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SURFACE SUPPORTED METAL CLUSTER CARBONYLS. CHEMISORPTION DECOMPOSITION AND REACTIVITY OF $Rh_4(CO)_{12}$ SUPPORTED ON SILICA AND ALUMINA

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Summary

Chemisorption of $Rh_4(CO)_{12}$ on to a highly divided silica (Aerosil "0" from Degussa), leads to the transformation: $3\ Rh_4(CO)_{12} \rightarrow 2\ Rh_6(CO)_{16} + 4\ CO$. Such an easy rearrangement of the cluster cage implies mobility of zerovalent rhodium carbonyl fragments on the surface. Carbon monoxide is a very efficient inhibitor of this reaction, and $Rh_4(CO)_{12}$ is stable as such on silica under a CO atmosphere. Both $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ are easily decomposed to small metal particles of higher nuclearity under a water atmosphere and to rhodium(I) dicarbonyl species under oxygen. From the $Rh^I(CO)_2$ species it is possible to regenate first $Rh_4(CO)_{12}$ and then $Rh_6(CO)_{16}$ by treatment with CO ($P_{CO} \geqslant 200$ mm Hg) and H_2O ($P_{H_2O} \geqslant 18$ mm Hg). The reduction of $Rh^I(CO)_2$ surface species by water requires a nucleophilic attack to produce an hypothetical $[Rh(CO)_n]_m$ species which can polymerize to small Rh_4 or Rh_6 clusters in the presence of CO but which in the absence of CO lead to metal particles of higher nuclearity. Similar results are obtained on alumina.

Analogies between molecular metal clusters and very small metallic particles have been recently discussed [1], and at the same time experimental studies have been carried out in different laboratories of the behaviour of metal carbonyl clusters of different metals and varying nuclearity supported on highly divided oxides [2—8]. The main purpose of supporting the clusters on highly divided oxides is to prevent an aggregation to large particles in order to investigate the possible reversible ligand dissociation from the cluster framework.

In an IR investigation of the behaviour of $Rh_6(CO)_{16}$ on silica [2] and on alumina [3] we observed both fragmentation of the initial cluster frame to monomeric species and aggregation to particles of higher sizes depending on the heating conditions and on the presence of water, carbon monoxide, hydrogen or oxygen. We wish to report here an infrared investigation on the behaviour of a small cluster such as $Rh_4(CO)_{12}$ supported on silica. Some work was also carried out on the same cluster supported on alumina.

Experimental

$Rh_4(CO)_{12}$ was prepared as described by Chini and Martinengo [9], the various gases used were supplied by Air-Liquide or SIO. They had a purity higher than 99.99%. In all cases they were stored under activated 5 A molecular sieves. Chloroform and pentane were purchased from FLUKA, they were distilled over $P_2O_5(CHCl_3)$ or Na (pentane) and stored under argon over 5 A molecular sieves.

The η-Al_2O_3 had a surface area of 315 m^2/g and an average pore size of 30 Å, SiO_2 was a non-porous silica "Aerosil 0", with a surface area of 200 m^2/g.

Infrared spectra were obtained on a Perkin-Elmer 225 or 621 spectrophotometer. The technique used to obtain infrared spectra of supported clusters has been described elsewhere [10].

Results

When a hexane solution of $Rh_4(CO)_{12}$ is adsorbed on a silica disc previously dehydroxylated at 500°C under vacuum (10^{-5} mm Hg) for 16 hours, the resulting IR spectrum (Fig. 1a) shows ν(CO) bands at 2080s, 2051m(sh), 2036m(sh) and 1795m(br). These bands are quite different from those expected for $Rh_4(CO)_{12}$ (ν(CO) at 2075s, 2048m, 2036m, 2028m, 1878s, 1870s cm^{-1} in Nujol), particularly in the region of bridging carbonyl groups, and they are closer to those observed for $Rh_6(CO)_{16}$ adsorbed on dehydrated silica [2].

The same result is obtained when a hexane solution of $Rh_4(CO)_{12}$ is adsorbed on a silica disc pretreated at 25°C under vacuum (10^{-5} mm Hg) for 16 hours. It appears however that the bridging carbonyls exhibit broader ν(CO) absorption bands, probably due to some particular hydrogen bonding with OH groups of the support (Fig. 1b). Moreover the transformation of the Rh_4 cluster into the Rh_6 cluster is supported by the detection of CO in significant amounts in the gas phase.

