were approximately 5%.

The spectrum of $\text{Rh}_6(\text{CO})_{16}$ in solution is characterized by two intense bands in the $\nu(\text{CO})$ region (Fig. 1, spectrum A): a sharp band at about 2080 cm^{-1} corresponding to the symmetric vibration mode of terminal carbonyl groups and a broad band at about 1800 cm^{-1} assigned to the vibration of bridged carbonyls, each bonded to three rhodium atoms [9,10]. The deposit of $\text{Rh}_6(\text{CO})_{16}$ on the silica surface gives a grey colour to the pellet. The two carbonyl vibration bands of the cluster appear alone in the $\nu(\text{CO})$ region (Fig. 1, spectrum B-2) and remain identical for days. However, by comparison of the IR spectrum of $\text{Rh}_6(\text{CO})_{16}$ in solution with its spectrum on a silica surface (Fig. 1, spectra A and B-2), a modification of relative intensities of the two bands at about 2080 and 1800 cm^{-1} is observed. The intensity of the $\nu(\text{CO})$ vibration band corresponding to terminal carbonyls has diminished, compared to the intensity of the bridged carbonyl band. Simultaneously, bands at 2345 and 2365 cm^{-1} assigned to carbon dioxide appear. Thus the deposit of $\text{Rh}_6(\text{CO})_{16}$ on a silica surface partly leads to the oxidation of the terminal carbonyls to carbon dioxide.

Introduction of carbon monoxide (1 atm) at 50°C on the surface compound thus partially decarbonylated, does not give any modification of the IR spectrum in the $\nu(\text{CO})$ region. However, under more drastic conditions of temperature

