[Rh(CO)$_2$X]$_2$ (X = Cl, CH$_3$COO) species supported on highly decarbonated magnesium oxide: observation of a strong effect of chloride ion on the surface organometallic chemistry

C. Dossi [a], R. Psaro [b] and R. Ugo [a]

[a] *Dipartimento di Chimica Inorganica e Metallorganica dell'Universita' and* [b] *Centro C.N.R., Via Venezian, 21 20133 Milano (Italy)*

(Received May 11th, 1988)

Abstract

When [Rh(CO)$_2$(CH$_3$COO)]$_2$ or [Rh(CO)$_2$Cl]$_2$ are chemisorbed on to the surface of a decarbonated magnesium oxide their surface organometallic chemistry depends on the nature of the anionic moiety. The presence of surface chloride ions probably modify the basic character of some sites of chemisorption through formation of acidic Mg-Cl species. As on other acidic or amphoteric oxides, selective carbonylation of the surface Rh^I(CO)$_2$ species to give physisorbed Rh$_6$(CO)$_{16}$ takes place even at room temperature on the surface of chlorine-doped magnesium oxide. The same behaviour is observed when hydrated RhCl$_3$ is used. In the absence of surface chloride ions, the previously reported surface reaction to give surface carbonyl cluster anions is observed.

Introduction

Much attention is currently being given to the characterization of rhodium-supported catalysts because of their potential industrial applications, mainly in the field of carbon monoxide reduction. The catalysts are usually supported rhodium carbonyl complexes; in particular, much work has been carried out with acidic or amphoteric oxides as supports, such as silica [1], zeolites [2] or alumina [3].

With alumina as support, some recent EXAFS studies have shown that carbon monoxide can disrupt even the supported rhodium crystallites obtained by reduction with hydrogen, ultimately leading to isolated rhodium dicarbonyl species [4]. Furthermore, under carbon monoxide, a mixture of metallic rhodium and Rh^I dicarbonyl species encapsulated in the support is always obtained, the Rh^0/Rh^I ratio being related both to the metal loading and to the nature of the support [5].

We have described the ready surface reactions of these Rh^I(CO)$_2$ species to generate polynuclear rhodium clusters "in-situ". With acidic or amphoteric oxides,

the synthesis of physisorbed $Rh_6(CO)_{16}$ occurs under an atmosphere of carbon monoxide and in the presence of traces of water [1,3]. However, on the surface of highly decarbonated magnesium oxides, high nuclearity carbonyl anions are formed, in keeping with the basic properties of the support [6].

The use of basic supports with rhodium catalysts is of special interest, because they enhance the activity and selectivity (towards oxygenates) under Fischer-Tropsch or hydroformylation conditions [7]. Preformed molecular Rh^I carbonyls have also been used as catalyst precursors [7].

In the work described below we studied the surface organometallic chemistry of molecular $[Rh(CO)_2X]_2$ [X = Cl, CH_3COO] or $RhCl_3$ species supported on various kinds of magnesium oxide, particularly on a highly decarbonated one. The anionic ligand of the molecular precursor seems to play a significant role through a selective doping of the active sites of the support [8], with production of new surface sites associated with new types of organometallic species. Particular attention has therefore been devoted to the relation between the surface organometallic chemistry and the nature of the anionic ligand.

Experimental

$[Rh(CO)_2Cl]_2$ and $[Rh(CO)_2(CH_3COO)]_2$ were prepared by published methods [9,10]. Hydrated $RhCl_3$ was purchased from Aldrich and used as received.

Infrared spectra were recorded in the FT mode on a Nicolet MX-1E spectrophotometer. The procedure used for recording infrared spectra under a controlled atmosphere has been described [3].

The untreated magnesium oxide (MgO_{air}) was obtained by evacuation ($p < 10^{-5}$ torr) of the commercial oxide (MgO Merck RP) overnight at room temperature. Further thermal treatments were by Zecchina's method [11]; the support was treated at $250°C$ for 8 h at 10^{-5} torr, then in oxygen at $500°C$ for 16 h, and finally evacuated at $500°C$ for 8 h at 10^{-5} torr, to give a highly dehydrated, carbon-dioxide-free magnesium oxide (MgO^{500}) (B.E.T. specific surface area 250 m^2 g^{-1}).

The samples were studied as compressed wafers (18 mm diameter) in a Pyrex cell with CaF_2 windows which was attached to a vacuum and gas line.