In order to confirm that the transformation of $Rh_4(CO)_{12}$ to $Rh_6(CO)_{16}$ had occurred the following experiment was carried out: 2 g of silica were treated at 500°C under vacuum (10^{-5} mm Hg) overnight, then 57.1 mg of $Rh_4(CO)_{12}$ in hexane solution was absorbed on the silica. After stirring for a few hours the solvent was removed in a liquid nitrogen trap. Then a well degassed solution of $CHCl_3$ was introduced and the suspension left for a few hours. After filtration of the solid, a mixture of $Rh_6(CO)_{16}$ (major component) and $Rh_4(CO)_{12}$ (very minor component) was detected by IR spectroscopy in the $CHCl_3$ solution (Fig. 2). We thus have reasonable evidence that upon absorption of $Rh_4(CO)_{12}$ on silica a rapid transformation to $Rh_6(CO)_{16}$ occurs at the silica surface.

However different results were obtained under a CO atmosphere (250 mm

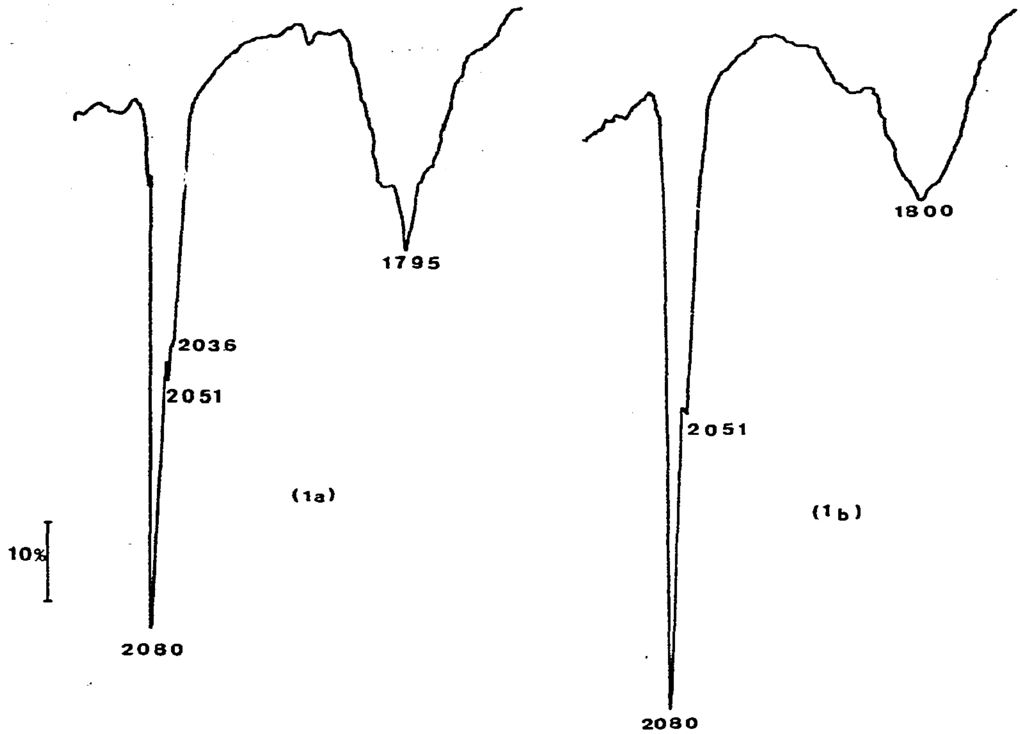


Fig. 1. (1a) Infrared spectrum in the ν(CO) region of $Rh_4(CO)_{12}$ adsorbed on a silica disc previously dehydroxylated at 500°C for 16 hours under a vacuum of 10^{-5} torr. (1b) Infrared spectrum in the ν(CO) region of $Rh_4(CO)_{12}$ adsorbed on a silica disc previously dehydroxylated at 25°C for 16 hours under a vacuum of 10^{-5} torr.

