Journal of Organometallic Chemistry, 279 (1985) 147–158
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE WATER GAS SHIFT REACTION CATALYZED BY $Rh_6(CO)_{16}$ ADSORBED ON ALUMINA OR $[Rh(CO)_2Cl]_2$ ADSORBED ON ALUMINA, Na–Y ZEOLITE AND H–Y ZEOLITE *

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(Received March 7th, 1984)

Summary

$Rh_6(CO)_{16}$ chemisorbed on η-alumina or $[Rh(CO)_2Cl]_2$ chemisorbed on η-alumina, Na–Y zeolite and H–Y zeolite catalyze the water gas shift reaction to various degrees. The following order of activity was observed: alumina > Na–Y > H–Y zeolite. With alumina the reaction occurs between 25 and 100 °C. Turnover numbers as high as 255/Rh atom/h are obtained at 50 °C and under 50 atm. These turnover numbers are the same whether the precursor complex is $Rh_6(CO)_{16}$ or $[Rh(CO)_2Cl]_2$. The mechanism of such a reaction has been deduced from infrared studies, mass balance and labeling experiments. It involves three steps: electrophilic attack by surface protons on the metallic frame with formation of $Rh^{I}(CO)_2(OAl\langle)(HOAl\langle)$ and possibly $Rh^{III}(H)(H)(OAl\langle)HOAl\langle)$; reductive elimination of H_2 from $Rh(H)(H)(OAl\langle)(HOAl\langle)$ under CO pressure; and nucleophilic attack by water on CO coordinated to rhodium(I) with formation of CO_2, H^+ and regeneration of $Rh_6(CO)_{16}$. If the CO pressure is too low or if liquid water is used, aging of the catalyst occurs which seems to be due to the formation of metallic rhodium. The intermediacy of $[Rh(CO)_4]^-$ is also suspected in the step of metal–metal bond formation.

I. Introduction

A great variety of molecular cluster carbonyls have been used as precursor catalysts in the water gas shift [1] or related reactions [2,3]. In some cases, catalytic cycles were proposed which suggested that a cluster frame could be retained during the catalytic reaction [4].

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* Deditated to Prof. J. Halpern on the occasion of his 60th birthday.

0022-328X/85/$03.30

We report in this paper that $Rh_6(CO)_{16}$ supported on alumina, or $[Rh(CO)_2Cl]_2$ supported on alumina or encapsulated within Na–Y or H–Y zeolites, catalyze the water gas shift reaction to various degrees. With $Rh_6(CO)_{16}$ supported on alumina, and under CO pressure (50 atm), the catalyst may be extremely active at low or moderate temperature. In this particular case, the mechanism of the reaction apparently involves the destruction of the cluster frame and its reconstruction as two of the major steps of the catalytic cycle.

II. Experimental section

All the experiments were carried out in a batch reactor either at atmospheric pressure (type A experiments) or at 50 atm (type B experiments).

"Type A" experiments were carried out in the glass equipment described in Fig. 1 which allowed us to prepare the catalyst in situ. The solvent (CH_2Cl_2, $CHCl_3$ or THF) was first carefully dehydrated over 5A zeolite which had previously been treated at 250 °C under vacuum and then degassed by repeated freezing (tube A of Fig. 1A). The solvent was condensed through a break-seal into tube B, which contained a known amount of $Rh_6(CO)_{16}$ or $[Rh(CO)_2Cl]_2$. Tube A was then separated (arrow 1 in Fig. 1A) from the apparatus. The solution of the cluster (or of the dimer) in tube B was then introduced into tube C, through a break-seal. The solids in tube C (alumina, H–Y or Na–Y zeolite) had previously been degassed or thermally treated at 500, 300 and 350 °C, respectively). After chemisorption of the organometallic compound on the support, the solvent was removed from tube C by trapping with liquid nitrogen in tube B. Reactor B was then separated from reactor C. Traces of solvent in tube C were then eliminated by vacuum treatment (10^{-4} Torr) for 1 h. The solid C was then equilibrated with 20 Torr of well-degassed water and a given pressure of CO (99.995% pure) was introduced into reactor C maintained at a given temperature. Gas phase analysis of CO_2 and H_2 was carried out by removing, with a syringe, a sample from vessel F. This vessel (F) was isolated from tube C by a stopcock in order to avoid contamination by traces of air which might be present in the gas syringe. Quantitative analysis of H_2 was carried out by gas chromatography using a molecular sieve column at 650 °C with Ar as carrier gas. Analysis of CO_2 was achieved through a PORAPAK R column at 50 °C with H_2 as carrier gas. A methanation catalyst (Ni/MgO at 350 °C) was located in front of the flame ionization detector and transformed all the CO_2 to CH_4. The activities were expressed as mole of H_2 or CO_2 per mole of $Rh_6(CO)_{16}$ or per mole of $[Rh(CO)_2Cl]_2$. Preliminary experiments showed that equivalent amounts of H_2 and CO_2 are obtained [5].

"Type B" experiments were carried out in the following way: first the catalyst was prepared as in type A experiments and stored under vacuum (10^{-4} Torr) in the glass equipment. Then the glassware was introduced, under Ar, into a 250 ml autoclave and broken in situ. The catalyst was then equilibrated with water by passing a stream of CO ($P = 1$ atm) saturated with water at 20 °C. Then dry CO was introduced into the autoclave at 50 °C. Analysis of the gas phase was then carried out as in Type A experiments.

