Catalysis by Supported Clusters: Two Examples of Catalytic Reactions that Involve a Molecular Cluster Frame [and Discussion]

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Catalysis by supported clusters: two examples of catalytic reactions that involve a molecular cluster frame

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Two examples of catalysis by supported clusters are given that involve a molecular cluster frame during the catalytic cycle.

$(H)Os_3(CO)_{10}(OSi\leqslant)$ is able to hydrogenate ethylene between 343 and 373 K. The mechanism of this reaction, which involves the molecular cluster frame, requires the opening of the bridging three-electron oxygen ligand as the key step of the catalytic process.

$Rh_6(CO)_{16}$ adsorbed on alumina is a catalyst for the water-gas shift reaction carried out between 293 and 393 K. The mechanism of this reaction involves three steps: (i) electrophilic attack by surface protons on the metallic frame with formation of $Rh^{I}(CO)_2$ and $Rh^{III}(H)(H)$ species; (ii) reductive elimination of H_2 favoured by CO coordination to the $Rh^{III}(H)(H)$ species; (iii) nucleophilic attack by molecular water on CO coordinated to Rh^{I} with regeneration of the starting cluster, release of CO_2 and surface protons.

INTRODUCTION

Catalysis by molecular clusters (Smith & Basset 1977; Laine 1982; Jackson *et al.* 1982) remains of great interest in the field of homogeneous and heterogeneous catalysis. Among the various reasons for such an interest there are the 'cluster–surface analogy' (Johnson & Lewis 1975; Muetterties *et al.* 1979; Johnson 1981; Ugo 1975; Muetterties 1975*a*, *b*; Basset & Ugo 1977; Primet *et al.* 1975), the availability of an increasing number of new clusters of increasing nuclearity (Eady *et al.* 1975; Jackson *et al.* 1980; Chini 1980), and the increasing number of molecular cluster carbonyls used as precursor (or effective) (Chini 1980; Pruett & Walker 1974; Robertson & Webb 1974; Anderson & Howe 1977) catalysts in 'CO catalysis' or related reactions. Consider also the great variety of catalytic reactions that can be carried out on metal surfaces and that are not yet known for mononuclear complexes. It appears that one of the main motivations for trying to develop the field of cluster catalysis is to carry out selectively, at a molecular level, catalytic reactions that occur on metal surfaces but with poor selectivities.

Initially, the immobilization of a cluster onto a support, followed by a thermal or photochemical decarbonylation, appeared to be a way to transform a molecular cluster carbonyl 'poisoned' by its carbonyl ligands into a very small particle of metal (Robertson & Webb 1974; Smith *et al.* 1975, 1978; Ichikawa 1976; Anderson & Howe 1977; Kuznetzov *et al.* 1980; Knözinger & Rumpf 1978; Lieto & Gates 1980*a*, *b*). In fact such an approach proved to be much more complicated than expected (Smith *et al.* 1979; Bilhou *et al.* 1978; Besson *et al.* 1980; Psaro *et al.* 1981). The direct immobilization of a molecular cluster carbonyl onto the surface of an inorganic oxide has contributed to the recent development of two different fields, which can be called 'surface organometallic chemistry' and 'catalysis by supported clusters'.

In the former field one considers, *inter alia*, the reactions of the metallic frame or of the ligands with the functional groups present at the surface of an oxide such as the hydroxyl groups, the Lewis centres, and the siloxane or aloxane bridges. It is only after a careful study of the immobilized system or the reaction product of a cluster with a surface that it is possible to consider whether any catalytic reaction involves a cluster catalyst. Cluster catalysis on surfaces may then be compared with clusters in solution, i.e.: (i) the catalytic reaction involves a molecular metal cluster frame throughout the complete catalytic cycle; (ii) the catalytic reaction involves a molecular cluster in some steps of the catalytic cycle and mononuclear fragments in other steps; (iii) the catalytic reaction involves a metal particle derived from the molecular cluster. This last has been the most commonly encountered situation (Smith & Basset 1977).

We shall present two examples where the two first situations have been encountered, namely: (i) the catalytic hydrogenation of ethylene with $HOs_3(CO)_{10}(O\text{-}Si\lessgtr)$, and (ii) the catalytic water-gas shift reaction carried out with $Rh_6(CO)_{16}$ adsorbed on alumina.

