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Surface-supported metal carbonyl clusters: an IR investigation of the behaviour of $Rh_6(CO)_{16}$ supported on highly decarbonated magnesium oxide

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Abstract

This paper investigates, by means of infrared spectroscopy, the organometallic chemistry of $Rh_6(CO)_{16}$ adsorbed on magnesium oxide treated in various ways. When the magnesia surface has a high content of carbonates, simple physisorption is slowly followed by complete and irreversible decarbonylation without formation of metallic rhodium. When the magnesia surface is highly decarbonated but highly hydrated, the anion $[Rh_6(CO)_{15}(COOMg-)]^-$ is initially generated, and this followed by slow formation of an unknown carbonyl anion of high nuclearity, which gives a reproducible and specific infrared spectrum. When the magnesia is highly decarbonated but also fairly anhydrous, the anions $[Rh_6(CO)_{15}]^{2-}$ or $[Rh_7(CO)_{17}]^{3-}$ are initially quickly formed. They are transformed by a very fast process into the same carbonyl anion of high nuclearity. The presence of traces of oxygen causes a fast oxidation to $Rh^I(CO)_2$ surface species, which, however, are readily recarbonylated to the original carbonyl anion.

This surface organometallic chemistry can form the basis of a reexamination of the reason why the catalytic behaviour of $Rh_6(CO)_{16}$ supported on magnesium oxide is different from that when the support is a more acidic oxide.

Introduction

The chemistry of metal carbonyl clusters supported on inorganic oxides [1] offers several possibilities for innovative research, because (a) a new type of interaction takes place between the cluster and the surface sites of the support to give surface species which can often be well-characterized; (b) the carbonyl ligands are more or less easily removed from the metallic frame, so that they do not interfere, by doping or promotion effects, on the activity of the resulting supported metallic catalyst; and (c) the size of the supported metal particles may be related to and sometimes controlled by the nuclearity of the original cluster precursor.

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Often there are strong chemical interactions between the cluster and the support when basic or amphoteric oxides (such as MgO, La_2O_3, Al_2O_3) are used [1]; at the same time the catalytic activity and selectivity of the final supported catalyst is strongly influenced by the nature and treatment of the support. Because of this strong "support effect", some rhodium metal catalysts, typically supported on basic oxides such as lanthanum or magnesium oxides, exhibit unusual activities and selectivities, e.g. for alcohol formation under Fischer–Tropsch conditions [2].

Although the above catalytic results are relevant, only very little work has been done on the surface chemistry of rhodium clusters (mainly $Rh_6(CO)_{16}$) supported on highly basic oxides. In particular it has been briefly reported that on magnesium oxide fast chemisorption occurs, but while some authors have described a surface chemistry, leading to "metal-like" structures [3] others have reported formation of oxidized Rh^I species [4]. Both investigations were of a preliminary nature, and it is possible that the different results were due to the different thermal treatment of the magnesium oxide, which greatly influences the physico-chemical properties of the support (surface area, number and type of the surface sites, presence of carbonates on the surface, etc.), and therefore its surface reactivity [5].

We have previously described the large effect of thermal treatments of the support on the surface reaction of a metal cluster such as $Os_3(CO)_{12}$ with the surface of magnesium oxide [6].

The aim of the present work was to investigate in detail how the thermal pretreatment of the magnesium oxide would affect the surface reactivity of $Rh_6(CO)_{16}$, in order to arrive at a better knowledge of its surface organometallic chemistry and to prepare well defined catalysts for selective reactions such as heterogeneous hydroformylation of olefins or synthesis of ethanol from syngas.

Experimental

Infrared spectra were recorded on a Nicolet MX-1E FT spectrophotometer. The techniques used for recording infrared spectra under a controlled atmosphere has been described previously [4]. The samples were studied as compressed wafers (18 mm diameter) in a Pyrex cell with CaF_2 windows, the cell being attached to a vacuum and gas line.

The untreated magnesium oxide (MgO_{air}) was obtained by evacuation ($p < 10^{-6}$ torr) of the support (MgO Merck RP) overnight at room temperature. Further thermal treatments were performed by Zecchina's method [5]; the support was heated at 250 °C in vacuo, then in oxygen at 500 °C, and finally evacuated under high vacuum at 500 °C, to give a highly dehydrated, CO_2-free, oxide (MgO^{500}), some of which was rehydrated with water vapour at room temperature to give a support designated as MgO^{25}.

The magnesia wafers were impregnated under argon by adding a saturated solution of $Rh_6(CO)_{16}$ [7] in CH_2Cl_2 dropwise through a break seal.