"Turnover numbers" (TN) under CO pressure were deduced from the following experiment: 5.72 g of alumina catalyst containing 0.82% Rh was introduced into a 250 ml autoclave under Ar atmosphere and purged under dry CO. The alumina was then saturated with water by introducing 47.6 l of CO saturated with water (0.052 mole H_2O). After introduction of 50 atm of dry CO, the catalyst was heated at 50 °C for 1 h. Analysis of the gas phase gave 12.5% mole H_2 corresponding to 0.055 mole. The corresponding turnover number was therefore 0.055 mole H_2 for 0.0000758 mole of $Rh_6(CO)_{16}$ i.e. 130 h^{-1} per Rh atom. This experiment was repeated and almost identical quantitative results were obtained.

Infrared spectra were recorded on a Perkin-Elmer 225 spectrophotometer. The impregnation technique used to obtain infrared spectra of supported complexes in the absence of air was as follows (Fig. 1B). First, a solution (CH_2Cl_2 or THF) of the complex was prepared in a glass tube equipped with a break-seal as described in type A experiments. The infrared cell (Fig. 1B) allowed the support to be thermally treated under vacuum (10^{-4} Torr). Then the solution of the complex was dripped gradually onto the disc of support via a break-seal and a funnel. The solvent was then removed by trapping in liquid nitrogen and the infrared cell was sealed under vacuum (arrow 2, Fig. 1B). The solid could then be treated under various atmospheres (vacuum, H_2, CO, H_2O, Ar, etc.) and (or) at various temperatures.

Volumetric measurements were carried out with the same reactor as that depicted in type A experiments. Volumetric measurements of H_2 adsorption were carried out with a Precision Pressure Gauge from Texas Instrument (0–400 Torr).

The alumina used for type A experiments and for infrared studies was an η-Al_2O_3 with a surface area of 300 m^2/g and an average pore size of 30 Å. The alumina used under pressure was a cubic γ-Al_2O_3 with a surface area of 255 m^2/g, an average pore

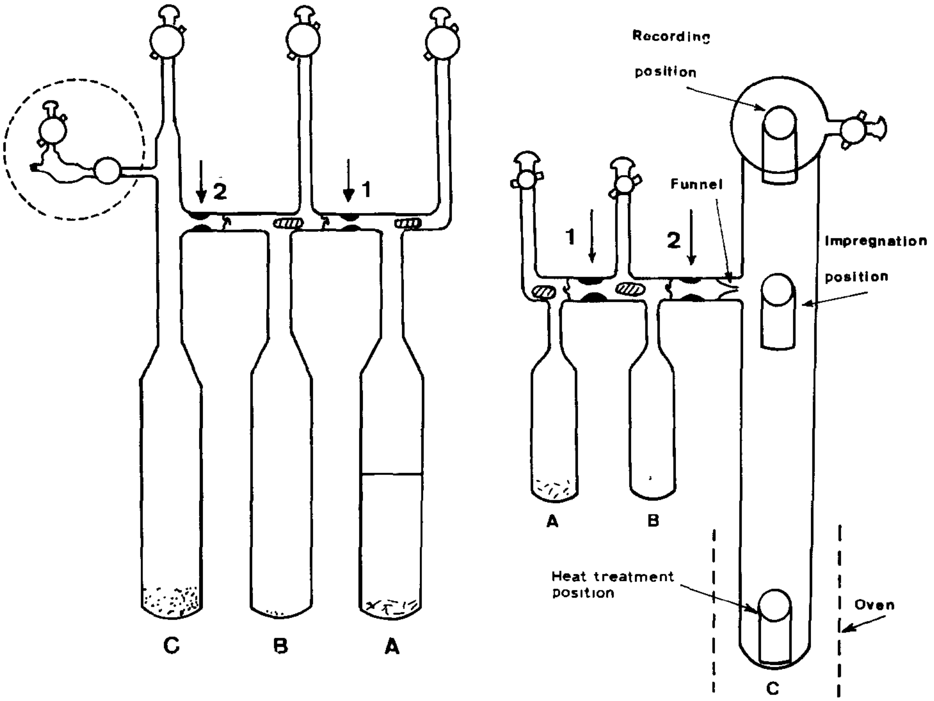


Fig. 1. (left) Glass equipment used to carry out preparation of the supported catalyst and catalytic runs. (right) Infrared cell used to study the "in situ" chemisorption of organometallic complexes on a disc of alumina.

size of 100 Å and a pore volume of 0.59 cm^3/g. The Na-Y zeolite (SK 40) was purchased from Linde.

The H–Y zeolite was obtained by Na^+/NH_4^+ exchange of the Na–Y zeolite. The solid was washed several times with water to remove the NaCl. The resulting NH_4^+ zeolite was treated under O_2 by increasing the temperature slowly up to 350 °C to give the H–Y zeolite.

III. Results

III.1. $Rh_6(CO)_{16}/Al_2O_3$

When $Rh_6(CO)_{16}$/alumina is contacted with CO and H_2O, the water gas shift reaction occurs at 25 °C or above.

Typical data are given in Fig. 2 and 3 corresponding to the effect of temperature and CO pressure ($P < 1$ atm). The loss of activity which occurs at 80 °C does not seem to be due to aging of the catalyst since, upon introduction of a new CO, H_2O loading, similar results are obtained. It appears that this loss of activity is due to the total consumption of water introduced into the reactor. Calculations indicate that when the reaction is over, the amount of hydrogen produced corresponds to the amount of water introduced. The apparent activation energy deduced from Fig. 2 is equal to 15 kcal/mole.

Figure 3 indicates that the reaction is first order in CO ($P(CO) < 1$ atm) and probably first order in water (shape of the curve in a batch reactor). At 80 °C and for $P(CO)$ 300 Torr, the initial turnover number is equal to 0.37 mole H_2/Rh atom/h, which corresponds to a value of 2.8 mole H_2/Rh atom/h at 100 °C and 1 atm of CO, assuming an apparent activation energy of 15 kcal/mole. This value is comparable to that obtained by Sauvage [1] using $RhCl_3$ and water-soluble sulfonated diimine ligands at pH 5.4 (TN 23.3 h^{-1} at 100 °C for the most efficient catalyst).