The magnesia wafers were impregnated under argon introducing a saturated solution of the rhodium carbonyl compound through a break-seal. Solutions of $[Rh(CO)_2Cl]_2$ and $[Rh(CO)_2(CH_3COO)]_2$ were in CH_2Cl_2, and those of hydrated $RhCl_3$ in CH_3OH.

Chemical extraction of the supported species was performed on larger samples (1 to 5 g of MgO) which had been pretreated and impregnated under argon with a CH_3OH solution of hydrated $RhCl_3$.

Results and discussion

[Rh(CO)₂(CH₃COO)]₂ supported on thermally treated magnesium oxide

$[Rh(CO)_2(CH_3COO)]_2$ was used as the chlorine-free Rh^I carbonyl because the acetate anion should not substantially affect the basic properties of the surface of a carbon dioxide-free magnesium oxide such as MgO^{500}. After impregnation of the support under argon with a dichloromethane solution of $[Rh(CO)_2(CH_3COO)]_2$, a fast chemisorption process takes place, as evidenced by the formation of new
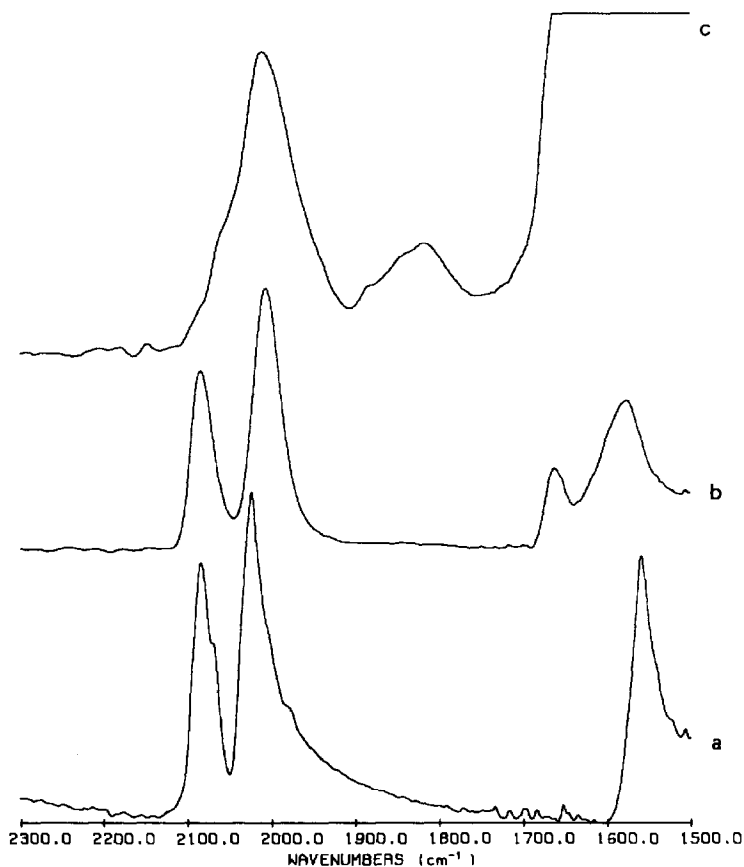
Fig. 1. Infrared spectra in the ν(CO) region (cm^{-1}): (a) [Rh(CO)$_2$(CH$_3$COO)]$_2$ in KBr, (b) [Rh(CO)$_2$(CH$_3$COO)]$_2$ supported on MgO^{500}, (c) as (b), after 10 d under CO (300 torr) at 25°C.

carbonyl bands at 2083 and 2004 cm^{-1} (Fig. 1b). We previously observed such a simple two-band spectrum, which is quite different from that of the original molecular complex dispersed in a KBr matrix (Fig. 1a), following oxygen oxidation of the high nuclearity surface rhodium carbonyl anions obtained after chemisorption of Rh$_6$(CO)$_{16}$ on MgO^{500} and MgO^{25} (Table 1) [6].

By comparison of this infrared spectrum with those of some anionic Rh^I carbonyls, such as [Rh(CO)$_2$Cl$_2$]$^-$ (Table 2), we suggest a two-point attachment of the Rh^I moiety to the surface of the support:
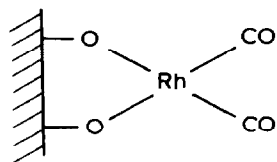
The strong basic O^{2-} sites of the surface of magnesium oxide should donate some electronic density to the rhodium atoms, the net effect being a red-shift of the IR stretching frequencies of the two carbonyl bands (Table 1). In confirmation, a simple calculation by Cotton and Kraihanzel's method [12], of the force constant of the C=O bond indicates that there has been a weakening of the carbon–oxygen