Results and discussion

$Rh_6(CO)_{16}$ supported on untreated magnesium oxide

$Rh_6(CO)_{16}$ is simply physisorbed on the surface of untreated magnesium oxide MgO_{air}; the infrared spectrum of the sample is identical to that of the hexanuclear cluster dispersed in a KBr matrix (Fig. 1a, b).

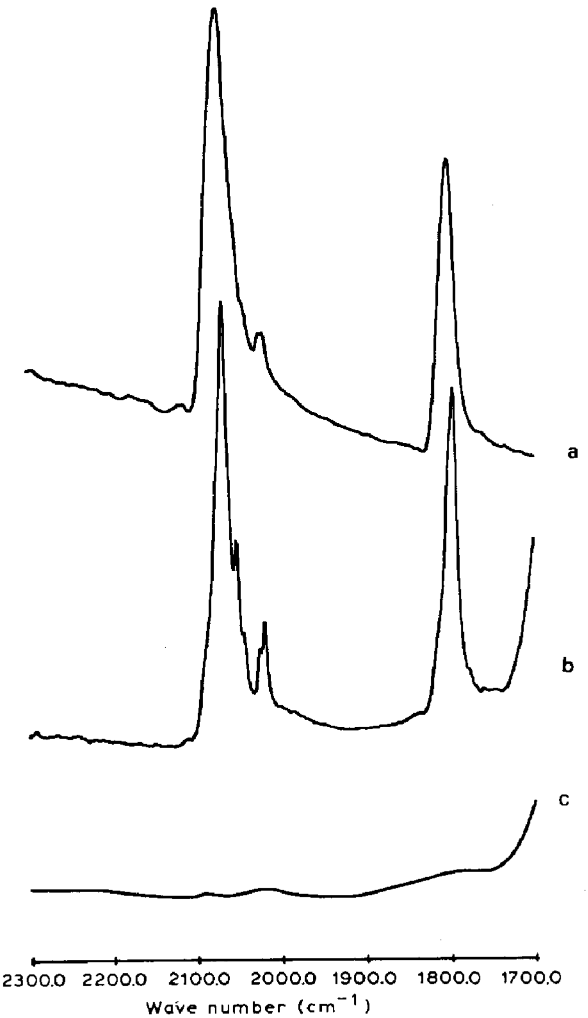

Fig. 1. Infrared spectra in the ν(CO) region (cm^{-1}): (a) $Rh_6(CO)_{16}$ in KBr; (b) $Rh_6(CO)_{16}$ supported onto a MgO_{air}; (c) as (b), after 1 h in vacuo at 80 °C and further 24 h under CO at 25 °C.

However, the supported cluster is stable only at room temperature, either in vacuo or under an inert atmosphere. When it is exposed to air or heated in vacuo or in an inert atmosphere at temperatures above 60 °C complete decarbonylation occurs (Fig. 1c), but, contrary to a previous report [4], no oxidized surface species $Rh^I(CO)_2$ are formed. Moreover, when the decarbonylated sample was exposed again to carbon monoxide, no metal carbonyl infrared bands were observable, suggesting that very stable, probably mixed oxide species, are probably formed. It is known that on magnesium oxide, a complete reduction to rhodium metal is quite difficult even under hydrogen [8]. This behaviour is related to the ready formation of mixed oxides, of general formula $Mg_xRh_yO_z$ [9], incorporated within the structure of the support, which are highly stable to reduction.

$Rh_6(CO)_{16}$ supported on thermally treated magnesium oxide

As previously mentioned, we carried out studies on thermally treated magnesium oxide samples such as MgO^{25} and MgO^{500} (see Experimental), in order to investi-