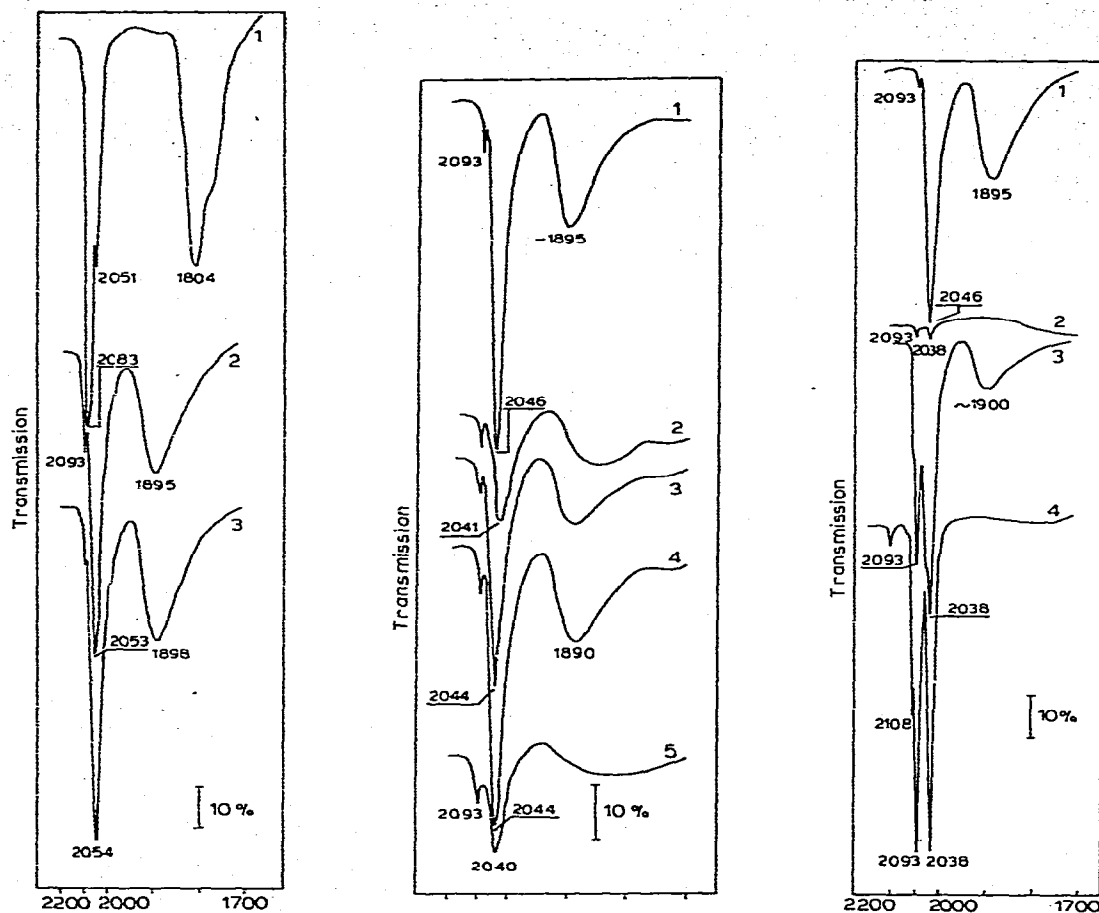


Fig. 2. Evolution of $\text{Rh}_6(\text{CO})_{16}$ on silica under vacuum versus temperature. 1. $\text{Rh}_6(\text{CO})_{16}$ on silica as obtained in Fig. 1, spectrum B-3. 2. After $\frac{1}{2}$ h under vacuum at 150°C . 3. Same sample after treatment under hydrogen (1 atm) at 50°C for 1 h.

Fig. 3. Reversible dissociation of CO adsorbed. 1. Spectrum obtained as described in Fig. 2, spectrum 2. 2. Following $\frac{1}{2}$ h evacuation of CO at 200°C . 3. Following exposure to 1 atm of CO at 25°C for $\frac{1}{2}$ h. 4. Following exposure to 1 atm of CO at 50°C for 1 h. 5. Following $\frac{1}{2}$ h evacuation of CO at 320°C and exposure to 1 atm of CO at 50°C for 2 h.

Fig. 4. Oxidation of the surface species characterized by the $\nu(\text{CO})$ vibration bands at 2046 and 1895 cm^{-1} . 1. Spectrum obtained as described in Fig. 2, spectrum 2. 2. Following exposure to 1 atm of O_2 at 50°C for $\frac{1}{2}$ h. 3. Following exposure to 1 atm of CO at 25°C for 45 min. 4. Same sample after exposure to O_2 (1 atm) at 50°C for $\frac{1}{2}$ h and exposure to CO (1 atm) at 50°C for $\frac{1}{2}$ h.

($T\ 200^\circ\text{C}$), the intensity of the band at about 2080 cm^{-1} increases, and the relative intensities of the two bands at 2080 and 1800 cm^{-1} then correspond closely to those exhibited in solution (Fig. 1, spectrum B-3) although bands are slightly broader in the adsorbed state. No change in the colour of the pellet is observed. Therefore, the initial molecular cluster is regenerated under carbon monoxide after being partially decarbonylated on the silica surface.

We have undertaken an investigation in order to determine to what extent carbonyl ligands can be removed while keeping the Rh_6 cluster frame. Upon

treatment under vacuum at 150°C, the rhodium carbonyl-silica material progressively changes to a brown-red colour. The two bands at 2083 and 1804 cm^{-1} of the initial cluster compound are removed whereas three new carbonyl stretching bands appear (Fig. 2, spectrum 2): an intense and relatively sharp band at 2053 cm^{-1} , an intense broad band at 1895 cm^{-1} and a small sharp band at 2093 cm^{-1} . Several experiments reveal that the intensities of the two bands at 2053 and 1895 cm^{-1} appear to change in parallel, suggesting that both bands are associated with a single carbonyl compound. The carbonyl band at 2093 cm^{-1} corresponds to another surface compound; for instance, a treatment under hydrogen (1 atm) at 50°C leads to the almost complete disappearance of the band at 2093 cm^{-1} whereas the intensities of the bands at 2053 and 1895 cm^{-1} increase simultaneously (Fig. 2, spectrum 3). Thus, a partial decarbonylation of the initial molecular cluster leads to the formation of a new surface carbonyl compound characterized by two carbonyl vibration bands at 2053 and 1895 cm^{-1} . Many experiments have been performed in order to determine chemical and spectroscopic properties of this new species, and the following features have been found: (a) The position in frequency of the vibration bands can slightly fluctuate; when their intensity increases, their position moves towards higher wave-numbers and conversely, when their intensity decreases their position moves towards lower wave-numbers. The positions of the bands have been found to be 2048 ± 7 and 1893 ± 10 cm^{-1} . (b) The carbonyl species is presumably in a "metallic state". A treatment under hydrogen (1 atm) up to 100°C does not lead to the appearance of any carbonyl band; only a slight decrease of the intensities of the bands at 2048 and 1893 cm^{-1} is observed after half an hour. It should be noted that the intensity variations when going from the molecular cluster to the "metallic" particle are relatively low. (c) The carbonyl group dissociation is reversible, provided that the temperature does not exceed 200°C at any time (Fig. 3). The surface decarbonylated species seems to be relatively stable under thermal treatment; but after a thermal treatment at 320°C under vacuum and an introduction of carbon monoxide, only a small amount of the previous carbonyl species is reobtained (Fig. 3, spectrum 5), (d) Under a carbon monoxide atmosphere and various conditions of temperature, it has not been possible to regenerate the initial cluster compound at any time.