Table 1

Infrared stretching frequencies and force constants of the C–O bonds in some supported *gem*-Rh$^{(I)}$(CO)$_2$ species

Compound	ν(CO) band (cm^{-1}) [a]		K [b]	K_I [c]	Reference
	A$_1$	B$_1$	(N/m)		
Rh(CO)$_2$(OMg–)/MgO^{500}					
from [Rh(CO)$_2$(AcO)]$_2$	2083	2004	1683	65.2	This work
from Rh$_6$(CO)$_{16}$	2086	2009	1693	63.7	[6]
from [Rh(CO)$_2$Cl]$_2$	2097	2020	1712	64.0	This work
from RhCl$_3$ [d]	2090	2018	1705	59.7	This work
Rh(CO)$_2$(OSi$\lessgtr$)	2093	2038	1723	45.9	[1]
Rh(CO)$_2$(OAl$\langle$)	2096	2020	1711	63.2	[3]
Rh(CO)$_2$(O$_2$T) [e]	2101	2022	1717	65.8	[2]
Rh(CO)$_2$(OH)(OT) [e]	2116	2048	1751	57.2	[2]
(T = Si or Al atoms of Y zeolite)					

[a] All spectra were recorded with pressed wafers. [b] Force constant. [c] Interaction constant of the CO groups. [d] After carbonylation at room temperature of RhCl$_3$/MgO$_{air}$. [e] After carbonylation at 100 °C of Rh^{III}-exchanged NaY zeolite.

bond compared to that in the same Rh^I dicarbonyl species supported on acidic or even amphoteric oxides (Table 1).

We could not obtain physisorbed Rh$_6$(CO)$_{16}$ by reaction under carbon monoxide at room temperature, contrary to what happens with Rh$^{(I)}$ surface species supported on acidic or amphoteric oxides (silica [1], alumina [3] and zeolite [2]). Instead we observed the formation of a new carbonyl species containing both bridged and terminal CO groups (Fig. 1c). Its infrared spectrum is very similar to that of the high nuclearity rhodium carbonyl anion (which we called species A [6]) generated by carbon monoxide reduction of the Rh^I(CO)$_2$ species obtained by oxidation of various rhodium clusters supported on several kinds of magnesium oxide.

However, in the present work a much lower rate of reaction was observed, more than 10 days being needed for complete reduction of the supported Rh^I dicarbonyl species. It is likely that when starting from chemisorbed mononuclear or dinuclear precursors, the surface rhodium dicarbonyl species are statistically dispersed over the surface of the support; an extensive and slow migration of the rhodium ions is therefore needed in order to make some aggregation possible and allow formation of a new polynuclear molecular species.

Table 2

Infrared stretching frequencies of some molecular Rh$^{(I)}$ carbonyls

Compound	ν(CO) (cm^{-1})	Reference
[Rh(CO)$_2$Cl]$_2$ [a]	2106m, 2091s, 2035vs	[9]
[Rh(CO)$_2$(CH$_3$COO)]$_2$ [b]	2096s, 2073m, 2024vs	[10]
	1574ms, 1438ms (ν(CO$_2$))	
[Rh(CO)$_2$Cl$_2$]$^-$ [a]	2067s, 1990s	[10]
[Rh(CO)$_2$](SO$_4$) [a]	2093vs, 2035s, 2014m	[10]
Rh(CO$_2$)(C$_5$H$_7$O$_2$) [b]	2083s, 2066w, 2015s, 1987w	[22]

[a] Dichloromethane. [b] Pentane.

Obviously, such a topological effect is not so relevant when the starting material is the rhodium dicarbonyl species produced by decomposition or oxidation of supported rhodium clusters [6], in which the rhodium atoms in the surface structure are already in close proximity.

[Rh(CO)₂Cl]₂ supported on different kinds of magnesium oxide

In order to investigate effects due to the presence of some chloride ions on the surface of magnesium oxide, a chlorine-containing species such as $[Rh(CO)_2Cl]_2$ was used as precursor. Impregnation of the support (MgO^{500}) was carried out under argon with a CH_2Cl_2 solution of the complex. The infrared spectrum of the impregnated material, showing two broad bands at 2097 and 2020 cm^{-1} (Fig. 2b), is different from that of the complex $[Rh(CO)_2Cl]_2$ (Fig. 2a). Chemisorption via the basic sites of the support has therefore occurred; new *gem*-dicarbonyl Rh^I species, covalently bonded to the surface via Mg–O–Rh bonds, are probably generated via the surface reaction:

$$[Rh(CO)_2Cl]_2 + MgO \rightarrow 2/n[Rh(CO)_2(OMg-)]_n + 2\ MgCl- \qquad (1)$$
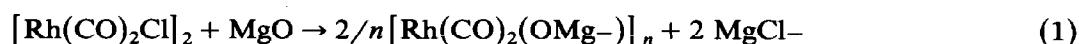
The $\nu(CO)$ frequencies are significantly higher than those observed when $[Rh(CO)_2(CH_3COO)]_2$ is supported and are close to those obtained when the same
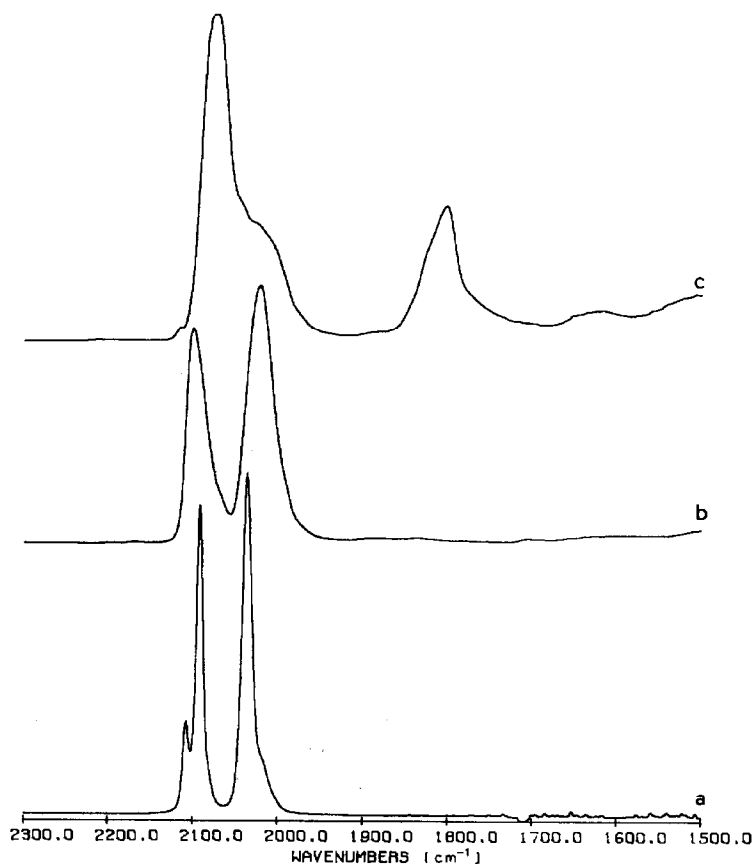

Fig. 2. Infrared spectra in the $\nu(CO)$ region (cm^{-1}): (a) $[Rh(CO)_2Cl]_2$ in CH_2Cl_2, (b) $[Rh(CO)_2Cl]_2$ supported on MgO^{500}, (c) same sample after recarbonylation at 25°C for 7 d.
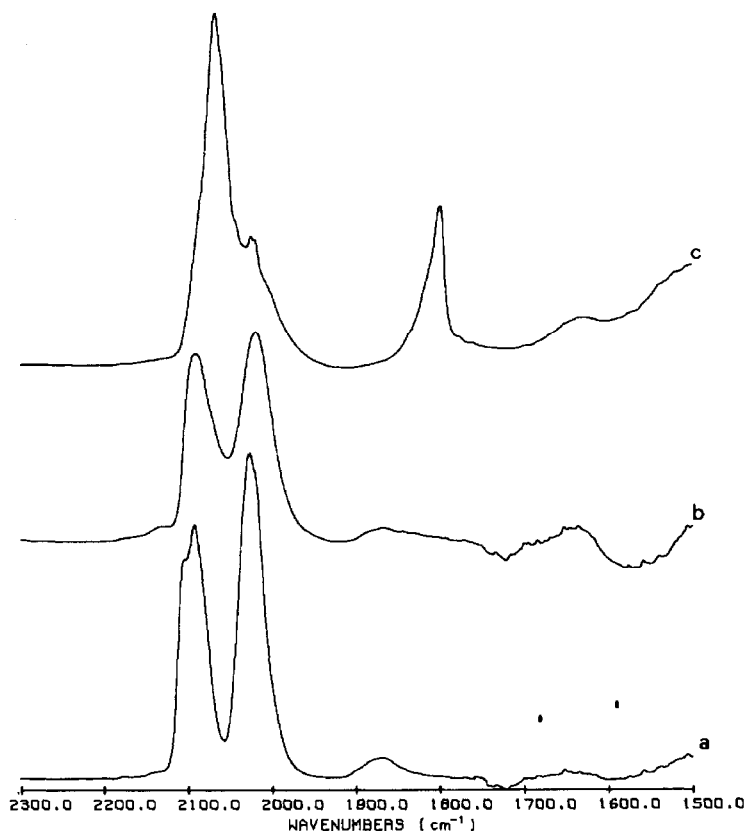
Fig. 3. Infrared spectra in the ν(CO) region (cm^{-1}): (a) [Rh(CO)$_2$Cl]$_2$ after impregnation on MgO$_{air}$, (b) same sample treated in vacuo at 100°C for 7 h, (c) same sample, after recarbonylation at 25°C for 7 d.