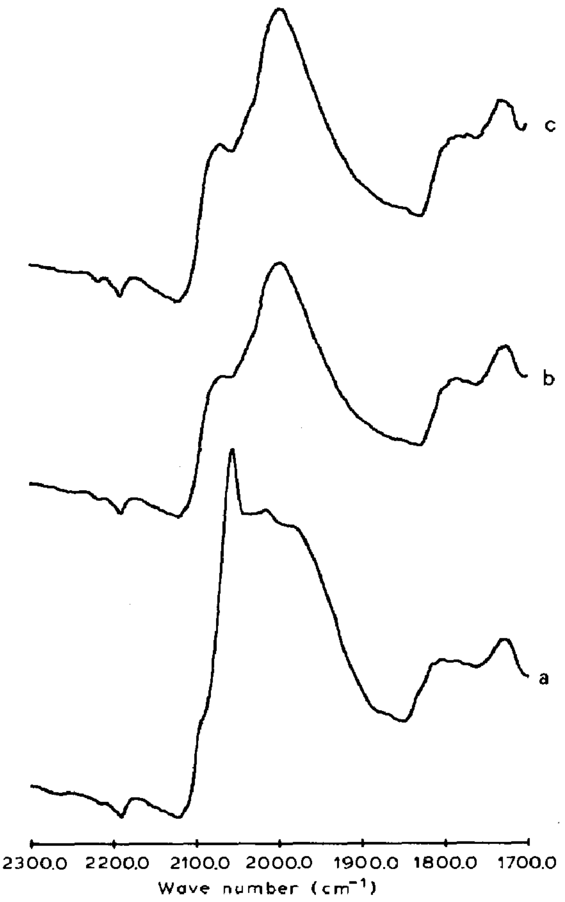

Fig. 2. Infrared spectra in the ν(CO) region (cm^{-1}): (a) $Rh_6(CO)_{16}$ after impregnation onto MgO^{25}; (b) same sample after treatment in vacuo at 25 ° C for 12 h; (c) same sample after further 24 h in vacuo at 25 ° C.

gate how Brönsted (MgO^{25}) or Lewis (MgO^{500}) basic sites might affect the surface chemistry of $Rh_6(CO)_{16}$.

In contrast to MgO_{air}, $Rh_6(CO)_{16}$ reacts quickly with the surface of MgO^{25}. An infrared spectrum with bands at 2078, 2055, 2016, 1981, 1802 and 1646 cm^{-1} can be recorded immediately after the impregnation (see Fig. 2a). In the light of the known organometallic chemistry of $Rh_6(CO)_{16}$ under basic conditions [10], nucleophilic attack of a Brönsted basic surface OH group can be suggested:

$$Rh_6(CO)_{16} + 2Mg\text{-}OH \rightarrow [Rh_6(CO)_{15}(COOMg\text{-})]^- Mg^+ + H_2O$$

This proposal is supported by the close similarity of the infrared spectrum (Fig. 2a) to that of the related molecular $[Rh_6(CO)_{15}X]^-$ species, where X is COOR (Table 1). This surface anion is not very stable even in vacuo; a final and reproducible species, characterized by a well-defined infrared spectrum is obtained at room temperature after 36 h (Fig. 2b, c).

A higher surface reactivity is observed with MgO^{500}. In the impregnation under argon a green colour immediately develops, suggesting the fast formation of anionic carbonyl clusters, probably $[Rh_6(CO)_{15}]^{2-}$ or $[Rh_7(CO)_{17}]^{3-}$, which are known to

Table 1

Stretching frequencies in the ν(CO) region

Compound	ν(CO) (cm^{-1})	Reference
$Rh_6(CO)_{16}$ [a]	2066, 2051ms, 2025w, 2019w, 1795s	[7]
$Rh_6(CO)_{16}/MgO_{air}$	2066s, 2050sh, 2019mw, 1795s	This work
$[Rh_6(CO)_{15}(COOMg\text{-})]^-$	2078m, 2055s, 2016ms, 1984s 1802m(br), 1646mw	This work
$[Rh_6(CO)_{15}(COOMe)]^-$ [b]	2085w, 2048s, 2020w, 1830w, 1780s 1654m, 1622m	[10]
$[Rh_n(CO)_m]^{(n/5)-}$ (species A)	2075w(sh), 2004vs, 1840m(br)	This work
$[Rh_{13}(CO)_{24}H_2]^{3-}$ [c]	1995s, 1840m	[14]
$[Rh_{15}(CO)_{27}]^{3-}$ [c]	2040vw, 1998s(br), 1850–1825m, 1805m(br)	[15]
$[Rh_{22}(CO)_{37}]^{4-}$ [c]	2020vs, 2010m(sh), 1990vw, 1940w, 1860m(br) 1845m(sh), 1803m(sh), 1765w	[16]
$[Rh_{22}(CO)_{35}H_x]^{5-}$ [a] ($x = 2,3$)	2010vs, 1860ms, 1820ms(br)	[17]

[a] KBr disc. [b] THF. [c] Acetonitrile.