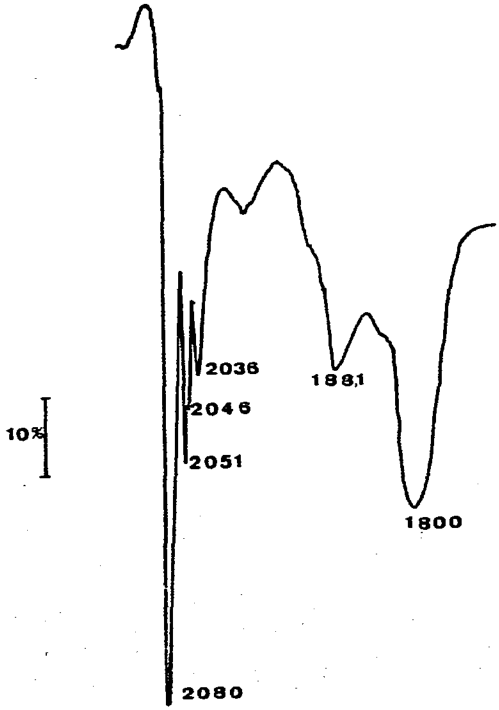


Fig. 2. Infrared spectrum in the ν(CO) region of the species extracted by $CHCl_3$ after adsorption of $Rh_4(CO)_{12}$ on $silica_{500}$.

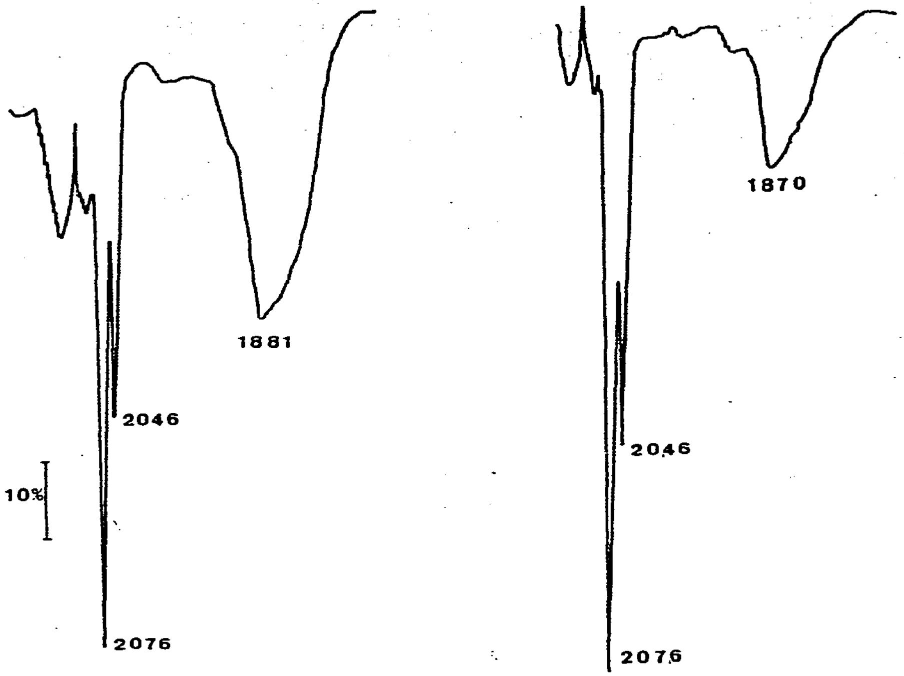


Fig. 3. (3a) Infrared spectrum in the ν(CO) region of $Rh_4(CO)_{12}$ adsorbed on $silica_{500}$ under 250 torr of CO. (3b) Infrared spectrum in the ν(CO) region of $Rh_4(CO)_{12}$ adsorbed on $silica_{25}$ under 300 torr of CO.

Hg) when the adsorption of $Rh_4(CO)_{12}$ was carried out on a disc of silica (treated under vacuum for 16 hours at 500° C). In these experiments, in order to preclude interference by the IR absorption bands of both silica and gaseous carbon monoxide, a blank disc of silica (treated under vacuum for 16 hours at the same temperature (500° C)) of identical weight was exposed to the same CO partial pressure and placed in the reference beam of the infrared spectrometer. In contrast with the previous case, ν(CO) bands at 2076s, 2045m and 1881m-(br) were observed, in agreement with those expected for physisorbed $Rh_4(CO)_{12}$ (Fig. 3a).

The same experiment was carried out on a sample of silica (treated under vacuum for 16 hours at 25°C) under CO atmosphere (300 torr): the ν(CO) bands obtained 2075s, 2046s and 1870m(br) cm^{-1}, are again very similar to those of $Rh_4(CO)_{12}$ (Fig. 3b). Obviously it is possible to maintain $Rh_4(CO)_{12}$ in its molecular form on the silica surface provided there is a partial pressure of CO above the solid.