Rh^I surface dicarbonyl species are encapsulated in acidic or even amphoteric supports, such as silica, alumina, or zeolites (Table 1).

This behaviour is probably related to the formation on the surface of MgO^{500} (see reaction (1)) of strongly acidic MgCl sites, located not too far from the rhodium dicarbonyl species. These sites can considerably modify the electronic and the physico-chemical properties of specific areas of the surface of magnesium oxide. Magnesium oxide is, in fact, known to react even with molecular chlorine with formation of surface chloride ions by displacement of a surface oxygen [13].

We could not detect any infrared bands below 1700 cm^{-1} although a further reaction of carbon monoxide (to generate surface carbonates, formates etc.) is a feature of thermally-treated magnesium oxide [14].

When [Rh(CO)$_2$Cl]$_2$ is supported on an untreated magnesium oxide (MgO$_{air}$), simple physisorption occurs (Fig. 3a), probably because the presence of large amounts of surface water and carbonates substantially inhibits the basic activity of the surface of the support [15]. Upon treatment in vacuo at temperatures above 100°C, some water and carbon dioxide are desorbed, with formation of basic surface sites. Under such conditions, the infrared spectrum changes and two new bands at 2090 and 2019 cm^{-1} appear, in agreement with the chemisorption of [Rh(CO)$_2$Cl]$_2$ (Fig. 3b).

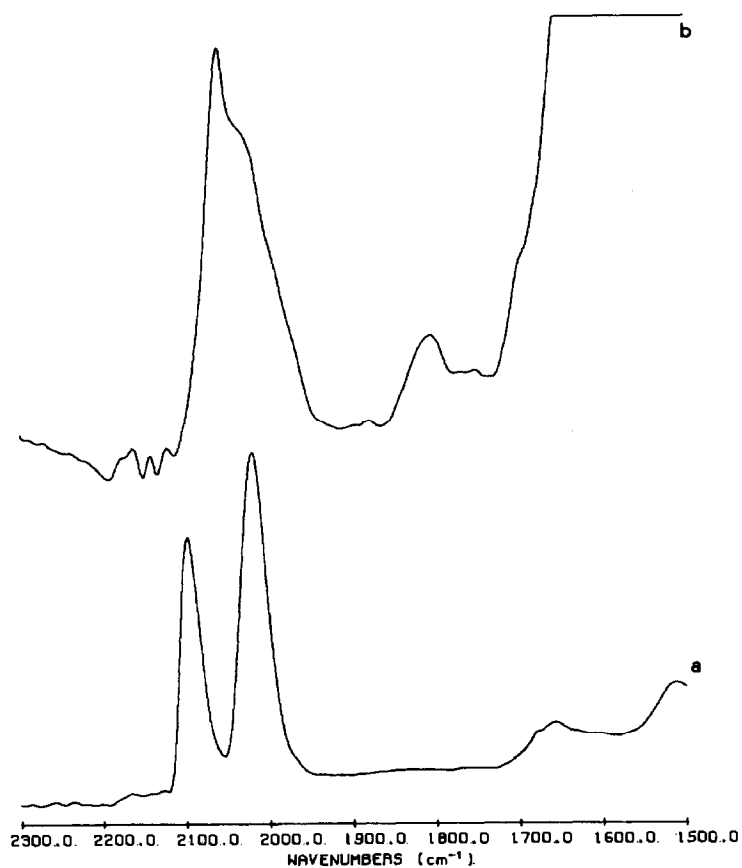Fig. 4. Infrared spectra in the ν(CO) region (cm^{-1}): (a) MgO^{500} impregnated with a low loading (<1%) of [Rh(CO)$_2$Cl]$_2$, (b) same sample, after recarbonylation under CO (300 torr) at 25°C for 25 d.