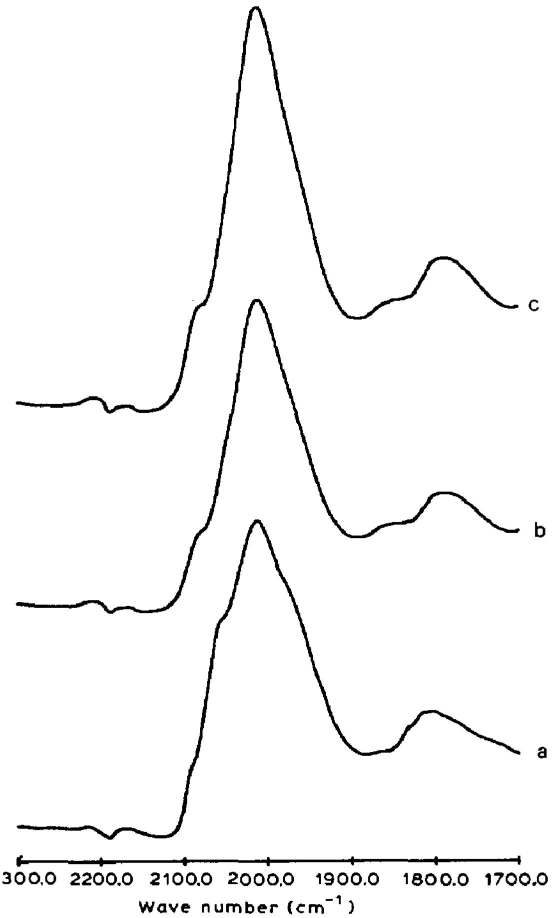

Fig. 3. Infrared spectra in the ν(CO) region (cm^{-1}): (a) $Rh_6(CO)_{16}$ after impregnation onto MgO^{500}; (b) same sample treated in vacuo at 25 °C for 48 h; (c) same sample thermally treated at 60 °C in vacuo for 3 h.

have this colour [11]. The anion is obtained by reaction of $Rh_6(CO)_{16}$ with the basic Lewis O^{2-} sites of the MgO surface. Ready formation of cluster carbonyl anions is to be expected because under similar conditions $Os_3(CO)_{12}$ selectively gives the anion $[Os_3(CO)_{11}]^{2-}$ [6]. However, this green species is highly reactive, and all attempts to record its infrared spectrum failed. In vacuo it rapidly turned brown, and the infrared spectrum then recorded was virtually identical to that finally observed on MgO^{25} (Fig. 2b, c and Fig. 3a). These results suggest that the same surface species, stable in vacuo, is finally formed independent of the nature of the thermal treatment of magnesium oxide. For convenience, this species will be called "species A".

A careful analysis of the infrared spectrum of species A by Chini's method [12] indicates that this surface species is probably anionic, with a ratio, R, between the number of metal atoms (MA) and the number of negative charges (NC) [R = MA/NC] of about 5, as in the generic anionic structure $[Rh_n(CO)_m]^{(n/5)-}$. The simplest structure, corresponding to the $[Rh_5(CO)_{15}]^-$ anion, should be red and give completely different infrared spectrum [13]. We thus suggest that a nucleation process occurs, and this is supported by comparison of the infrared spectrum of species A with those of some molecular high nuclearity carbonyl cluster anions of rhodium (Table 1). In addition, the formation of hydrido species, especially in the case of MgO^{25}, obtained by reaction with the protons of surface OH groups or adsorbed H_2O, cannot be ruled out, because the presence of hydrido groups in the framework of high nuclearity carbonyl cluster anion does not much affect its infrared spectrum (see Table 1). Unfortunately, a definitive conclusion about the nature of the species A could not be reached. Attempts at chemical extraction proved unsuccessful, probably owing to the very high reactivity of the anionic species A, which undergoes reaction during the chemical extraction with dilute aqueous HCl or H_2SO_4.

Reactivity of the species A in oxygen

Even at room temperature, in air or under a sub-atmospheric pressure of O_2, fast oxidation of species A takes place, as shown by the appearance of a new infrared spectrum, characterized by two strong bands, at 2086 and 2009 cm^{-1} (fig. 4a), which is consistent with the formation of $Rh^I(CO)_2$ species covalently bonded to the surface through Mg–O bonds [18].

The strongly basic nature of the oxygen donor atoms of these surface sites results in an increase of the electron density on the rhodium atoms, and this accounts for the red shift of the carbonyl frequencies compared to those of similar species on other supports such as alumina, silica, or even zeolites [4,19,20].

These Rh^I surface species react with carbon monoxide; even after a few hours the doublet at 2086 and 2009 cm^{-1} has disappeared and new bands at 1996 and 1807 cm^{-1} have appeared (Fig. 4b). The new spectrum is virtually identical to that of the species A, thus confirming the observations of Gates et al. about the possibility of generating anionic clusters on the surface of magnesium oxide by carbonylation of a mononuclear precursor [21].