Since presumably the $\nu(\text{CO})$ vibration bands at 2048 and 1893 cm^{-1} characterize a "metallic" surface species, it was interesting to study their behaviour under oxidation conditions. Under oxygen (1 atm) at 50°C, the colour of the pellet becomes rapidly black; the two carbonyl bands at 2046 and 1895 cm^{-1} (Fig. 4, spectrum 1) completely disappear after half an hour, and carbon dioxide is formed. Only two low intensity bands at 2093 and 2038 cm^{-1} are left in the $\nu(\text{CO})$ region (Fig. 4, spectrum 2). After introduction of carbon monoxide (1 atm) at 25°C onto such a decarbonylated species, the pellet turns a dark brown colour. A new IR spectrum is shown in the $\nu(\text{CO})$ region (Fig. 4, spectrum 3), consisting of two intense sharp bands at 2093 and 2038 cm^{-1} which presumably characterize an oxidized carbonyl species on the surface. However, the oxidation has not occurred completely since the bands at 2046 (sh) and at 1895 cm^{-1} of the initial "metallic" species remain. Introduction of oxygen (1 atm) at 50°C on the surface species thus obtained modifies neither the intensity nor the position of the bands at 2093 and 2038 cm^{-1} ; only the band at 1895 cm^{-1} and the

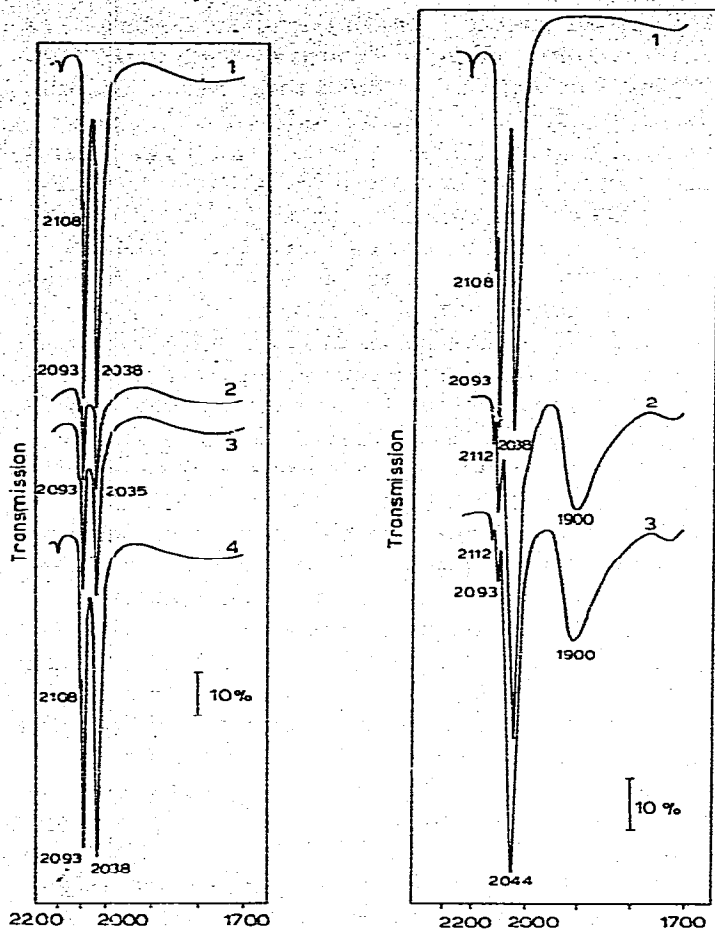


Fig. 5. Reversible dissociation of CO adsorbed. 1. Spectrum obtained as described Fig. 4, spectrum 4. 2. Following evacuation of CO at 200°C for $\frac{1}{2}$ h. 3. Following exposure to CO (1 atm) at 25°C for 1 h. 4. Following exposure to CO (1 atm) at 80°C for 1 h.

