$Ru_3(CO)_{12}$ supported on alumina samples with different dehydration degrees

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FTIR spectroscopy was used to characterise $Ru_3(CO)_{12}$ supported by chemical vapour deposition onto several γ-alumina samples with different dehydration degrees. The metal carbonyl was found to be molecularly physisorbed onto hydrated alumina; it undergoes oxidative addition of a surface OH group onto hydroxylated alumina; it forms Lewis type adducts, via a CO group, with Al^{3+} ions at the surface of dehydroxylated alumina.

Keywords: alumina, trirutheniumdodecacarbonyl, infrared spectroscopy

1. Introduction

The adsorption and reactivity of transition metal carbonyls on oxidic surfaces have attracted the attention of many research groups [1–6]. A number of these studies are motivated by the attempt to understand the chemical bonding between the surface of the support and the metal carbonyl, and to investigate the reactivity of the surface adduct thus formed.

As recently outlined by Zecchina and Otero Areán [4], there are several ways in which transition metal carbonyls can interact with oxidic surfaces, and most of them have their analogues in homogeneous chemistry. The main interaction modes can be divided into ligand-centred interactions and metal-centred interactions [2,4,7,8], and they depend on several parameters: the nature of both metal carbonyl and oxide support; the degree of dehydroxylation of the support; the method adopted to deposit the carbonyl on the support (chemical vapour deposition or impregnation); and the nature of the surrounding atmosphere.

The interaction of $Ru_3(CO)_{12}$ with alumina [9–12] has been studied mainly by IR spectroscopy, although EXAFS and temperature-programmed decomposition have also been used. The interaction is rather complex: on partially hydroxylated alumina, $Ru_3(CO)_{12}$ can undergo oxidative addition of a surface OH group with simultaneous release of two CO ligands [11,12]; slightly acidic OH groups on the alumina surface can also lead to several anchored subcarbonylic species. However, no well-documented reports appear to be available to date on the interaction between $Ru_3(CO)_{12}$ and highly dehydroxylated alumina.

Previous studies on other metal carbonyls supported on highly dehydroxylated supports indicated the formation of Lewis-type (donor–acceptor) σ-adducts where the oxygen atom of a CO ligand interacts with a coordinatively unsaturated metal ion at the oxide surface [2,4,8,13]. We report here on a detailed FTIR characterisation of $Ru_3(CO)_{12}$ sublimed onto highly dehydroxylated γ-alumina in order to investigate the possible interaction of the metal carbonyl with Lewis acid sites on the support. Also included in this paper is the FTIR characterisation of $Ru_3(CO)_{12}$ supported on hydrated and on hydroxylated alumina. The results on hydroxylated alumina will be compared with those obtained by other authors [11,12].

2. Experimental

High-purity trirutheniumdodecacarbonyl was supplied by Aldrich (Steinheim) and was used without further purification. The γ-Al_2O_3 sample was obtained by thermolysis at 873 K of synthetic boehmite and showed a BET surface area of 222 $m^2\,g^{-1}$ and a mesoporous texture with a most frequent pore diameter of 4 nm (although a small contribution from microporosity was also present). These pore openings allow free diffusion of $Ru_3(CO)_{12}$ molecules, which have dimensions of about 1.1×0.9 nm [14].

A quartz cell fitted with NaCl windows, similar to that described by Boccuzzi et al. [15], allowed in situ activation of the alumina sample and dosing of the metal carbonyl by vacuum sublimation at 380 K. This temperature ensured a vapour pressure of $Ru_3(CO)_{12}$, high enough for vapour deposition onto the alumina without causing thermolysis of the metal carbonyl. For activation, three portions of the alumina sample, in the form of thin self-supporting wafers, were heated (inside the IR cell) for 1 h at 273, 873 and 1173 K respectively, under a dynamic vacuum (residual pressure $< 10^{-3}$ Pa). These

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thermal treatments led to hydrated alumina (sample A273), hydroxylated alumina (sample A873), and dehydroxylated alumina (sample A1173), respectively. The hydration/hydroxylation degree was checked by IR spectroscopy in the O–H stretching region. After activation, contact with air was strictly excluded during vapour phase deposition of the metal carbonyl and acquisition of the spectra. Room temperature IR spectra were collected, at 3 cm^{-1} resolution, on a Bruker IFS66 spectrometer. For each sample, the spectrum taken before the dosage of $Ru_3(CO)_{12}$ has been used as background, and the spectra shown in the CO stretching region are background subtracted.