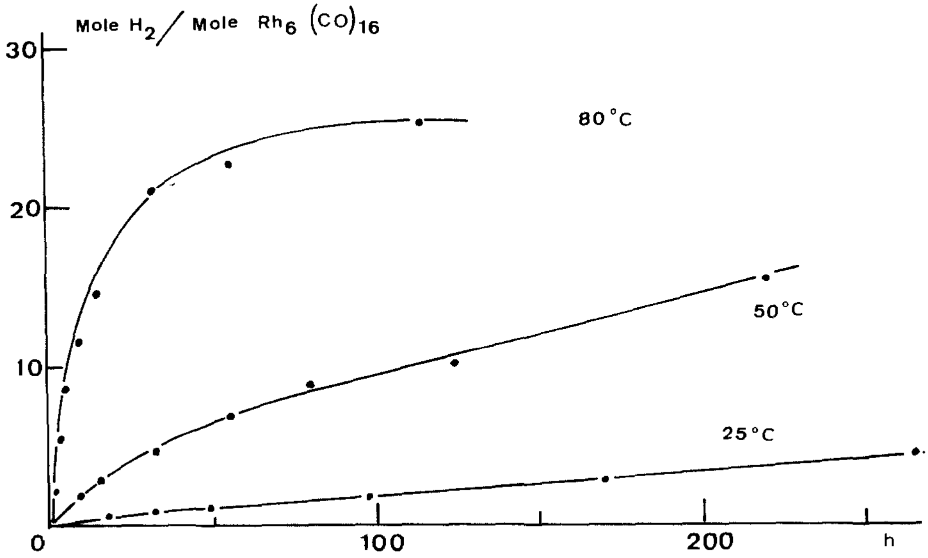


Fig. 2. Typical kinetic results of the water gas shift reaction obtained with catalyst I at various temperatures (batch reactor).

Much larger turnover numbers have been attained under CO pressure (P(CO) 50 atm) (type B experiments). Under these conditions and at temperatures as low as 50 °C, turnover numbers of 130 mole H_2/Rh atom/h could be reached. To our knowledge, this is the highest value reported for a low temperature rhodium-based water gas shift reaction. (The corresponding value at 100 °C would be close to 2600 h^{-1}.) If the reaction is carried out under CO pressure and with liquid water (instead of gaseous water), the TN reached are even greater than this value, in agreement with a positive order in water (TN 255 h^{-1} at 50 °C). Unfortunately, the catalytic lifetime seems to be decreased drastically by an excess of liquid water.

III.2. $[Rh(CO)_2Cl_2]_2/Al_2O_3$, Na–Y and H–Y zeolite

These experiments were carried out in order to see if the nature of the support and the nature of the starting complex play an important role in the resulting activity. Figure 4 indicates clearly that alumina is the most active support and H-Y zeolite is the least active. For the alumina support, the turnover numbers for $Rh_6(CO)_{16}$ and $[Rh(CO)_2Cl]_2$ at 80 °C and 300 Torr are equal to 0.37 and 0.50 mole H_2/Rh atom/h, respectively. Considering the experimental uncertainties, these two values can be regarded as very close.

III.3. Mechanistic studies

The reactivity of the molecular cluster $Rh_6(CO)_{16}$ and of the $[Rh(CO)_2Cl]_2$ dimer with the surface of alumina in the presence of CO and H_2O was studied by infrared spectroscopic analysis of the gas phase and adsorption measurements. When $Rh_6(CO)_{16}$ is adsorbed from a CH_2Cl_2 solution on $alumina_{500}$, the resulting infrared spectrum, after removal of the CH_2Cl_2 solvent, exhibits ν(CO) bands at

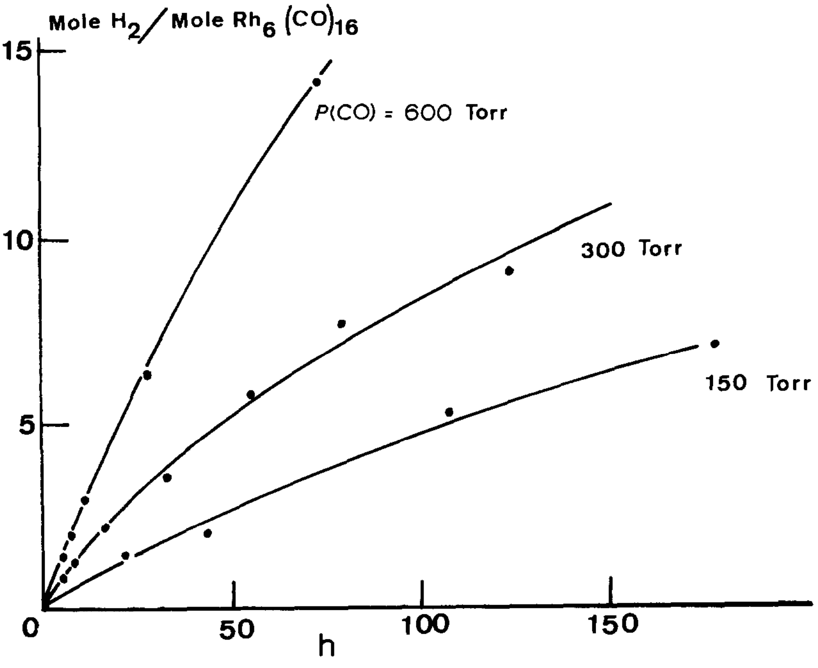


Fig. 3. Influence of the initial CO pressure on the initial rate of the water gas shift reaction (catalyst I; T 50 °C).