Fig. 6. Reduction of the surface species characterized by the $\nu(\text{CO})$ vibration bands at 2093 and 2038 cm^{-1} . 1. Spectrum obtained as described in Fig. 4, spectrum 4. 2. Following exposure to H_2 (1 atm) at 50°C for $\frac{1}{2}$ h. 3. Same sample after exposure to H_2 (1 atm) at 50°C for 2 h.

shoulder at about 2046 cm^{-1} disappear again. Reintroduction of carbon monoxide (1 atm) at 50°C finally leads to a spectrum consisting of two intense sharp bands of equal intensities at 2093 and 2038 cm^{-1} (Fig. 4, spectrum 4). Moreover, a sharp and relatively weak band is observed at 2108 cm^{-1} . This band presumably characterizes another adsorption site since its evolution appeared to be unrelated to the bands at 2093 and 2038 cm^{-1} .

After many experiments, the following features can be pointed out: (a) The oxidized species, to which the bands at 2093 and 2038 cm^{-1} correspond, is stable under oxygen (1 atm) up to 100°C. (b) The carbonyl groups can be removed and reassociated (Fig. 5) with a negligible loss of intensity of the bands at 2093 and 2038 cm^{-1} . (c) The oxidized species can be directly obtained by heating $\text{Rh}_6(\text{CO})_{16}/\text{SiO}_2$ at 100°C under oxygen (1 atm). (d) It has not been

possible to regenerate the initial cluster compound, even under CO and drastic conditions of temperature.

We finally took an interest in the behaviour of this oxidized surface species under reduction conditions. Under hydrogen (1 atm) at 50°C, the intensities of the carbonyl bands at 2093 and 2038 cm⁻¹, as well as that of the band at 2108 cm⁻¹, decrease rapidly. Simultaneously, the bands at 2043 and 1900 cm⁻¹, characterizing the "metallic" species previously observed, appear (Fig. 6, spectra 1 and 2). If the reduction under hydrogen is maintained for a longer time, one gets almost exclusively the "metallic" surface compound (Fig. 6, spectrum 3).

This sequence can be repeated several times without noticeably diminishing the intensities of the bands, provided that the temperature does not go above 80°C.

2. $RhCl_3, xH_2O/SiO_2$.

In order to investigate further the nature of the surface species obtained from $Rh_6(CO)_{16}$, we studied the adsorption of carbon monoxide onto the various species produced by reducing $RhCl_3, xH_2O$ on silica. $RhCl_3, xH_2O$ was dissolved in a few ml of ethanol; the solution was stirred for 3 h with silica. The ethanol was evaporated under vacuum at 40°C during a period of 20 h. The amount of rhodium on the silica was approximately 4%. Following the introduction of carbon