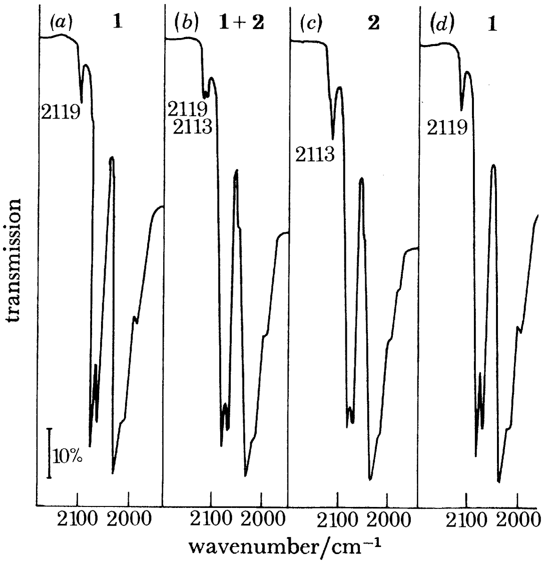


FIGURE 1. (*a*) Infrared spectrum in the ν(CO) region of $HOs_3(CO)_{10}(OSi\lessgtr)$. (*b*) As (*a*), after treatment under C_2H_4 (33 kPa) at 333 K for 1 h. (*c*) As (*b*), after treatment at 353 K for 1 h. (*d*) As (*c*), after vacuum (10 mPa) after treatment at 353 K.

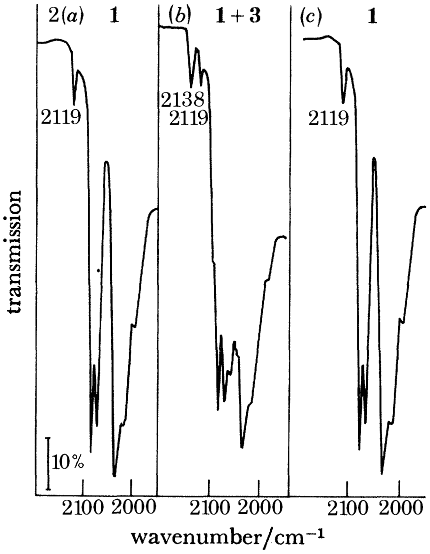
CATALYTIC HYDROGENATION OF ETHYLENE WITH $HOs_3(CO)_{10}(O\text{-}Si\lessgtr)$

The reaction between $Os_3(CO)_{12}$ or $Os_3(CO)_{10}(CH_3CN)_2$ and the silanol groups of silica gives at 423 K the grafted cluster $(H)Os_3(CO)_{10}(OSi\lessgtr)$ (**1**) (Besson *et al.* 1980; Psaro *et al.* 1981). This is a compound stable in air at room temperature and, under Ar, up to 473 K.

The hydrogenation of ethylene can be carried out with **1** between 343 and 373 K, in either batch or dynamic reactors. In a typical experiment, 100 mg of catalyst (**1**–SiO_2; 2 % Os by mass) were introduced in a flow reactor. After a purge with He, the catalyst was heated at 363 K under a mixture of H_2 (50.5 kPa), C_2H_4 (7.2 kPa) and He (42 kPa) with a flow rate of 0.66 ml s^{-1}. A steady-state activity was obtained without any break-in period with a turnover of 40 mmol per mole of cluster per second (differential conditions). The orders with respect to the olefin and to the hydrogen were found to be respectively 0 and 1. The apparent activation energy, determined between 343 and 363 K, was found to be 32 kJ mol^{-1}. The i.r. spectrum of the catalyst after several runs was identical to that of **1**, suggesting that **1** was the effective catalyst. Mechanistic studies were therefore carried out on **1**.

Compound **1** is able to coordinate C_2H_4 at 353 K: volumetric measurements indicate that under 14.4 kPa C_2H_4, 20 % of **1** is transformed into an adduct with C_2H_4. This behaviour is confirmed by i.r. spectroscopy (figure 1*a*–*c*). Under 33 kPa C_2H_4, **1** is transformed almost quantitatively into a new compound, **2**, which gives back **1** under vacuum at 353 K (figure 1*d*).