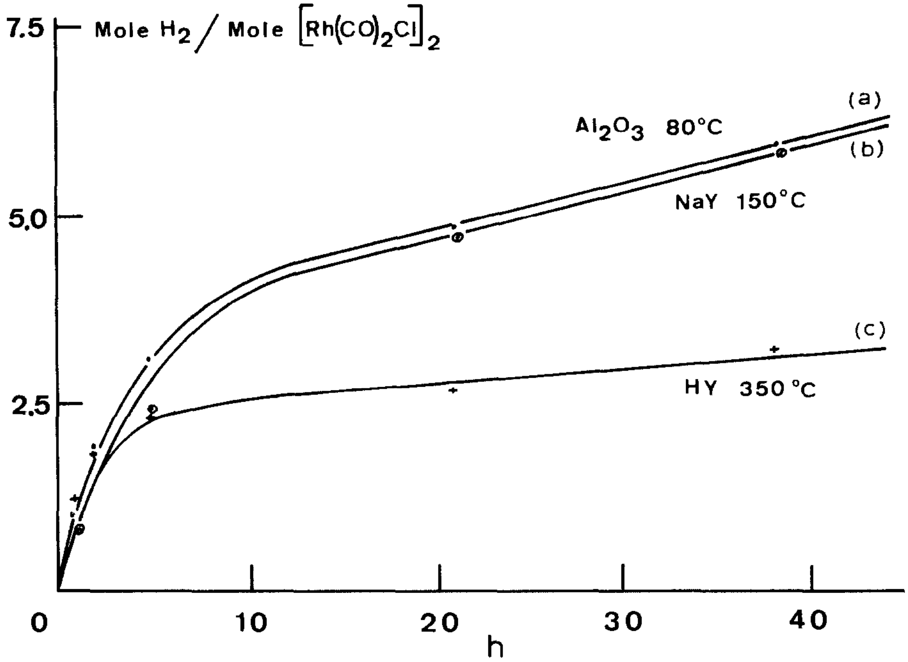


Fig. 4. Comparative activities in the water gas shift reaction between η-alumina (curve a), Na–Y zeolite (curve b) and H–Y zeolite (curve c)

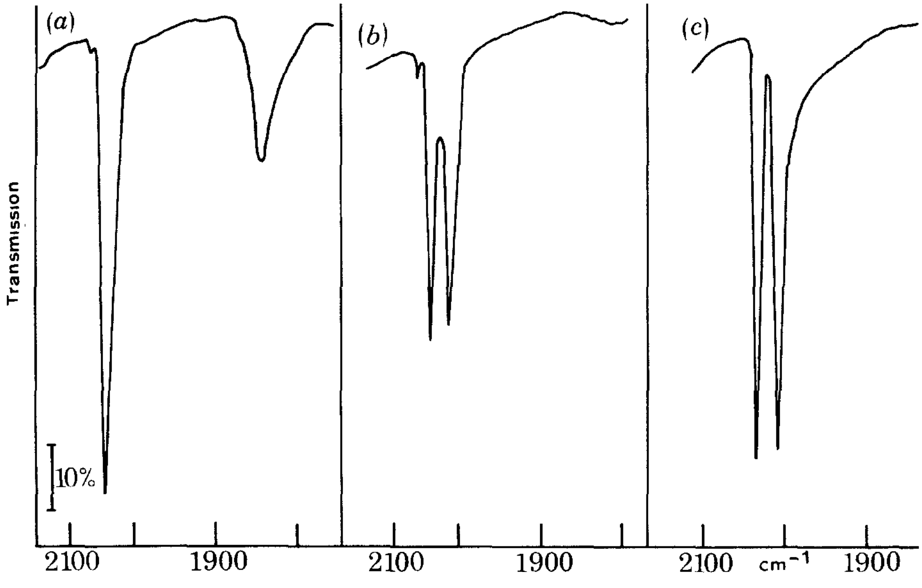
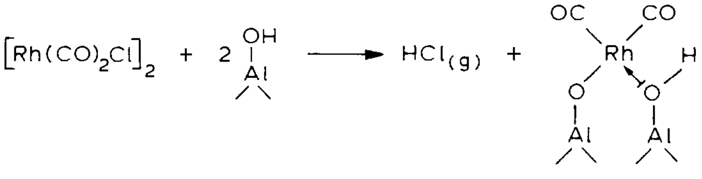


Fig. 5. (a) Infrared spectrum in the $\nu(CO)$ region of $Rh_6(CO)_{16}$ adsorbed on alumina$_{500}$ (20 mg). (b) Same as (a) after treatment of the catalyst with 5×10^{-6} mole of H_2O for 5 min. (c) same as (b) after treatment of the catalyst with 300 Torr of CO for 24 h.

2086(v.s.) and 1845(br, m) cm^{-1} corresponding to the values expected for the cluster supported on alumina [6] (Fig. 5). The cluster interacts only slightly with the partially dehydroxylated surface, since it can be quantitatively and selectively removed from the surface as $Rh_6(CO)_{16}$ by washing with CH_2Cl_2.

If 20 mg of the alumina-supported cluster is treated with 5×10^{-6} mole of H_2O for 5 min so that the coverage of the alumina by OH groups is almost unity, the cluster is transformed instantaneously into a new carbonyl compound (II) characterized by a doublet of almost equal intensity at 2097 and 2028 cm^{-1} (species II) [7] (Fig. 5b). Treatment of the resulting solid with 300 Torr of CO results in a slow but significant increase of the intensity of the doublet at 2097 and 2028 cm^{-1}. Simultaneously, H_2 is evolved with time (Fig.5c).