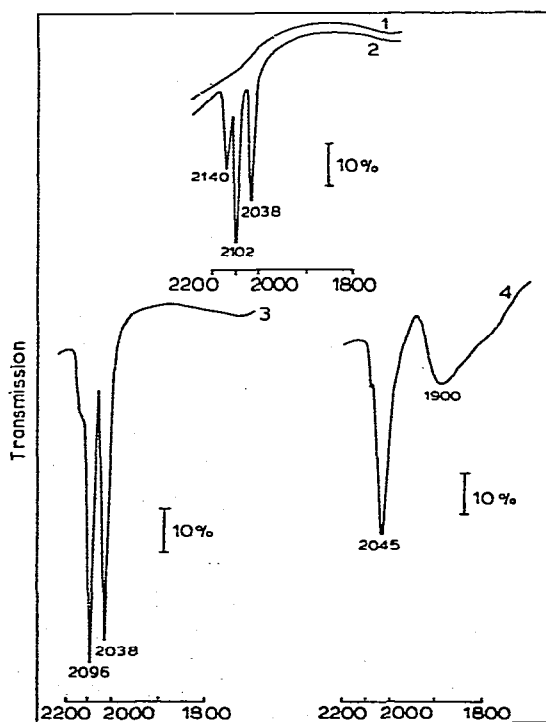


Fig. 7. Adsorption of CO onto various species produced by reduction of $RhCl_3, xH_2O/SiO_2$. 1. $RhCl_3, xH_2O/SiO_2$ after evaporation of ethanol. 2. Same sample after exposure to CO (1 atm) at 50°C for 1 h. 3. Same sample after exposure to H_2 (1 atm) at 50°C for $\frac{1}{2}$ h, and exposure to CO (1 atm) at 25°C for 2 h. 4. Same sample as used previously (spectrum 2); after treatment under vacuum at 300°C for 16 h, exposure to H_2 (1 atm) at 100°C for 1 h, and exposure to CO (1 atm) at 50°C for 1 h.

monoxide (1 atm) at 25°C, three carbonyl bands of relatively weak intensity appear at 2140, 2102 and 2038 cm⁻¹ (Fig. 7, spectrum 2).

After reduction under hydrogen at 50°C and introduction of carbon monoxide at room temperature, the band at 2140 cm⁻¹ disappears. Only two strong bands of equal intensities at 2096 and 2038 cm⁻¹ are left (Fig. 7, spectrum 3). The IR spectrum thus obtained in the $\nu(\text{CO})$ region is quite similar to that of the oxidized carbonyl surface compound previously observed.

If an identical sample of $\text{RhCl}_3 \cdot x\text{H}_2\text{O}/\text{SiO}_2$ is treated for 16 h under vacuum at 300°C and then reduced under hydrogen (1 atm) at 100°C, the adsorption of carbon monoxide will show an IR spectrum with only two carbonyl bands at 2045 and 1900 cm⁻¹ (Fig. 7, spectrum 4). Neither the number nor the position of the $\nu(\text{CO})$ bands is affected by a reduction at higher temperature. Only a decrease in the intensity of the bands at 2045 and 1900 cm⁻¹ is observed.

Discussion

It must be pointed out that the IR studies reported here are not sufficient by themselves to precisely describe the nature of the adsorbed species. Nevertheless, the relative simplicity of the IR spectra allows us to draw a number of interesting conclusions.

After the deposit of the cluster compound on the surface of the silica, a partial decarbonylation of the molecular cluster occurs spontaneously and almost instantaneously. The terminal carbonyl groups are preferentially decoordinated and oxidized, whereas the bridged carbonyl groups do not seem to be affected. Probably, the rhodium species remaining on the surface after the oxidation of the terminal carbonyl groups are partially oxidized by surface water or hydroxyl groups as indicated in the reaction step [12]:



The formation of hydride bonds is supported by the small shift of the carbonyl frequencies (we have only a change of the shape of the absorption band around 2080 cm⁻¹), a trend which, for instance, has been observed for the two similarly related clusters $\text{Ir}_4(\text{CO})_{12}$ [13] and $\text{Ir}_4(\text{CO})_{11}\text{H}_2$ [14] or $\text{Os}_6(\text{CO})_{18}$ [15] and $\text{Os}_6(\text{CO})_{18}\text{H}_2$ [16]. Moreover the introduction of CO at low temperature does not lead easily to recarbonylation since molecular hydrogen must be shifted from the cluster coordination sphere. This kind of shift requires a higher temperature [17], as we have observed in order to regenerate the original $\text{Rh}_6(\text{CO})_{16}$ cluster.

These results suggest that the Rh_6 cluster frame has been retained. Our observations with silica differ from those obtained on alumina in some previous works [8,18] where the decarbonylation of $\text{Rh}_6(\text{CO})_{16}$ occurs progressively and completely at room temperature [8], even though the rate of the decarbonylation reaction seems to depend upon the conditions of pretreatment of the support [18]. On silica once the initial cluster is regenerated, the IR spectrum remains practically unaffected for days. Therefore, the initial oxidation of part of the $\text{Rh}_6(\text{CO})_{16}$ terminal carbonyl groups seems to have occurred by means of particular oxidizing groups close to the coordination sphere of the rhodium atoms. No further oxidation occurs at room temperature under vacuum after the consumption of these oxidizing groups. This observation supports an oxidation by the few OH or H_2O surface species left after thermal treatment.