When $Rh_4(CO)_{12}$ is transformed into $Rh_6(CO)_{16}$ on silica treated at 500°C, it is possible to oxidixe with gaseous O_2 the cluster to "$Rh^I(CO)_2$" species as already observed [2] (Fig. 4). By treatment of the oxidized surface species at 25° C with CO (220 mm Hg) and H_2O (4 mm Hg), we could not observe any transformation, but when the partial pressure of H_2O was raised to 22 mm Hg both $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ were regenerated at 25° C (3 hours) (Fig. 5a). After 24 hours only $Rh_6(CO)_{16}$ was left on the surface (Fig. 5b). These results

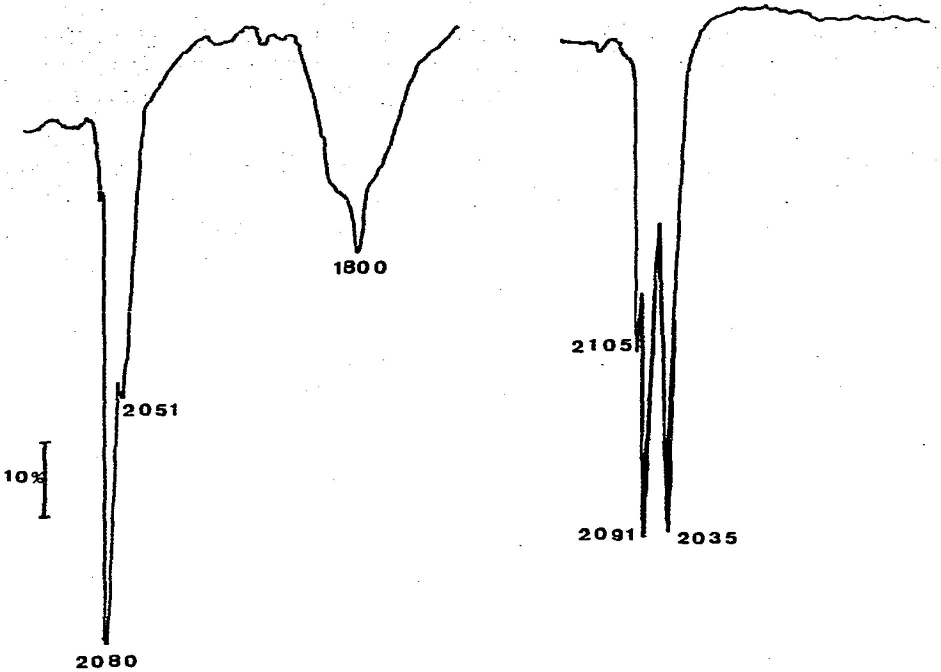


Fig. 4. (4a) (left) Infrared spectrum of $Rh_4(CO)_{12}$ adsorbed on silica$_{500}$. (4b) After treatment under O_2 (300 torr) for 2 hours at 50°C, vacuum treatment at room temperature followed by CO adsorption (200 torr) at room temperature.