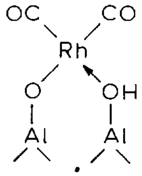
The chemisorption of $[Rh(CO)_2Cl]_2$ on $alumina_{500}$ or $alumina_{300}$ also gives a doublet of equal intensity at 2097 and 2028 cm^{-1} at the same position as that observed in the reaction of $Rh_6(CO)_{16}$ with OH groups on alumina. It is suspected, in agreement with previous studies [6,8], that species II corresponding to this doublet is a $Rh^I(CO)_2$ species having a 16-electron square-planar configuration (formalism developed in surface organometallic chemistry, see ref. 9).

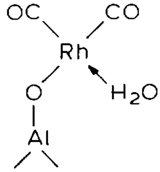


(II)

(1)

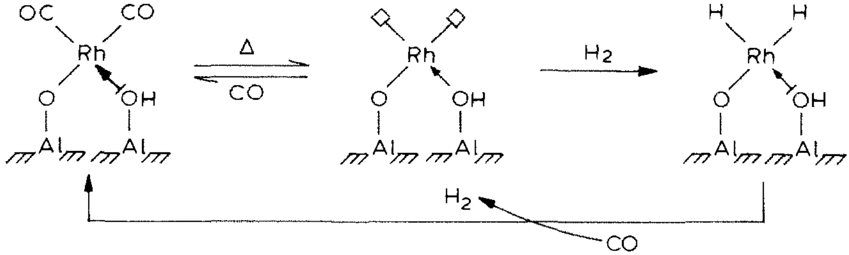
Species II generated either from $Rh_6(CO)_{16}$ + >AlOH + CO or from $[Rh(CO)_2Cl]_2$ + >AlOH is able to coordinate molecular water, as indicated by the shift of about 10 cm^{-1} towards low frequencies when about 20 Torr of H_2O is added to the alumina surface (ν(CO) 2090, 2021 cm^{-1}). This shift of frequency is cancelled when the system is evacuated above ca. 120 °C. It is restored under water adsorption at room temperature, indicating a kind of reversibility of water coordination on the rhodium(I) dicarbonyl.





Species II generated either from $Rh_6(CO)_{16}$ + >AlOH + CO or from $[Rh(CO)_2Cl]_2$ + >AlOH can be reversibly decarbonylated by treatment under vacuum (10^{-4} Torr) at 140 °C and then with CO (300 Torr) at 25 °C (Fig. 6).

Species II does not oxidatively add H_2 at room temperature, as shown by the volumetric measurement (no H_2 adsorption) and infrared spectroscopy (no modification of the IR spectrum under H_2). However, after decarbonylation at 140 °C, species II is able to coordinate hydrogen at 50 °C (0.62 mole H_2 per Rh atom under H_2 equilibrium pressure of 300 Torr). H_2 is then quantitatively evolved by introducing CO pressure, which suggests the occurrence of a reversible process as depicted in eq. 2.



(2)

When species II, generated either from $Rh_6(CO)_{16}$ + $\diagup$AlOH + CO or from $[Rh(CO)_2Cl]_2$ + $\diagup$AlOH, is treated with CO (700 Torr) and H_2O (20 Torr), the resulting spectrum changes slowly with time to give a new carbonyl complex with ν(CO) bands at 2065 and 1804 cm^{-1} typical for $Rh_6(CO)_{16}$ adsorbed on a fully hydrated alumina [6] (Fig. 7). Other bands at 1222, 1450, 1480 and 1640 cm^{-1} corresponding to CO_2 adsorbed on alumina are observed along with gaseous CO_2 [11]. The molecular cluster can then be extracted from the surface by $CHCl_3$ and characterized by its infrared spectrum. If the CO pressure is kept below a value of ca. 150 Torr, the transformation of species II into $Rh_6(CO)_{16}$ is not complete and ν(CO) bands characteristic of CO coordinated to metallic rhodium [6] are observed at ca. 2025 (s) and 1850 (br) cm^{-1}. The formation of metallic particles of rhodium (when the CO pressure is too low and the water pressure is too high) can be confirmed by electron microscopic measurements. The growth of the particles under water is such that particles of 500 Å can be detected.

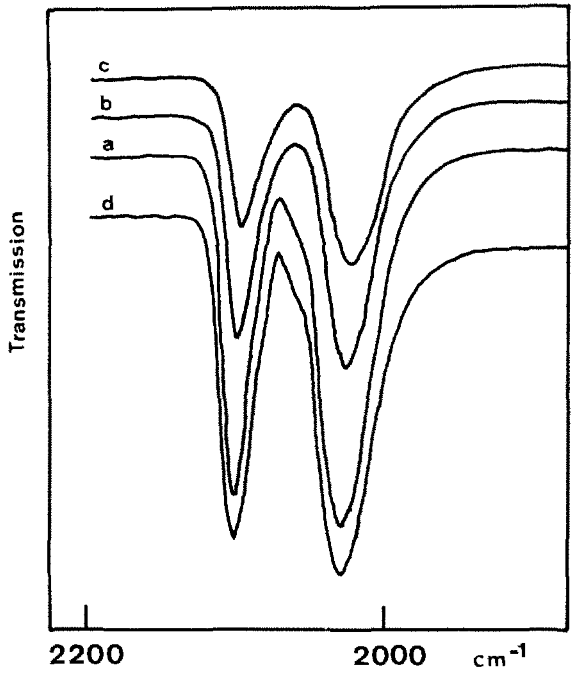


Fig. 6. (a) IR spectrum obtained after reaction of $[Rh(CO)_2Cl]_2$ with the $alumina_{500}$ surface (b) Same as (a) after vacuum treatment at 140 °C for 4 h. (c) Same as (b) after vacuum treatment at 140 °C for 20 h. (d) Same as (c) after admission of 300 Torr of CO at 25 °C.

Under catalytic conditions at temperatures ranging from 25 to 80 °C, and for CO pressure of 150 to 760 Torr, the infrared spectrum of the system contains bands corresponding to $Rh_6(CO)_{16}$ (ν(CO) 2065 and 1804 cm^{-1}) and $Rh^{I}(CO)_2(OAl{<})(H_2O)$ (ν(CO) 2090 and 2021 cm^{-1}).