In both cases, the presence of Rh^I species, bonded close to the acidic MgCl surface sites is supported by a surface reactivity similar to that shown by the silica- or zeolite-supported Rh^I dicarbonyl species. In fact, under carbon monoxide, even at room temperature physisorbed Rh$_6$(CO)$_{16}$ (Fig. 2c and Fig. 3c) is formed in a nucleation reaction which is highly selective towards the formation of the hexanuclear cluster, since the intermediate formation of Rh$_4$(CO)$_{12}$ [16], tricarbonyl Rh$^{(I)}$(CO)$_3$ [17], or other species is not observed. The supported Rh$_6$(CO)$_{16}$ so formed can be readily extracted from the surface with dichloromethane.

The surface nucleation reaction to generate a Rh$_6$ frame seems to be strongly dependent on the degree of loading of the surface with [Rh(CO)$_2$Cl]$_2$. Normally, the impregnation is carried out on one side only of the compressed wafer, so that high local surface concentrations of [Rh(CO)$_2$Cl]$_2$ are reached on the support, since the carbonyl rhodium compound immediately reacts with the surface of MgO^{500} and consequently cannot diffuse inside the wafer. In order to investigate the effect of metal loading, we repeated the impregnation, working at lower metal loadings, certainly < 1% (Fig. 4a). The same surface Rh^I carbonyl species are formed at low or high metal loadings. However, the reaction with CO, under similar conditions is much slower with low metal loadings; even after 25 d the conversion to Rh$_6$(CO)$_{16}$ is incomplete (Fig. 4b).

This effect may be associated both with the low surface concentration of the chloride ions and the higher dispersion of the Rh^I dicarbonyl species on the surface, which makes the nucleation process more difficult and the effect of the chlorine doping of the surface less specific.

$RhCl_3$ supported on untreated magnesium oxide

In order to confirm the doping effect of surface chlorides we started with a Rh^{III} salt, namely $RhCl_3$. This compound has been widely employed in catalysis as precursor for the preparation of supported rhodium metal catalysts. Much work has also been carried out on the chemistry of the hydrated $RhCl_3$ supported on silica, zeolites, and other oxides, with the purpose of bringing about an in-situ synthesis of molecular clusters under catalytic conditions [1,2]. We therefore investigated the stepwise reduction of supported $RhCl_3$ to Rh^0 clusters. This work was carried out on an untreated magnesium oxide only, because hydrated rhodium trichloride is readily soluble in protic solvents, such as water and alcohols, which would react with the surface of a thermally treated magnesium oxide [18]. After impregnation, the support takes an uniform and pink-red colour and shows no infrared bands in the carbonyl region, as expected (Fig. 5a).
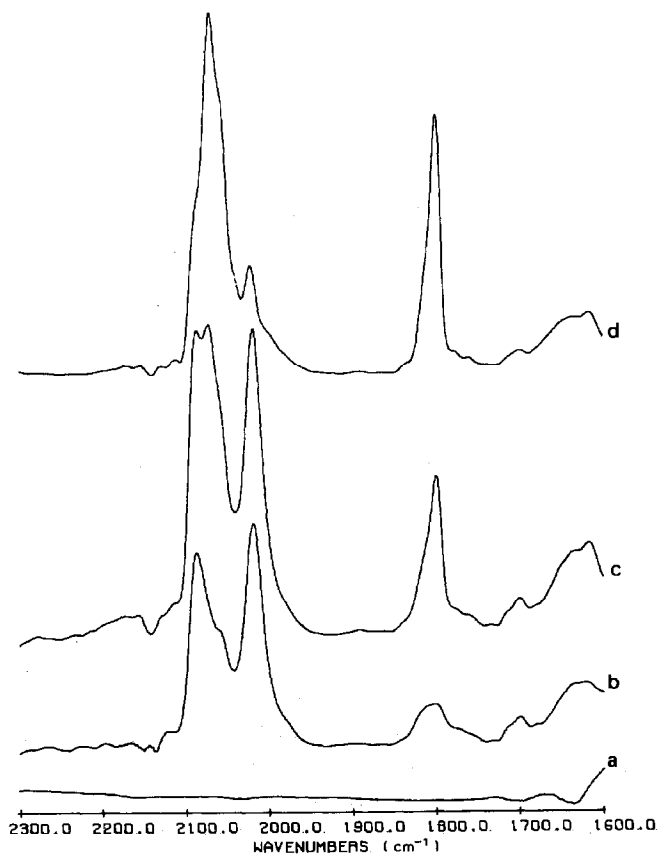

Fig. 5. Infrared spectra in the ν(CO) region (cm^{-1}): (a) Hydrated $RhCl_3$ after impregnation on MgO_{air}, (b) same sample, after recarbonylation under CO (300 torr) at 25°C for 24 h, (c) as (b), after further 2 d under CO at 25°C, (d) as (c), after further CO treatment in the same conditions.