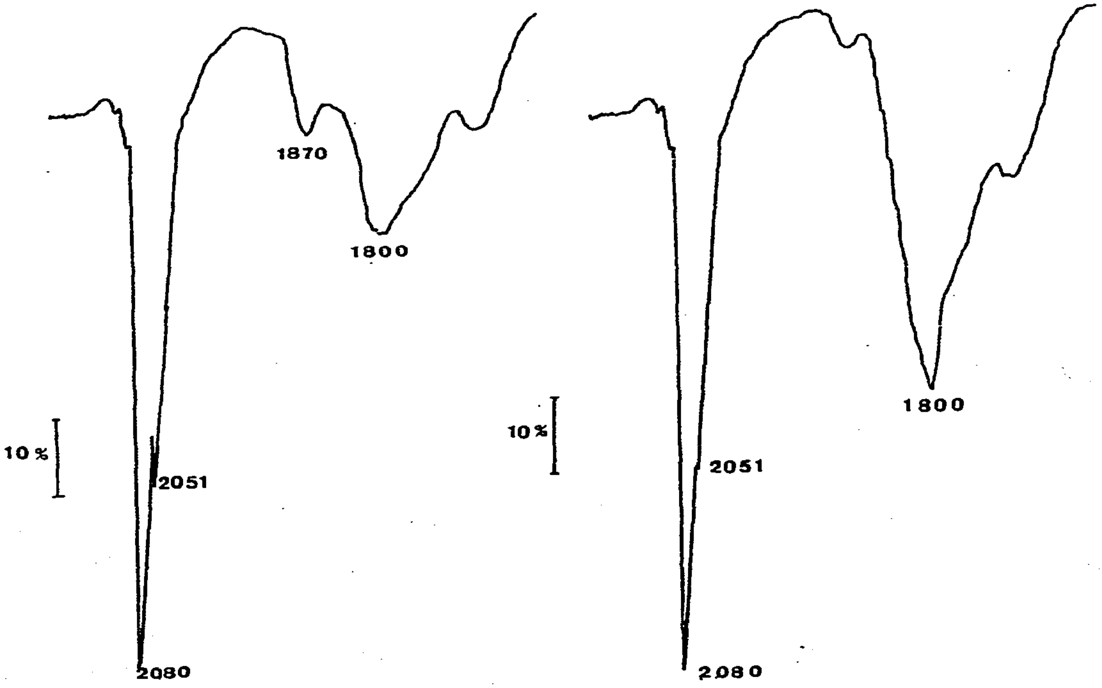


Fig. 5. (5a) Infrared spectrum in the $\nu(CO)$ region after treament of the oxidised $Rh^{I}(CO)_2$ species under H_2O (22 torr) and CO (220 torr) for 3 hours. (5b) Same as 5a after 24 hours under CO + H_2O.

not only confirm that on silica, as well as on alumina [3], "$Rh^I(CO)_2$" surface species can regenerate the zerovalent rhodium clusters, but also that $Rh_4(CO)_{12}$ is an intermediate step in the surface synthesis of $Rh_6(CO)_{16}$ from "$Rh^I(CO)_2$ species.

Interestingly, the decarbonylation of this $Rh_6(CO)_6$ synthesized on a surface, involving treatment at 130° C under vacuum (10^{-5} mm Hg) for 16 hours, produces metallic particles covered with CO (ν(CO) at 2034 and 1835 cm^{-1}) which show ν(CO) infrared absorptions much broader and very much less intense than those from the original cluster (Fig. 6a). We found rather different results on silica treated at 300° C [2]; in this case the close similarities of shapes and intensities of ν(CO) bands for the metallic particles and $Rh_6(CO)_{16}$ suggested a very low nuclearity of the metallic particles obtained by thermal decomposition of $Rh_6(CO)_{16}$.

The only difference between the two sets of experiments is the water content of the support. It seems that large particles are obtained in the presence of water, suggesting that the water on the support might favour in same way the migration of carbonylated zerovalent rhodium species. In the presence of water we were able to detect by electron microscopy particles of rhodium having

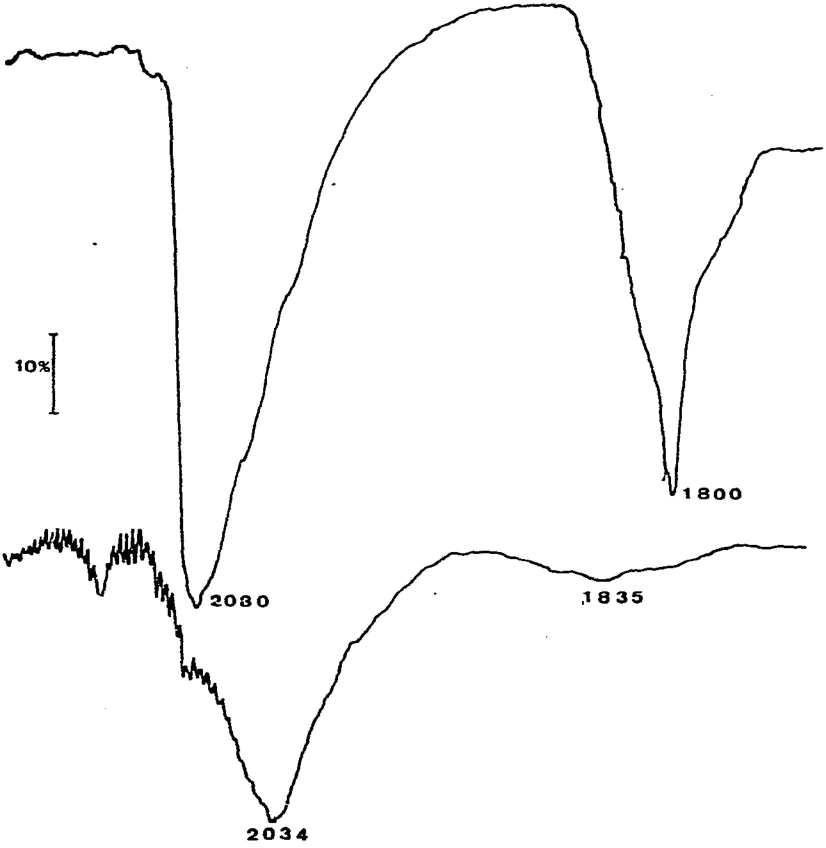


Fig. 6a. Decomposition under vacuum (10^{-5} torr) at 130° C for 16 hours of the $Rh_6(CO)_{16}$ species obtained on Fig. 5b: upper spectrum $Rh_6(CO)_{16}$, lower spectrum after decomposition to metallic rhodium.