The stoichiometric oxidation of $Rh_6(CO)_{16}$ by ${>}AlOH$ to $Rh(CO)_2(OAl{<})(HOAl{<})$ should produce molecular hydrogen in significant amount: $Rh_6(CO)_{16} + 12{>}AlOH \rightarrow 3H_2 + 6Rh(CO)_2(OAl{<})(HOAl{<}) + 4CO$.

In fact, such a surface reaction between the cluster and OH groups gives only 0.5 mole H_2/mole of cluster, suggesting that intermediate hydrides have been produced according to the possible oxidative addition reaction:

$$Rh_6(CO)_{16} + 12{>}AlOH \rightarrow 3Rh^{III}(H)(H)(OAl{<})(HOAl{<})$$
$$+ 3Rh^{I}(CO)_2(OAl{<})(HOAl{<})$$

It was not possible to detect the rhodium dihydride by infrared spectroscopy probably due to the low intensity expected for the Rh–H or Rh–D vibrations. However, the presence of a rhodium hydride can be suggested by the following experiment: 2.6×10^{-5} mole of $Rh_6(CO)_{16}$ supported on alumina is treated with 4×10^{-4} mole of D_2O. Such a solid when treated for 1 h at 353 K with excess C_2H_4 gives 3×10^{-5} mole of $C_2H_4D_2$ and a smaller amount of C_2H_5D and C_2H_6. In fact, 7.8×10^{-5} mole of D_2 should be expected from the complete reaction [12]:

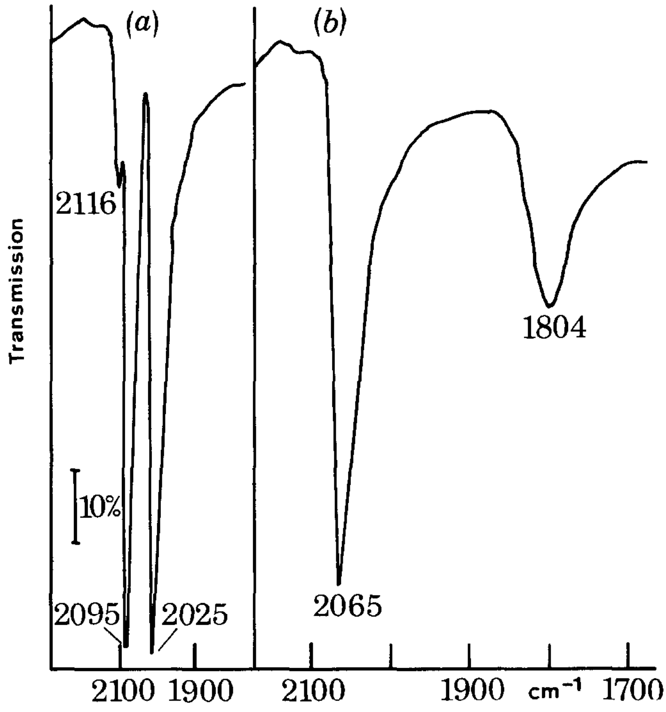
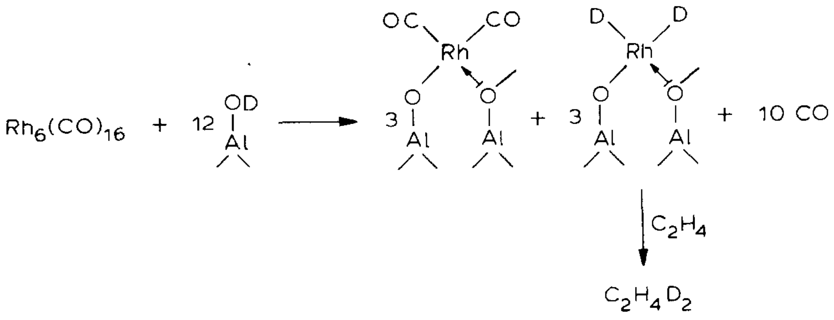


Fig. 7. (a) Infrared spectrum in the ν(CO) region of the catalyst resulting from treatment of $Rh_6(CO)_{16}$ adsorbed on $(Al_2O_3)_{300}$ with a small amount of water. (b) As (a), after treatment with CO (700 Torr) and H_2O (20 Torr) for 24 h

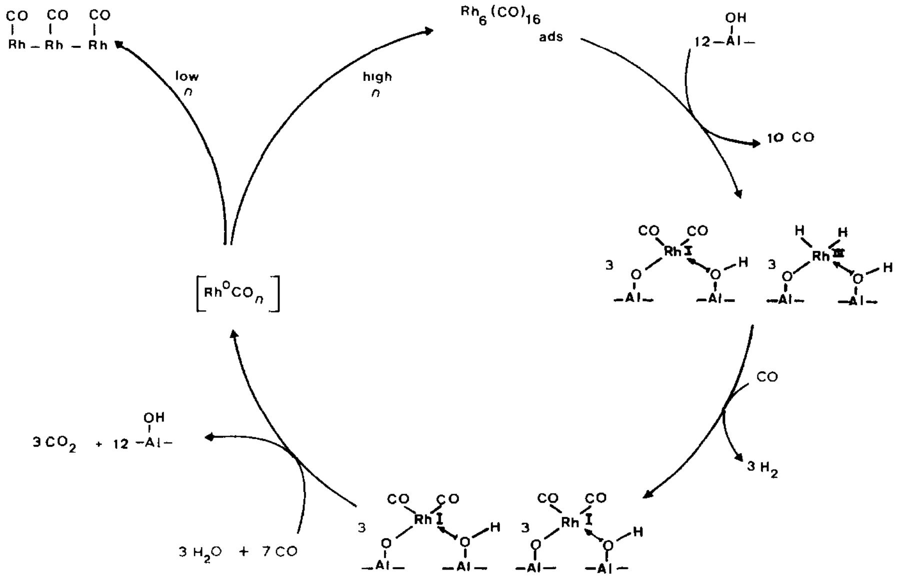


IV. Discussion

The water gas shift reaction is catalyzed by $[Rh(CO)_2Cl]_2$ chemisorbed on alumina, Na–Y zeolite or H–Y zeolite. It is also catalyzed by $Rh_6(CO)_{16}$ chemisorbed on alumina. With $[Rh(CO)_2Cl]_2$ the following order of activity is observed: $Al_2O_3 > Na\text{–}Y \gg H\text{–}Y$.