The reversibility of the coordination process and the similarity of the i.r. spectra of **1** and **2** suggest that **2** has the structure $(H)(C_2H_4)Os_3(CO)_{10}(\mu_{-1}O\text{-}Si\leqslant)$ or $(C_2H_5)Os_3(CO)_{10}(\mu_{-2}O\text{-}Si\leqslant)$. Compound **1** does not coordinate H_2 at 353 K as determined by i.r. and volumetric measurements carried out at 273 or 353 K. However, under H_2 at 373 K, i.e. above reaction temperature, **1** gives compound **3** (figure 2*a*, *b*), which gives back **1** under vacuum at the same temperature (figure 2*c*). Compound **3** can also be easily obtained from **2** by H_2 treatment at 323 K (figure 3).



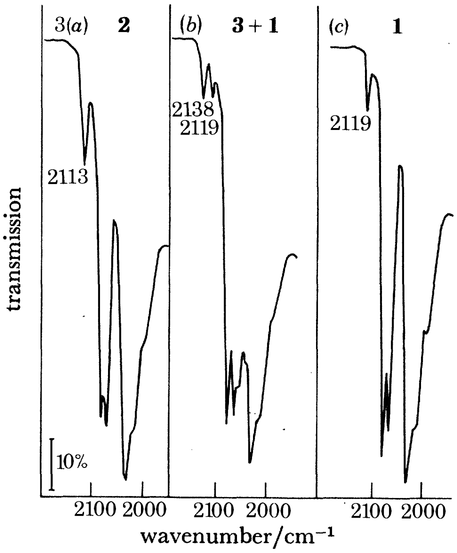
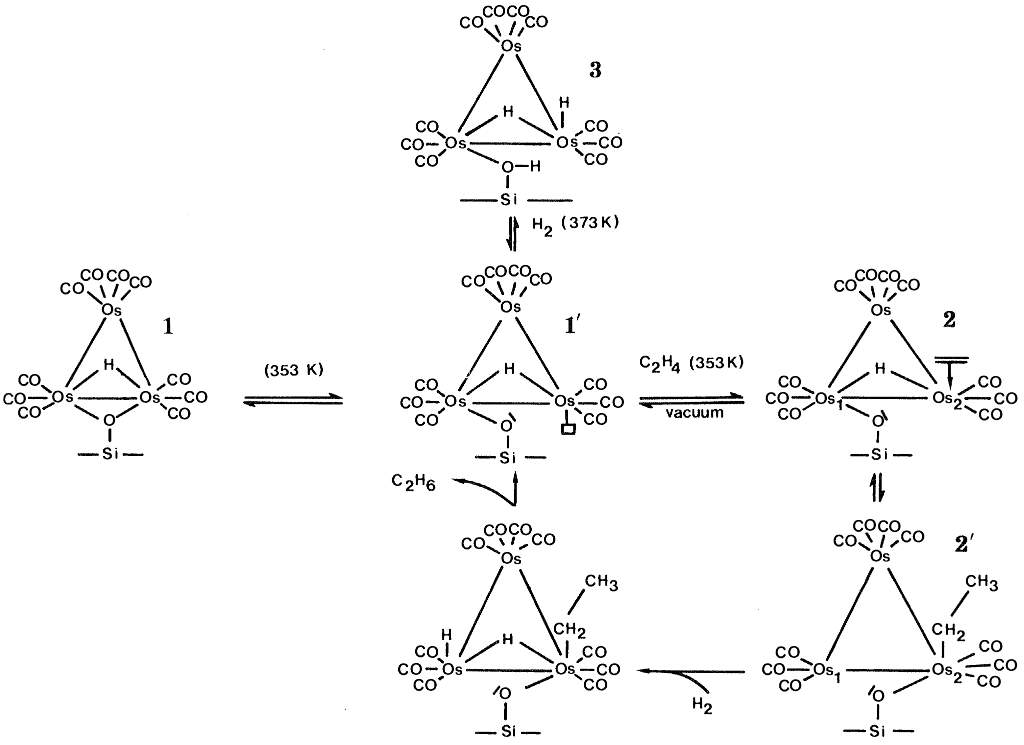


FIGURE 2. (*a*) Infrared spectrum in the ν(CO) region of **1**. (*b*) As (*a*), after H_2 treatment (32 kPa) at 373 K. (*c*) As (*b*), after vacuum treatment (10 mPa) at 273 K.