A similar oxidation/carbonylation cycle between mononuclear and cluster rhodium surface species was observed previously on alumina under actual catalytic water gas shift conditions, but involving only $Rh_6(CO)_{16}$ [22]. The different behaviour observed on magnesium oxide is clearly linked to the stronger basic

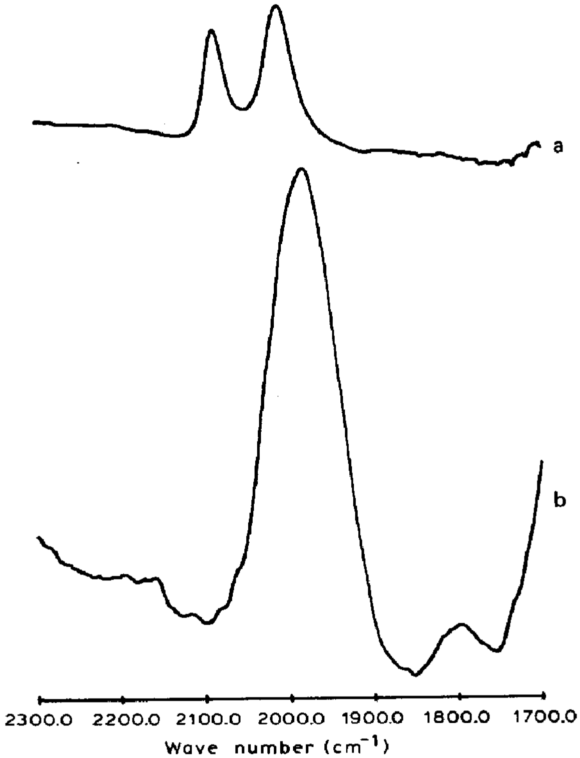

Fig. 4. Infrared spectra in the ν(CO) region (cm^{-1}): (a) $Rh_6(CO)_{16}$ on MgO^{500} after treatment under O_2 (200 torr) at room temperature for 2 h. (b) same sample, after recarbonylation under CO (300 torr) at 25 °C for 7 h.

character of the support compared to that of alumina, which acts to stabilize anionic species preferentially. If $Rh_6(CO)_{16}$ were formed as an intermediate species in the recarbonylation process, the above-mentioned reaction with the basic support would take immediately place, with the formation of species A. In contrast, on a highly dehydrated γ-alumina, $Rh_6(CO)_{16}$ is simply physisorbed, being quite stable at room temperature [4].

The stabilization of high nuclearity cluster species under carbon monoxide and the evidence for an oxidation/recarbonylation cycle provide clues to understanding of the unusual activity and selectivity observed by Ichikawa when using as catalysts rhodium clusters supported on some basic oxides, particularly magnesium oxide [2].

It is, in fact, quite possible that the formation of alcohols, and especially ethanol from syngas can be ascribed to the carbonyl anion A, because evidence for high nuclearity anionic carbonyl clusters has been obtained during the catalytic formation of alcohols (in particular ethanol, methanol and glycols) in the reaction of syngas in the homogeneous phase catalyzed by $Rh_6(CO)_{16}$ or $Ru_3(CO)_{12}$ [23,24].

Conclusions

The results have revealed that $Rh_6(CO)_{16}$ can be physisorbed with retention of its nuclearity only when supported on the rather inert and highly carbonated surface of untreated MgO_{air}, as in the case with $Os_3(CO)_{12}$ [6].

Magnesium oxide, thermally treated under various specific conditions, behaves as a strongly basic reagent through its Brönsted or Lewis basic surface sites, leading to a series of fast reactions with $Rh_6(CO)_{16}$ with ultimate formation of a single anionic rhodium carbonyl species of unknown formula, but certainly of high nuclearity. In the presence of traces of oxygen, this latter species gives rise to a reversible, oxidation/recarbonylation cycle. These observations may open new pathways to understanding of the surface species involved in catalytic reactions induced by $Rh_6(CO)_{16}$ supported on a basic oxide, such as magnesium oxide, as a heterogeneous catalyst [2,23].

This behaviour is quite different from that observed for $Rh_6(CO)_{16}$ supported on silica [19] or alumina [4], and so the very different properties of rhodium catalysts prepared by supporting $Rh_6(CO)_{16}$ on a series of oxides can be now be interpreted in terms of the formation of the surface of various molecular rhodium species, depending on the nature of the support. These species are probably the actual catalytic entities.

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