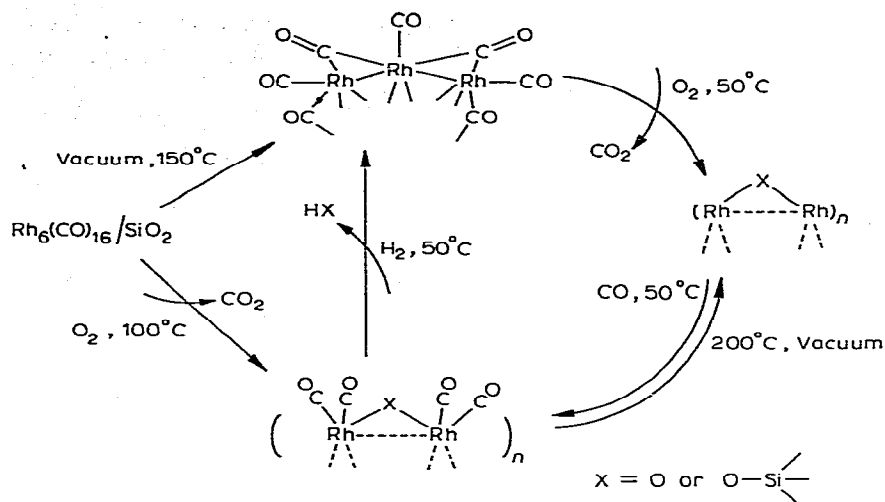


Fig. 8. Carbonyl species obtained from $\text{Rh}_6(\text{CO})_{16}$ deposited on silica.

As soon as the partial decarbonylation of the cluster compound occurs at 100°C or above, one or the other surface species is produced according to the experimental conditions used (Fig. 8).

1. Under vacuum, a carbonyl surface species, exhibiting two $\nu(\text{CO})$ vibration bands, is obtained. Our observations suggest that the rhodium atoms have kept an oxidation state equal to zero: the vibration bands of the carbonyl groups adsorbed on these "metallic" particles are stable under hydrogen, up to 100°C , whereas they disappear at once under oxygen at room temperature; moreover, a virtually identical spectrum is shown in the $\nu(\text{CO})$ region after adsorption of carbon monoxide on the surface species formed by reduction at relatively high temperature of the system $\text{RhCl}_3, x\text{H}_2\text{O}/\text{SiO}_2$.

The strong band at approximately 2048 cm^{-1} corresponds to terminal carbonyl groups and the broad and relatively weak band at about 1893 cm^{-1} presumably corresponds to bridged carbonyls each bonded to two rhodium atoms [11].

The positions of the carbonyl bands at 2048 and 1893 cm^{-1} may vary with their intensities; the band at 2048 cm^{-1} can be shifted from 2041 cm^{-1} for a weak intensity to 2055 cm^{-1} when it reaches its highest intensity. Similar observations have been reported in chemisorption of carbon monoxide over platinum [19]. This phenomenon may be regarded as being the result of electronic changes on the surface of very small particles and may be explained in the following manner. At small coverage of the Rh surface, the availability of Rh d electrons for back bonding to the π^* orbitals of CO is relatively high; it decreases when the surface coverage increases, which contributes to a strengthening of the C=O bond and causes an increase in the vibrational frequency of the C=O bond.

2. Under oxygen at 100°C , one gets a carbonyl surface species presenting two sharp $\nu(\text{CO})$ vibration bands of equal intensity at 2093 and 2038 cm^{-1} ; the same surface species can also be obtained when a treatment under oxygen at room