FIGURE 3. (*a*) Infrared spectrum in the ν(CO) region of **2**. (*b*) As (*a*), after H_2 treatment (32 kPa) at room temperature. (*c*) As (*b*), after vacuum treatment (10 mPa) at 273 K.

These results are interpreted in scheme 1. The coordination of the olefin at 353 K is likely to involve the opening of the Os–O–Os bridge, which creates a vacant coordination site on one metal atom. This process is similar to that reported with the bridging sulphur ligand of $Os_3(CO)_9H(SMe)$ (Johnson *et al.* 1978*a*), which coordinates C_2H_4 to give $Os_3(CO)_9H(C_2H_4)(SMe)$ (Johnson *et al.* 1978*b*). It is difficult at present to decide if the structure of the adduct compound contains the π-coordinated olefin (**2**) or the σ-alkyl group (**2′**). The reversibility of the olefin addition suggests only that if the σ-alkyl group is present, the β-H elimination is a facile and reversible process. The insertion process might be favoured by the concerted migration of the one-electron ligands σ-O and σ-H from the Os_1 to the Os_2 after π coordination of the olefin (scheme 1). The next step of the catalytic cycle involves the oxidative addition of H_2 on a coordinatively unsaturated Os_1 atom. The order of unity with respect to H_2 indicates that this step is rate-determining. The formation of **3** (hypothetical structure) from **1**, or from **2** or **2′**, indicates that H_2 can, under certain conditions, oxidatively add to the unsaturated cluster **1′**, which can be obtained either from **2** or **2′** after oxidative addition of H_2 and reductive elimination of C_2H_6 or from **1** by thermal activation under H_2. In the absence of C_2H_4 or after total consumption of C_2H_4, **1′** gives **3** under H_2.



SCHEME 1

This example constitutes, to our knowledge, the first case of catalysis by a molecular cluster grafted onto unmodified silica. With functionalized silica, there is one reported case of ethylene hydrogenation and but-1-ene isomerization with the clusters $Os_3(CO)_{11}(PPh_2\text{-SiL})$ and $H_2Os_3(CO)_9(PPh_2\text{-SiL})$ (Brown & Evans 1981; Freeman *et al.* 1982). In our case the presence of a bridging hydride and of a bridging oxygen would be responsible for the appearance of catalytic properties. The absence of ageing of such a catalyst is probably due to grafting, which may stabilize coordinative unsaturation and avoid secondary reactions.

THE WATER-GAS SHIFT REACTION CATALYSED BY $Rh_6(CO)_{16}$ ADSORBED ON η-ALUMINA

A great variety of molecular cluster carbonyls have been used as precursor catalysts or as catalysts in the water-gas shift reaction (Ungermann *et al.* 1979; Ford *et al.* 1978; Laine *et al.* 1977; Kang *et al.* 1977; Marnot *et al.* 1981) or related reactions (Laine *et al.* 1978; Laine 1978;

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Niwa *et al.* 1979; Cole *et al.* 1980).† In some cases catalytic cycles were proposed on spectroscopic evidence that suggested that a cluster frame could be retained during the catalytic reaction (Ford 1981). We report here that $Rh_6(CO)_{16}$, when supported on alumina, is an effective catalyst for the water-gas shift reaction; the mechanism of this reaction involves the destruction of the cluster frame and its reconstruction as two of the major steps of the catalytic cycle.