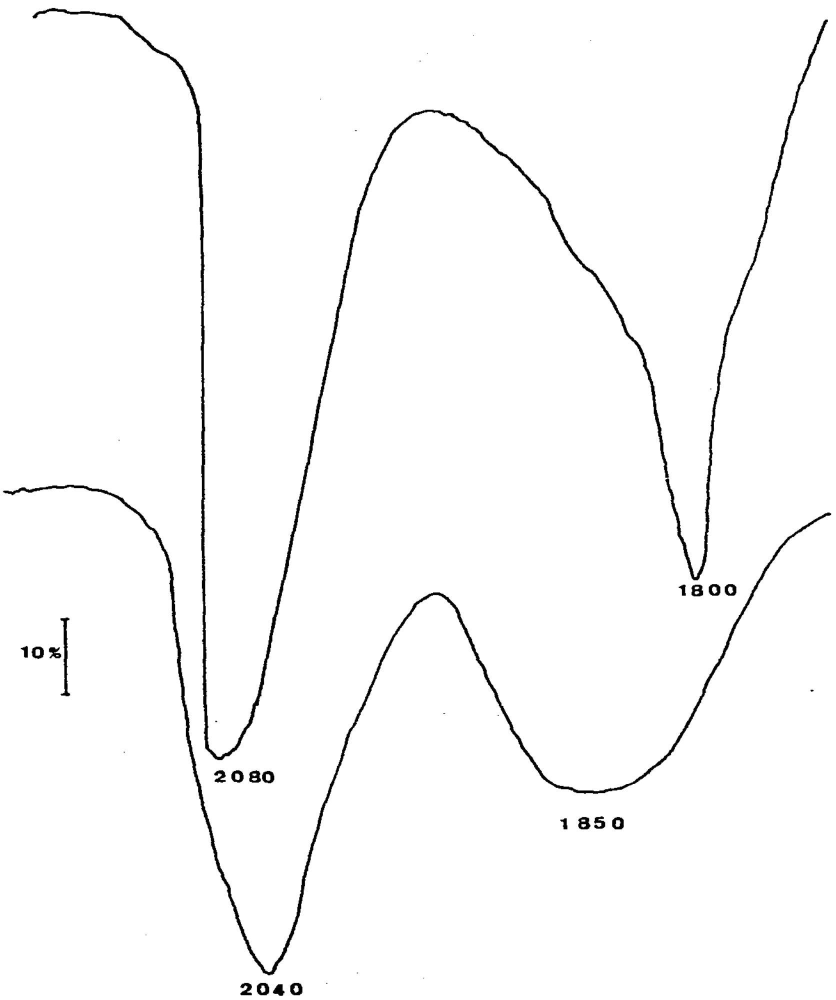


Fig. 6b. Decomposition under H_2O (23 torr) on $Rh_6(CO)_{16}$ supported on $silica_{25}$, upper spectrum $Rh_6(CO)_{16}/silica_{25}$, lower spectrum after decomposition under H_2O (23 torr).

an average size of about 30—40 Å. Metallic particles of rhodium can also be obtained by simple treatment at 50—100° C for one hour of supported $Rh_6(CO)_{16}$ with H_2O (23 mm Hg) in the absence of CO (Fig. 6b). The ν(CO) bands obtained (2040s and 1850m(br) are characteristic of CO coordinated to metallic particles. This CO is easily oxidized by admission of O_2 (520 mm Hg) into CO_2, and the resulting spectrum does not exhibit any ν(CO) vibration. Admission of CO to the solid produces a spectrum typical of "$Rh^I(CO)_2$" surface species (ν(CO) bands at 2106w(sh), 2093s and 2037s; such a behaviour was observed for $Rh_6(CO)_{16}$ adsorbed on silica [2].