It is known that hydrated rhodium trichloride interacts with both acidic or amphoteric oxides, such as silica, alumina, or silica-alumina [19] by the following surface reaction:

$$\underset{\text{H}}{\underset{|}{\text{RhCl}_3 \cdot 3\text{H}_2\text{O} + \text{MOH}}} \rightarrow \text{MORhCl}_3 \cdot (3-n)\text{H}_2\text{O} + n\text{H}_2\text{O}$$

(M = Si, Al)

With an untreated magnesium oxide, whose surface is completely covered by surface water and carbonates, a ligand substitution reaction with the surface carbonate ions or even the residual basic OH groups is likely.

The reaction with carbon monoxide at room temperature was monitored by infrared spectroscopy. After 24 h the reduction of Rh^{III} to Rh^I was evidenced by the appearance of two bands, at 2090 and 2018 cm^{-1}, which fall in the range previously observed for the surface $\text{Rh}^I(\text{CO})_2$ species bonded to chlorine-doped OMg sites (Fig. 5b). After a further 24 h the colour of the impregnated wafer changed to pink-violet, and new bands appeared at 2070 and 1798 cm^{-1}, in keeping with the formation of physisorbed $\text{Rh}_6(\text{CO})_{16}$ (Fig. 5c). In order to confirm the presence of these surface organometallic species, we carried out some chemical extractions with larger samples (1 to 5 g of supported MgO). When the material was extracted with dichloromethane, $\text{Rh}_6(\text{CO})_{16}$ was recovered from the solvent as the sole product. The solid residue left after extraction was treated with dilute HCl. Extraction of the aqueous phase with a CH_2Cl_2 solution of PPN^+Cl^- gave a light yellow compound which was identified as $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-\ \text{PPN}^+$ by infrared spectroscopy and TLC.

The formation of $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ is consistent with the occurrence of the following surface reaction:
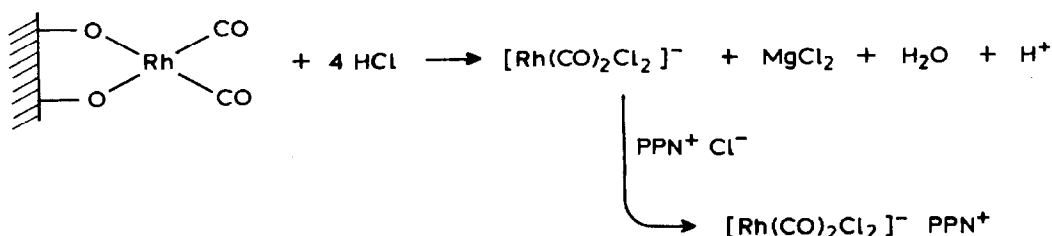
This experiment can be also considered as further direct evidence for the oxidized state of the rhodium atoms in the rhodium dicarbonyl species supported on magnesia. The selective formation on the surface of the hexanuclear cluster then occurs during a long period (Fig. 5d). The formation of $\text{Rh}_6(\text{CO})_{16}$ on the surface of MgO thus takes place in a two-step process:

1) $\text{RhCl}_3 \cdot 3\text{H}_2\text{O} + 3\,\text{CO} + \text{MgO} \rightarrow \left[\text{Rh}(\text{CO})_2{<}\right]^+\text{Cl}^- + \text{MgCl}_2 + \text{CO}_2$

2) $6\left[\text{Rh}(\text{CO})_2{<}\right]^+\text{Cl}^- + 7\,\text{CO} + 3\,\text{MgO} \rightarrow \text{Rh}_6(\text{CO})_{16} + 3\,\text{MgCl}_2 + 3\,\text{CO}_2$

where $[\text{Rh}(\text{CO})_2{<}]^+\text{Cl}^-$ indicates Rh^I species bound to the chlorine-doped surface sites of magnesium oxide

These surface reactions are similar to those involved in the homogeneous synthesis of $\text{Rh}_6(\text{CO})_{16}$ from RhCl_3 in basic media [20]; they indicate that similar

"organometallic reactions" occur on the surface of an inorganic support under actual heterogeneous conditions.