In a typical experiment 2 g η-alumina (315 $m^2\,g^{-1}$) was degassed under vacuum (10 mPa) at 773 K for 15 h ($(Al_2O_3)_{773}$). The resulting solid was contacted in a vacuum line with a solution of $Rh_6(CO)_{16}$ (30 μmol) in CH_2Cl_2. After removal of the solvent under vacuum, the resulting catalyst (**4**) was contacted with 2.9 kPa H_2O and 39 kPa CO in a glass reactor. The water-gas shift reaction was observed by the appearance of equivalent amounts‡ of gaseous CO_2 and H_2 at temperatures as low as 298 K and up to about 373 K, temperature at which the lifetime of the catalyst was very short (less than 2 h). With **4**, for a temperature of 353 K, the initial turnover number was equal to 2 mol H_2 or CO_2 per mole of $Rh_6(CO)_{16}$ per hour (figure 4). At 323 K the order with respect to CO and H_2O were respectively 1 (figure 5) and 0. The apparent activation energy, taken in the temperature range 298–353 K and for a CO pressure of 39 kPa was 65 kJ mol^{-1}. The catalyst aged with time at temperatures equal or above *ca.* 323 K or at CO pressures below *ca.* 20 kPa.

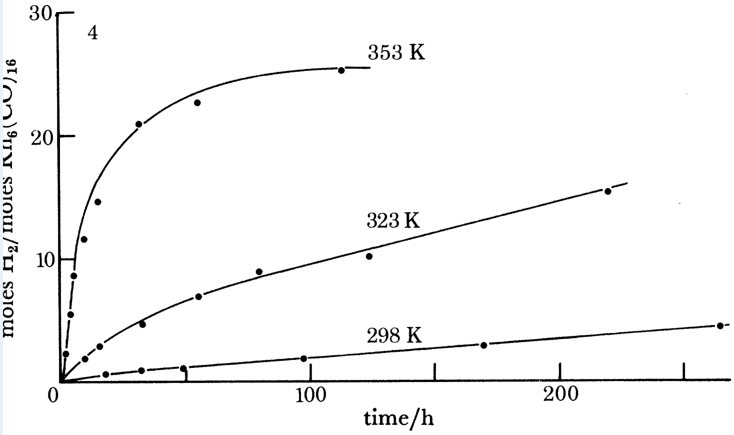

FIGURE 4. Typical kinetic results of the water-gas shift reaction obtained with catalyst **4** at various temperatures (batch reactor) (p_{CO} = 40 kPa).

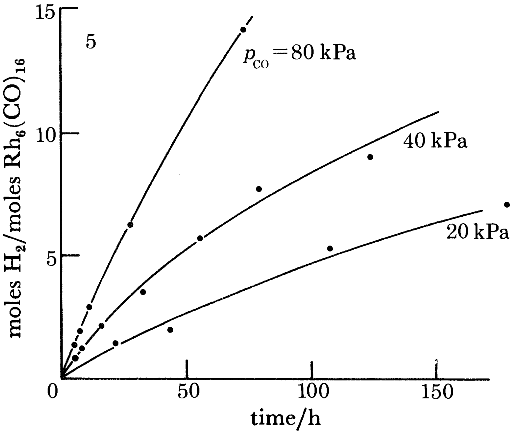

FIGURE 5. Influence of the initial CO pressure on the initial rate of the water-gas shift reaction (catalyst **6**; T = 323 K).

The reactivity of the molecular cluster adsorbed onto η-alumina in the presence of CO or H_2O, or both, was studied by infrared spectroscopy and analysis of the gas phase. When $Rh_6(CO)_{16}$ was adsorbed on $(Al_2O_3)_{773}$, the resulting infrared spectrum, after removal of the CH_2Cl_2 solvent, exhibited ν(CO) bands at 2086 (vs) and 1845 (br, m) cm^{-1}. The cluster was only slightly interacting with the partly dehydroxylated surface, because it could be removed

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† There are also a number of mononuclear complexes that catalyse the water-gas shift reaction under alkaline or acidic conditions (see, for example, Cheng *et al.* 1977; Cheng & Eisenberg 1978; Yoshida *et al.* 1978; King *et al.* 1980; Baker *et al.* 1980).