Treatment of the carbonylated "$Rh^I(CO)_2$" surface species with H_2 (50°C) or H_2O (30 mm Hg) at room temperature again produces small particles of rhodium covered with CO.

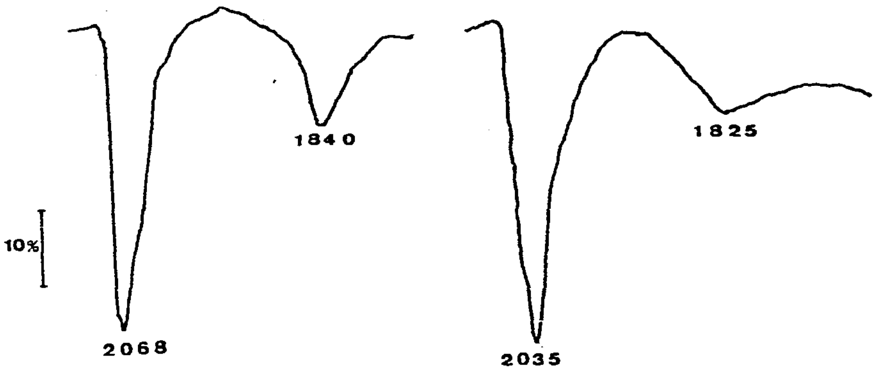


Fig. 7. Infrared spectrum in the ν(CO) region of $Rh_4(CO)_{12}$ adsorbed on alumina$_{500}$ (left). Decomposition to metal particle covered with CO after vacuum treatment at 25°C for 30 minutes (right).

Some experiments on η-Al_2O_3 were carried out. Adsorption of $Rh_4(CO)_{12}$ in hexane solution on η-Al_2O_3 treated at 500°C under vacuum (10^{-5} mm Hg) for 16 hours produces an infrared spectrum, with ν(CO) bands at 2068s and 1840m cm^{-1}, very similar to that observed for $Rh_6(CO)_{16}$ chemisorbed on η-Al_2O_3 treated at 500°C under vacuum (10^{-5} mm Hg) overnight. By subsequent treatment under the same vacuum at 25°C for half an hour, the ν(CO) bands shift at 2035s and 1825m(br), characteristic of small metallic particles covered with CO (Fig. 7). The intensities of these bands (when compared to those of the original $Rh_6(CO)_{16}$) suggest that the transformation to the metallic state has not produced a very significant change of the nuclearity to the original metal atom aggregate.

Discussion

The results supplement the information previously obtained in studies of $Rh_6(CO)_{16}$ adsorbed on silica [2], alumina, silica-alumina and magnesia [3]. They are summarized in Scheme 1. Moreover we have shown that the transformation:

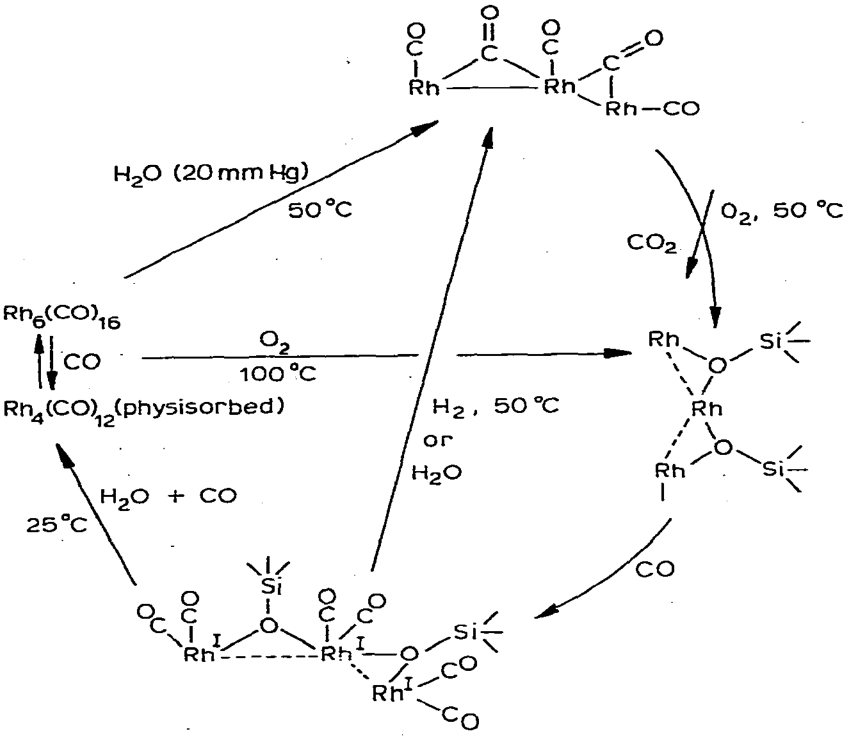
$$3\ Rh_4(CO)_{12} \rightarrow 2\ Rh_6(CO)_{16} + 4\ CO$$