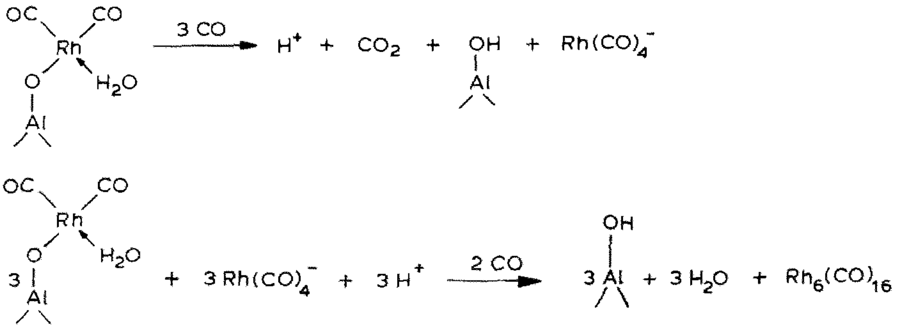
With alumina the reaction is first order in CO ($P(CO) < 1$ atm) and probably first order in water. High turnover numbers can be reached under CO pressure (TN 130 mole H_2/Rh atom/h for a CO pressure of 50 atm). In the presence of liquid water and under CO pressure, the resulting turnover number can be even greater (TN 255 mole H_2/Rh atom/h for a CO pressure of 50 atm). Unfortunately, in this particular case, the lifetime of the catalyst seems to be limited to a few hours. It is interesting to observe, on alumina, that the turnover numbers expressed in mole of H_2 per rhodium atom are very close if $Rh_6(CO)_{16}$ and $[Rh(CO)_2Cl]_2$ are used as the precursor complexes: obviously common intermediates are involved regardless of the nature of the starting complex (Scheme 1).

SCHEME 1



Spectroscopic studies carried out with $Rh_6(CO)_{16}$ and $[Rh(CO)_2Cl]_2$ also support the existence of common intermediates. $Rh_6(CO)_{16}$ reacts with surface protons to give $Rh^{I}(CO)_2(OAl<)(HOAl<)$ and probably $Rh^{III}(H)(H)(OAl<)(HOAl<)$ surface species. The formation of $Rh^{I}(CO)_2(OAl<)(HOAl<)$ from $Rh_6(CO)_{16} + {>}AlOH$ is confirmed by the fact that an identical compound is also obtained from chemisorption of $[Rh(CO)_2Cl]_2$ on alumina, which occurs by the reaction with ${>}AlOH$ groups with evolution of HCl [8]. The formation of a $Rh^{III}(H)(H)(OAl<)HOAl<)$ species cannot be proved spectroscopically but almost quantitative formation of $C_2H_4D_2$ can be observed by the stoichiometric reaction of $Rh_6(CO)_{16}$ with deuterated alumina. Besides, H_2 does not oxidatively add to $Rh^{I}(CO)_2(OAl<)(HOAl<)$ but can coordinate on the decarbonylated form of such species. Reductive elimination of H_2 under CO can then be observed.

$Rh^{I}(CO)_2(OAl<)(HOAl<)$ seems to be able to coordinate molecular water as indicated mainly by infrared spetroscopy. The surface complex probably has the formula $Rh(CO)_2(OAl<)(H_2O)$ [13]. This complex, arising either from $Rh_6(CO)_{16} + {>}AlOH + H_2O$ or from $[Rh(CO)_2Cl]_2 + {>}AlOH + H_2O$, is reduced by CO and water to $Rh_6(CO)_{16}$. This well-known reduction process (it is the procedure used for the synthesis of $Rh_6(CO)_{16}$ from $[Rh(CO)_2Cl]_2$ [14]) occurs at high CO pressure probably by a complicated pathway. It is possible that the formation of the metal–metal bond occurs by the reaction of $Rh(CO)_4^-$ on a $Rh^{I}(CO)_2(OAl<)(H_2O)$ surface species according to:



Nucleophilic attack by water probably occurs intramolecularly from $Rh^{I}(CO)_2(OAl<)(H_2O)$ with formation of the anionic mononuclear complex: $Rh(CO)_4^-$, CO_2, surface proton and ${>}AlOH$ group. This anionic species would be extremely reactive and mobile on the surface and could react with $Rh^{I}(CO)_2$-$(OAl<)(H_2O)$ to give a zerovalent cluster (such as $Rh_2(CO)_8$, $Rh_4(CO)_{12}$ or $Rh_6(CO)_{16}$). The fact that $Rh_6(CO)_{16}$ and $Rh(CO)_2(OAl<)(H_2O)$ are the main species detected during the catalytic reaction does not constitute proof in itself that the two species are involved in the catalytic process (see Scheme 1). However, we have seen that $Rh_6(CO)_{16}$ is oxidized to $Rh(CO)_2(OAl<)(HOAl<)$ (and probably $Rh(H)(H)(OAl<)(HOAl<)$) by surface protons. Besides, $Rh(CO)_2(OAl<)(H_2O)$ can be reduced by $Rh_6(CO)_{16}$ with formation of CO_2. It is therefore logical to assume that both species belong somehow to the overall catalytic process. Nevertheless, one cannot rule out that other zerovalent carbonyls give rise to oxidative addition with ${>}AlOH$ groups ($Rh_4(CO)_{12}$, $Rh_2(CO)_8$ etc.), however, we were not able to detect those species.