‡ The amounts of CO_2 and H_2 were nearly equivalent within 5 % of experimental error. However, in the early stages of the reaction the amount of CO_2 was slightly lower than that of H_2, presumably due to the absorption of CO_2 on the hydrated support (carbonate).

from the surface as $Rh_6(CO)_{16}$ by washing with CH_2Cl_2. If 20 mg of the alumina-supported cluster was treated with 5 μmol H_2O for 5 min, so that the coverage of the alumina by OH groups was close to but less than unity, the cluster was transformed instantaneously into two new carbonyl compounds, **5** and **6**, characterized respectively by a doublet of equal intensity at 2094 and 2026 cm^{-1}, and a single band of smaller intensity at 2115 cm^{-1}. Simultaneously about 0.5 mol of H_2 per mole of cluster and about 5 mol of CO per mole of cluster were evolved without any gaseous CO_2 or bands that could arise from the adsorption of CO_2 on the alumina support, when carbonate species are observed by bands at 1222, 1450, 1480 and 1640 cm^{-1}. The $\nu(CO)$ band corresponding to the carbonyl compound **6** was eliminated under vacuum at 353 K. It is probably due to CO coordinated to a Rh^{III} surface complex. Treatment of the resulting solid with 39 kPa CO resulted in a slow and significant increase of the intensity of the doublet at 2094 and 2026 cm^{-1}. Simultaneously H_2 was slowly evolved with time (figure 6).

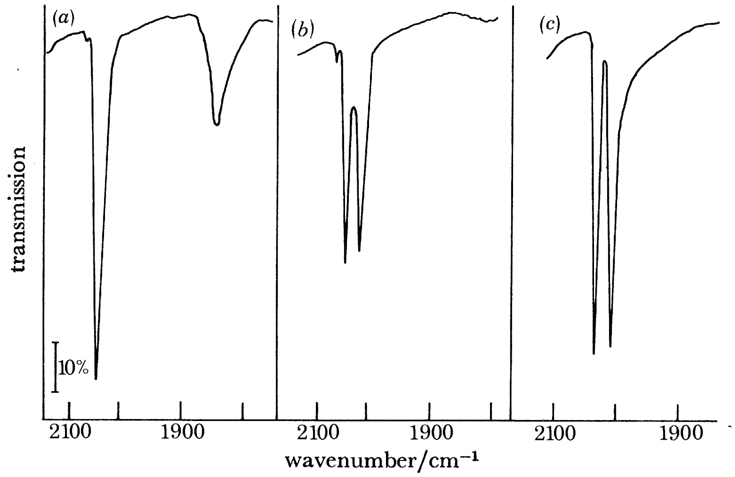
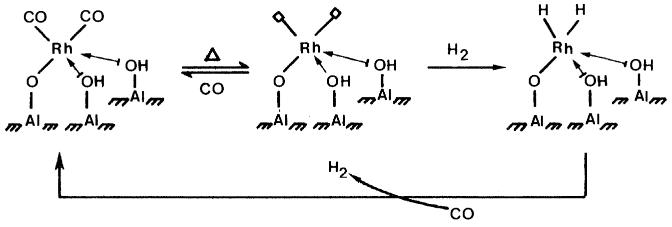


FIGURE 6. (*a*) Infrared spectrum in the $\nu(CO)$ region of $Rh_6(CO)_{16}$ adsorbed on $(Al_2O_3)_{773}$ (20 mg). (*b*) As (*a*), after treatment of the catalyst with 5 μmol H_2O for 5 min. (*c*) As (*b*), after treatment of the catalyst with 39 kPa CO for 24 h.

Compound **5** could also be obtained by reacting $[Rh(CO)_2Cl]_2$ with the surface of an alumina previously degassed at 573 K either from CH_2Cl_2 or from pentane solution, which suggests that this species is of the type $(CO)_2Rh^I(O{-}Al<)$ (Smith *et al.* 1979). Such carbonyl species (**2**) generated either from $Rh_6(CO)_{16}$ adsorbed on hydroxylated alumina or from $[Rh(CO)_2Cl]_2$ can be reversibly decarbonylated by treatment under vacuum (10 mPa) at 673 K and then with CO (40 kPa) at 273 K. Compound **5** does not oxidatively add H_2 at room temperature as determined by volumetric measurement and infrared spectroscopy.



SCHEME 2

However, **5**, after decarbonylation at 673 K, is able to coordinate hydrogen reversibly at 298 K (0.62 mol H_2 per mole of Rh), under an H_2 equilibrium pressure of 39 kPa, which suggests the occurrence of a reversible process as depicted in scheme **2**.