occurs readily during absorption of $Rh_4(CO)_{12}$ on both SiO_2 and η-Al_2O_3. Gaseous carbon monoxide is effectively produced at 25°C without significant amounts of other gases (e.g. H_2, CO_2, hydrocarbons). Such an ready rearrangement of the cluster cage implies a mobility of zerovalent rhodium carbonyl fragments at the surface of oxides.

Carbon monoxide, even under small pressure is a very efficient inhibitor of this reaction, suggesting that it proceeds through carbon monoxide dissociation from the Rh_4 cage as the preliminary step.

Both Rh_4 and Rh_6 clusters are easily decomposed to small metallic particles of higher nuclearity or oxidized to Rh^I surface species. From the latter species it is possible to regenerate first $Rh_4(CO)_{12}$ and subsequently $Rh_6(CO)_{16}$, by treatment with CO ($p_{CO} \geqslant 200$ mm Hg) and enough H_2O ($p_{H_2O} \geqslant 18$ mm Hg); the reaction does not take place if less water is present.

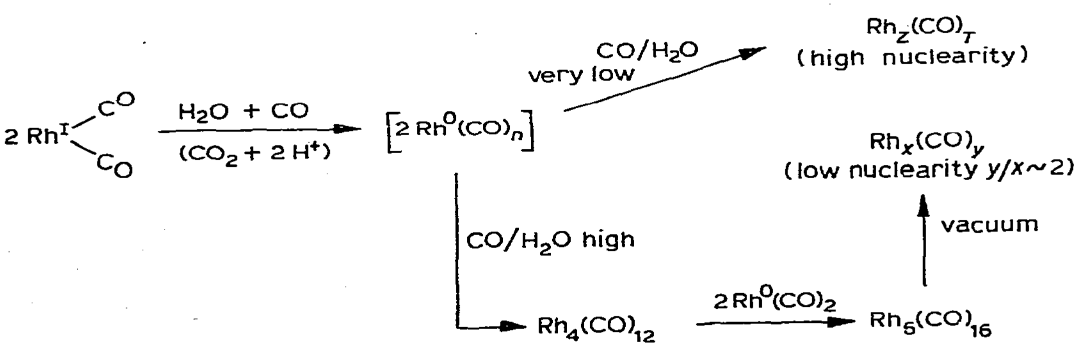
SCHEME 1



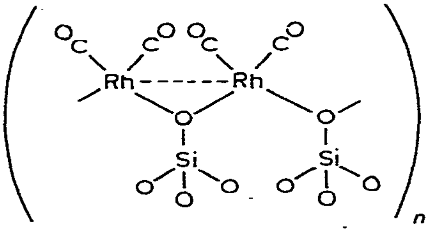
Obviously the reduction of "$Rh^I(CO)_2$" surface species by water requires a nucleophilic attack to produce "$Rh^0(CO)_n$" species, which can polymerize to small Rh_4 or Rh_6 clusters in the presence of CO, but which in the absence of CO show a higher mobility since metallic particles of high nuclearity are obtained (see Scheme 2).

The proposed formulation of the oxidised species as "$Rh^I(CO)_2$" moieties

SCHEME 2



bound to the SiO_2 support [2] by SiO bonds, e.g.



is supported also by the infrared characterisation of $[Me_3SiO\text{-}Rh(CO)_2]_2$ [11], which shows two strong absorption bands in hexane at 2088 cm^{-1} and 2007 cm^{-1} in good agreement in both shape and position with those observed on the SiO_2 surfaces. The compound separates as a very unstable yellow orange solid, whose spectrum in Nujol still shows two strong $\nu(CO)$ bands at about 2070 and 2015 cm^{-1} (shoulder at about 2090 cm^{-1}); however in the presence of traces of water it is transformed quickly into a black material, probably metallic rhodium, which does not show any appreciable carbonyl infrared absorption. Such an easy reduction by water to metallic particles, which has also been observed for the surface "$Rh^I(CO)_2$" species, is in agreement with a good parallelism of the chemical behaviour of rhodium in the two homogeneous and heterogeneous species.

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