temperature and a carbonylation are successively applied to the previous "metallic" compound (Fig. 8). Let us consider the study of chemisorption of carbon monoxide on the reduction products of the system $\text{RhCl}_3 \cdot x\text{H}_2\text{O}/\text{SiO}_2$. Initially, the IR spectrum of CO adsorbed on the system $\text{RhCl}_3 \cdot x\text{H}_2\text{O}/\text{SiO}_2$ shows three bands at 2140, 2102 and 2038 cm^{-1} of low intensities, corresponding to the coordination of CO on oxidized metallic atoms presenting vacant coordination sites [20]. Presumably, the highest frequency band is assigned to CO adsorbed on oxidized metallic atoms as rhodium(III). The reduction under mild conditions of rhodium(III) and the chemisorption of CO on the species formed cause the disappearance of the band at 2140 cm^{-1} , and the appearance of two intense bands at 2096 and 2038 cm^{-1} assigned to the chemisorption of CO on rhodium atoms which have an oxidation state equal to one, by analogy with the frequencies of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ [21]. Both intense bands at 2093 and 2038 cm^{-1} obtained from the system $\text{Rh}_6(\text{CO})_{16}/\text{SiO}_2$ are associated with a single form of adsorption as represented by: $\text{Rh}^{\text{I}}(\text{CO})_2$. Each $\text{Rh}^{\text{I}}(\text{CO})_2$ fragment of localized C_{2v} symmetry gives rise to two infrared-active terminal C=O stretching vibrations; the lack of any vibrational coupling between different $\text{Rh}^{\text{I}}(\text{CO})_2$ fragments would suggest that they are connected only by rather weak interactions [22]. In agreement with this latter assumption we have observed that in the "oxidised" surface rhodium(I) species, as well as on the previous metallic particles, carbonyl groups can be reversibly removed but in this case only a negligible shift in frequency is observed for the band at 2038 cm^{-1} when the "surface" coverage by CO decreases. This would support the absence of collective properties of *d* electrons in these particular species, as expected for weak intermetallic interactions between the different $\text{Rh}^{\text{I}}(\text{CO})_2$ surface fragments.

However, in a certain way the original nuclearity must be kept since it is possible to regenerate the zerovalent carbonyl "metallic" rhodium particle under very mild reduction conditions (Fig. 8). This latter experiment confirms the monovalent oxidation state of rhodium in these particular surface species because the easy reduction of dimeric rhodium(I) compounds, such as $(\text{Rh}(\text{CO})_2\text{Cl})_2$, to zerovalent polynuclear clusters is a well established feature [23]. The band at 2108 cm^{-1} , which is present whenever the bands at 2093 and 2038 cm^{-1} are shown, could not be assigned to any of the previous surface compounds observed. It may correspond to the adsorption of carbonyl groups on rhodium atoms with a higher oxidation state (Rh^{III} or Rh^{II}).

We must point out that once being in the reaction cycle as described in Fig. 8, it has not been possible to regenerate the initial cluster compound. Presumably the surface species thus obtained have not kept the Rh_6 cluster frame. However, infrared data seem to indicate a very small size for these particles: the adsorbed CO groups lead to very intense $\nu(\text{CO})$ bands, comparable to those initially obtained from $\text{Rh}_6(\text{CO})_{16}$, in agreement with low aggregation. For instance, the comparable intensities of the carbonyl absorptions of the "oxidised" rhodium(I) and "metallic" rhodium(0) surface species would suggest that, during the reduction step, a terminal carbonyl group for each $\text{Rh}^{\text{I}}(\text{CO})_2$ fragment is transformed into a bridged group bonded to two rhodium atoms in the zerovalent particle.

Conclusion

Interesting facts about the evolution of $\text{Rh}_6(\text{CO})_{16}$ on a silica surface have been revealed in these studies. The silica surface can form a decarbonylated rhodium species by simple room temperature oxidation, from which it is possible to regenerate the initial cluster compound. Decarbonylation of $\text{Rh}_6(\text{CO})_{16}$ on the surface at higher temperatures leads to very small carbonylated "metallic" particles in which both terminal and bridged carbonyl groups are present. Oxidation of these species takes place very easily under an oxygen atmosphere at room temperature and gives surface species in which rhodium atoms are present as rhodium(I); carbonylation leads to the adsorption of two CO molecules in a terminal position of each Rh^{I} site. The conversion from the oxidized surface species to the "metallic" one occurs easily under mild reduction conditions; one of the two terminal carbonyl groups gives, then, a bridged carbonyl group bonded between two rhodium atoms. It is not known yet whether or not these two surface species have kept the cluster nuclearity. Nevertheless, we have reached a level where CO dissociation is reversible and where it is possible to go from one form to the other without any apparent change in nuclearity. Studies are under way to determine the sizes as well as the catalytic properties of these surface species.

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