Compound **5** can also coordinate molecular water as determined by the small but significant shift of frequency observed by the adsorption of 2.9 kPa H_2O at 298 K: ν(CO) bands are shifted respectively from 2094 and 2026 cm^{-1} to 2089 and 2019 cm^{-1}. This process probably involves the substitution of the π donating –OH or –O– ligands of the surface coordinated to the rhodium I dicarbonyl by molecular water.

If compound **5** derived from $Rh_6(CO)_{16}$ adsorbed on hydroxylated alumina or from $[Rh(CO)_2Cl]_2$ was treated with CO (100 kPa) and H_2O (2.9 kPa), the resulting spectrum changed slowly with time to give a new carbonyl complex with ν(CO) bands at 2070 and 1804 cm^{-1}, typical of $Rh_6(CO)_{16}$ adsorbed on a fully hydrated alumina (Smith *et al.* 1979) (figure 7). Other bands at 1222, 1450, 1480 and 1640 cm^{-1}, corresponding to CO_2 adsorbed on alumina, were observed along with gaseous CO_2. The molecular cluster could then be extracted from the surface by $CHCl_3$ and characterized by its infrared spectrum. If the CO pressure was kept below *ca.* 20 kPa, the transformation of **5** into $Rh_6(CO)_{16}$ was incomplete and ν(CO) bands characteristic of CO coordinated to metallic rhodium (Smith *et al.* 1979) were observed at *ca.* 2025 (s) and 1850 (br.) cm^{-1}. Under catalytic conditions at temperatures between 298 and 353 K, and for CO pressures between 20 and 90 kPa, the infrared spectrum of the system indicated the presence of a $(CO)_2Rh^I(OAl\lessdot)$ species and $Rh_6(CO)_{16}$.

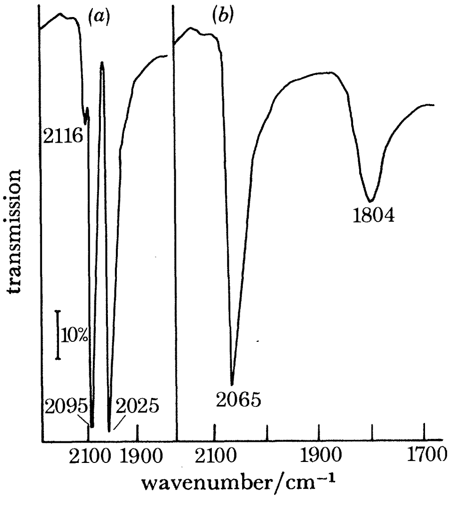


FIGURE 7. (*a*) Infrared spectrum in the ν(CO) region of the catalyst resulting from the treatment by a small amount of water of $Rh_6(CO)_{16}$ adsorbed on $(Al_2O_3)_{773}$. (*b*) As (*a*), after treatment with CO (100 kPa) and H_2O (2.9 kPa) for 24 h.

It was not possible to detect by infrared spectroscopy any rhodium hydride species; this may be due to the low intensity expected for the Rh–H or Rh–D vibrations. However, the ν(CO) frequency of **6** corresponded to CO coordinated to a Rh^{III} species that could be formulated as $Rh^{III}(CO)(H)(H)(O\text{–}Al\lessdot)$.† The presence of a rhodium hydride was also demonstrated by the following experiment: 25 mmol $Rh_6(CO)_{16}$ supported on $(Al_2O_3)_{773}$ were treated by