Conclusions

A new and different surface organometallic chemistry has been observed when chloride ions are present on the surface of magnesium oxide. The formation of some surface MgCl sites, which are strongly acidic, accounts well for the generation of a controlled Lewis acidity on the surface. This "chloride effect" causes strong local modifications of the basic properties of the support, which thus behaves locally like an anphoteric oxide such as γ-alumina. In confirmation, the selective carbonylation of supported $Rh^{(I)}$ dicarbonyl species to $Rh_6(CO)_{16}$ has observed, as on γ-alumina [3]. From the catalytic point of view, this coexistence of both acidic and basic sites could therefore open new and promising possibilities for the use of such a "doped" magnesium oxide, particularly when activation of bi- or poly-functional molecules (carbon monoxide, unsaturated ketones, etc.) is required. It is noteworthy that similar MgCl surface species have been observed to play an important role in specific catalysis, particularly as active sites in the third generation Ziegler-Natta catalysts [21].

References

1 J.L. Bilhou, V. Bilhou-Bougnol, W.F. Graydon, J.M. Basset, A.K. Smith, G.M. Zanderighi and R. Ugo, J. Organomet. Chem., 153 (1978) 73.
2 P. Gelin, Y. Ben Taarit and C. Naccache, J. Catal., 59 (1979) 357; E.J. Rode, M.E. Davis and B.E. Hanson, ibid., 96 (1985) 574; E. Mantovani, N. Palladino and A. Zanobi, J. Mol. Catal., 3 (1977/78) 285.
3 A.K. Smith, F. Hugues, A. Theolier, J.M. Basset, R. Ugo, G.M. Zanderighi, J.L. Bilhou, V. Bilhou-Bougnol and W.F. Graydon, Inorg. Chem., 11 (1979) 3104.
4 H.F.J. van't Blik, J.B.A.D. van Zon, T. Huizinga, J.C. Vis, D.C. Koningsberger and R. Prins, J. Am. Chem. Soc., 107 (1985) 3139.
5 S.D. Worley, C.A. Rice, G.A. Mattson, C.W. Curtis, J.A. Guin and A.R. Tarrer, J. Phys. Chem., (1982) 2714.
6 C. Dossi, R. Psaro and R. Ugo, J. Organomet. Chem., 353 (1988) 259.
7 M. Ichikawa, Bull. Chem. Soc. Jpn., 51 (1978) 2268; M. Ichikawa, ibid., 51 (1978) 2273.
8 B.J. Kip, F.W.A. Dirne, J. van Grondelle and R. Prins, Appl. Catal., 25 (1986) 43.
9 J.A. McCleverty and G. Wilkinson, Inorg. Synth., 8 (1966) 211.
10 D.N. Lawson and G. Wilkinson, J. Chem. Soc, (1965) 1900; M.J. Cleare and W.P. Griffith, J. Chem. Soc. (A), (1970) 2788.
11 E. Guglielminotti, S. Coluccia, E. Garrone, L. Cerruti and A. Zecchina, J. Chem. Soc. Faraday Trans. I, 75 (1979) 96.
12 F.A. Cotton and C.S. Kraihanzel, J. Amer. Chem. Soc., 84 (1962) 44.
13 A.J. Tench and J.F.J. Kibblewhite, Chem. Phys. Lett., 14 (1972) 220; J.F.J. Kibblewhite and A.J. Tench, J. Chem. Soc., Faraday Trans. I, (1973) 72.
14 E. Guglielminotti and A. Zecchina, J. Chim. Phys., 78 (1981) 891.
15 R. Psaro, C. Dossi and R. Ugo, J. Mol. Catal., 21 (1983) 331.
16 A. Theolier, A.K. Smith, M. Leconte, J.M. Basset, G.M. Zanderighi, R. Psaro and R. Ugo, J. Organomet. Chem., 191 (1980) 415.
17 M.P. Keyes and K.L. Watters, J. Catal., 100 (1986) 477.
18 J. Kondo, Y. Sakata, K. Maroya, K. Tamaru and T. Onishi, Appl. Surf. Sci., 28 (1987) 475; R.I. Razouk and R.Sh. Mikhail, J. Am. Chem. Soc., 62 (1958) 920.
19 A. Krzywicki and M. Marczewski, J. Mol. Catal., 6 (1979) 431.
20 P. Chini and S. Martinengo, Inorg. Chim. Acta, 3 (1969) 315.
21 S.I. Maktarulin, E.M. Moroz, E.E. Vermel and V.A. Zakharov, React. Kinet, Catal. Lett., 3 (1978) 269; K. Soga and M. Terano, Makromol. Chem., 182 (1981) 2439.
22 F. Bonati and G. Wilkinson, J. Chem. Soc., (1963) 3156.