We have also observed that in the presence of liquid water and under CO pressure the lifetime of the catalyst is in someway limited. It is possible that the presence of liquid water, which favours the formation of metal particles, will also destroy the catalytic activity due to these metal particles.

Finally, the mechanism which takes place within Na–Y or H–Y zeolite has not been studied in detail. Apparently the transformation of $Rh(CO)_2(OAl^{\prime}\ )(H_2O)$ to $Rh_6(CO)_{16}$ also occurs within the zeolite framework [15] in the presence of CO and H_2O. Besides, $Rh_6(CO)_{16}$ can be oxidized by the protons of the zeolite to give a $Rh^I(CO)_2(OAl^{\prime})$ species. These preliminary results obtained in the laboratory seem to indicate a similar mechanism within the zeolite framework [15].

References

1 C. Ungermann, V. Landis, S.A. Moya, H. Cohen, H. Walker, R.G. Pearson, R.G. Rinker and P.C. Ford, J. Am. Chem. Soc., 101 (1979) 5922; P. Ford, R.G. Rinker, C. Ungermann, R.M. Laine, V. Landis and S.A. Moya, ibid., 100 (1978) 4595; R.M. Laine, R.G. Rinker and P. Ford, ibid., 99 (1977) 252; H.C. Kang, C.H. Mauldin, T. Cole, W. Slegeir, K. Cann and R. Pettit, ibid., 99 (1977) 8323; P.A. Marnot, R.R. Ruppert and J.P. Sauvage, Nouv. J. Chim., 5 (1981) 543; M. Iwamoto, H. Kusano, S. Kagawa, Chem. Lett., (1983) 1483; A.A. Frew, R.H. Hill, L. Manojlovic-Muir, K.W. Muir and R.J. Puddephatt, J. Chem. Soc., Chem. Comm., (1982) 198; J.C. Bricker, C.C. Wagel, S.G. Shore, J. Am. Chem. Soc., 104 (1982) 1444.

2 R.M. Laine, D.W. Thomas, L.W. Cary and S.E. Buttrill, J. Am. Chem. Soc., 100 (1978) 6527; R. Laine, ibid., 100 (1978) 6451; M. Niwa, T. Itzuka and J. Lunsford, J. Chem. Soc. Chem. Comm., (1979) 684; T. Cole, R. Ramage, K. Cann and R. Pettit, J. Am. Chem. Soc., 102 (1980) 6128.

3 There are also a number of mononuclear complexes which catalyse the water gas shift reaction in alkaline or acidic conditions, see e.g. C.H. Cheng, D.E. Hendriksen and R. Eisenberg, J. Am. Chem. Soc., 99 (1977) 2791; C.H. Cheng and R. Eisenberg, ibid., 100 (1978) 5968; T. Yoshida, Y. Ueda and S. Otsuka, ibid., 100 (1978) 3941; A.D. King, R.B. King and D.B. Yang, J. Chem. Soc. Chem. Comm., (1980) 529; E.C. Baker, D.E. Hendriksen and R. Eisenberg, J. Am. Chem. Soc., 102 (1980) 1020.

4 P.C. Ford, Acc. Chem. Res., 143 (1981) 312.

5 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 adsorption of CO_2 on the hydrated support (carbonate).

6 A.K. Smith, F. Hugues, A. Theolier, J.M. Basset, R. Ugo, G.M. Zanderighi, J.L. Bilhou, V. Bougnol and W.F. Graydon, Inorg. Chem., 18 (1979) 3104.

7 Another band of very small intensity at 2115 cm^{-1} was also obtained when CH_2Cl_2 was used as solvent. However, this band was not obtained in THF. With THF, the reaction of $Rh_6(CO)_{16}$ with ,AlOH groups gave exclusively the doublet at 2097, 2028 cm^{-1}. It is therefore suggested that the band of small intensity at 2115 cm^{-1} corresponds to CO coordinated to a Rh^{III} arising from the formation of strong Brönsted acidity: J.M. Basset, M.V. Mathieu and M. Prettre, Rev. Chim. Min., 5 (1968) 879. The $\nu(CO)$ band corresponding to this carbonyl compound was eliminated under vacuum at 50 °C.

8 W.M. Bowser and W.H. Weinberg, J. Am. Chem. Soc., 103 (1981) 1453 and ref. therein.

9 J.M. Basset and A. Choplin, J. Mol. Cat., 21 (1983) 95.

10 Bond angles were calculated from the intensity ratio of the $\nu(CO)$ doublet.

11 When CO_2 is adsorbed on η-alumina, carbonate species are observed by bands at 1222, 1450, 1480 and 1640 cm^{-1}. Those bands are due to species of the type AlO(=O)OH see for example: N.D. Parkyns, J. Chem. Soc. A, (1969) 410.

12 The value obtained is lower than expected because vacuum treatment was carried out before introduction of C_2H_4 into the reactor which removed gaseous H_2.

13 One could also propose the formation of an aquo complex of the type $Rh(CO)_2(OH)(H_2O)$. However, this complex should go into solution. Apparently it is not possible to extract $Rh^I(CO)_2$ from the surface with water which is not in favour of this aquo complex.

14 P. Chini and S. Martinengo, Inorg. Chim. Acta, 3 (1969) 315.

15 F. Lefebvre and Y. Ben Taarit, Nouv. J. Chim., in press.