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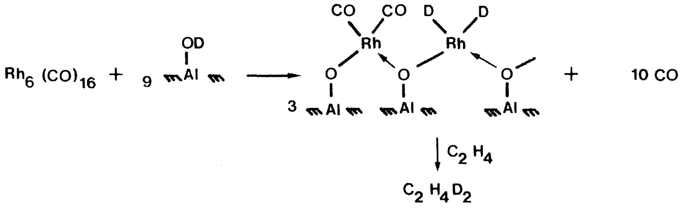
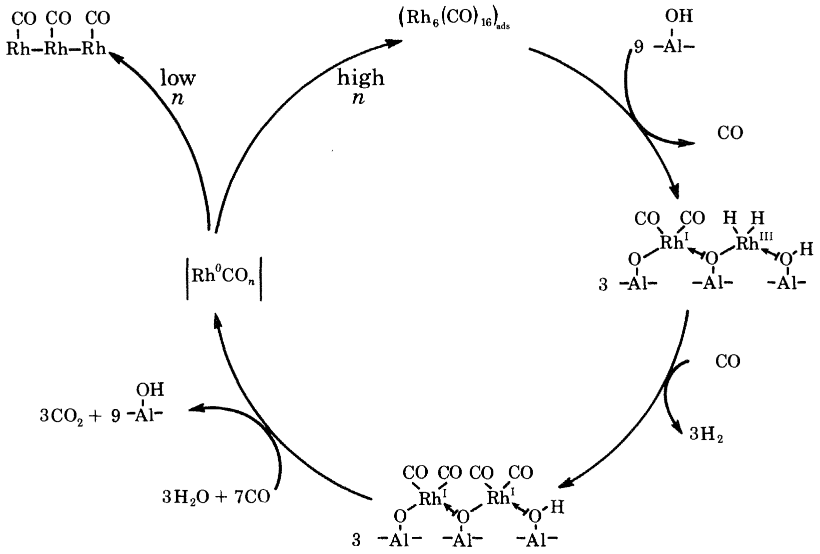
† A similar species has been obtained on silica by Ward & Schwartz (1981) by reacting $Rh(\pi\ allyl)_3$ with silanol groups of silica. In his case the (νRh–H) band could be observed more easily than in ours, owing to the absence of ν(CO) bands.

0.4 mmol D_2O. This solid, when treated for 1 h at 373 K with excess C_2H_4, gave 30 μmol of $C_2H_4D_2$ and smaller amounts of C_2H_5D and C_2H_6; 50 μmol of H_2 would have been expected from the complete reaction depicted in scheme 3.



SCHEME 3



SCHEME 4

Scheme 4 rationalizes the catalytic cycle that occurs in the temperature range 293–393 K. The primary step would be the oxidative addition of Al–OH groups of the alumina to the cluster frame with the formation of $Rh^I(CO)_2$ and $Rh^{III}(H)(H)$ species. CO could coordinate to the $Rh^{III}(H)(H)$ species. The slow step of the process seems to be the expulsion of dihydrogen from the $Rh^{III}(H)(H)$ species. It is likely that this process involves the replacement by CO of water molecules or of OH groups or aloxane groups π coordinated to the $Rh^{III}(H)(H)$ species. The next step of the process seems to be a nucleophilic attack by molecular water on CO coordinated to the $Rh^I(CO)_2$ species with regeneration of a $Rh^0(CO)_n$ species and of a proton, as an Al–OH group.

The $Rh^0(CO)_n$ species may then regenerate the starting cluster. This occurs at low temperature ($T < 393$ K) and at high CO:H_2O ratios. Otherwise the $Rh^0(CO)_n$ species agglomerates to metal particles, which are inactive in the catalytic reaction. This process leading to the formation of metal particles seems to be the origin of the ageing of the catalyst.

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Discussion

R. Whyman (*I.C.I. New Science Group*, *Runcorn*, *U.K.*). The three $\nu(CO)$ absorptions (two bands and one shoulder) assigned to the presence of mononuclear $Rh(CO)_2$ fragments on the surface of alumina might more preferably be accounted for in terms of dinuclear rhodium dicarbonyl units with a structure analogous to that of $[Rh(CO)_2Cl]_2$ (with chloride ions replaced by surface oxide ions). We obtained spectroscopic and chemical evidence consistent with such an interpretation with silica as support material. The occurrence on the surface of a $Rh_6 \rightleftharpoons 3Rh_2$ reversible rearrangement might perhaps be more plausible than a $Rh_6 \rightleftharpoons 6Rh_1$ transformation and of course it has a clear precedent in the solution chemistry of rhodium carbonyls, i.e.

$$\begin{gathered}\rightarrow \text{increasing pressure}\\ Rh_6(CO)_{16} \overset{CO}{\rightleftharpoons} Rh_4(CO)_{12} \overset{CO}{\rightleftharpoons} Rh_2(CO)_8.\\ \leftarrow \text{increasing temperature}\end{gathered}$$