3. Results and discussion

3.1. Hydration/hydroxylation degree of the alumina samples

Figure 1 depicts IR spectra, in the O–H stretching region, for the different alumina samples. Sample A273 shows three main bands at 3692, 3740 and 3786 cm^{-1}, and a very broad IR absorption starting at about 3650 cm^{-1} and extending down to 3200 cm^{-1}. The three main bands correspond to three isolated O–H groups which are characteristic of γ-Al_2O_3 [16]; and the broad band can be assigned to H-bonded hydroxyl groups, coupled with physisorbed water molecules. This last contribution was confirmed by an intense IR absorption band centred at 1620 cm^{-1} (not shown), which corresponds to the H_2O bending mode. Activation at 873 K (sample A873) results in elimination of adsorbed water (the band at 1620 cm^{-1} was no longer present), while in the corresponding IR spectrum only the bands due to isolated hydroxyl groups remain. Heating at 1173 K (sample A1173) causes the virtual disappearance of O–H groups. From the results shown in figure 1, it can be concluded that, in a broad sense, sample A273 is hydrated, sample A873 is hydroxylated, and sample A1173 is dehydroxylated.

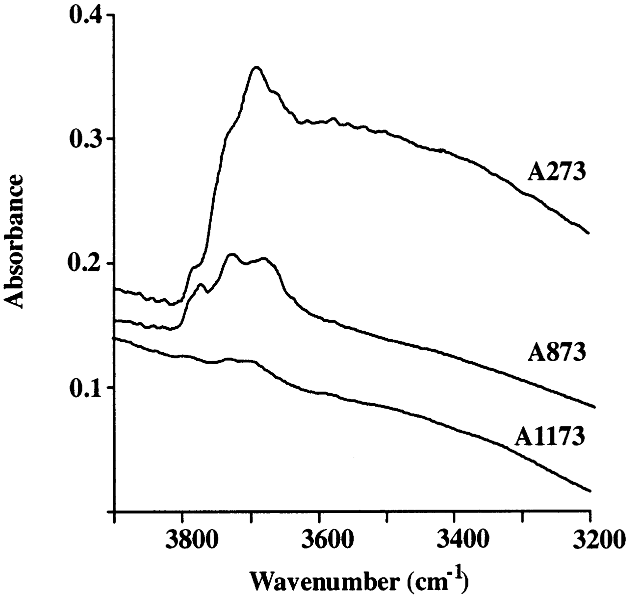


Figure 1. IR spectra in the O–H stretching region of samples A273, A873, and A1173.

3.2. $Ru_3(CO)_{12}$ adsorbed on the alumina samples

Figures 2, 3 and 4 show the IR spectra, in the C–O stretching region, of $Ru_3(CO)_{12}$ adsorbed at increasing doses on samples A273, A873 and A1173, respectively. In every case, we checked that the spectrum obtained after the last dose of $Ru_3(CO)_{12}$ was not altered after 1 h.

IR spectra of the metal carbonyl adsorbed onto the sample A273 (figure 2) show two main bands: a symmetric band at 2063 cm^{-1} and a broad band centred at 2029 cm^{-1} showing a shoulder at 2014 cm^{-1}. A very weak band is also observed at 2119 cm^{-1}. All these bands grow in parallel when the amount of adsorbed $Ru_3(CO)_{12}$ is increased, thus suggesting that they all belong to the same surface species. The IR spectra obtained on sample A873 (figure 3) show a broad absorption in the 2150–1950 cm^{-1} range with several components at 2131 (vw), 2090 (w,sh), 2057 (m), 2028

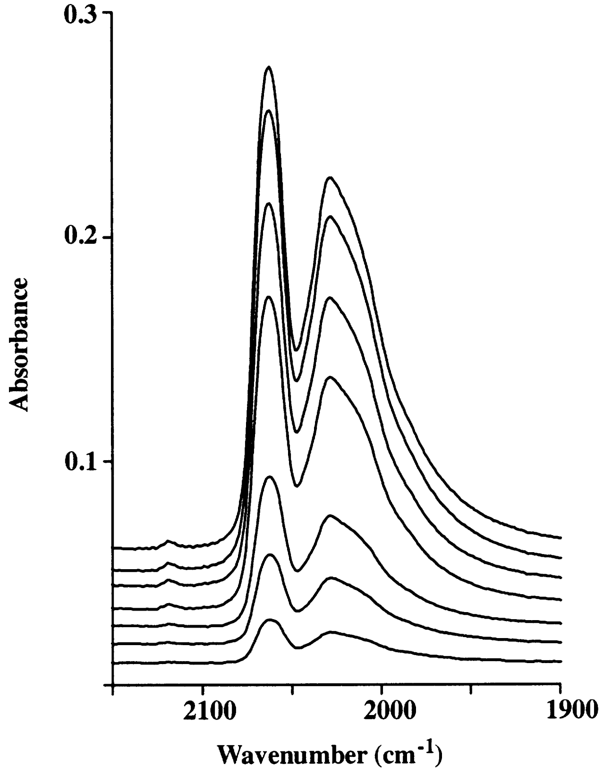


Figure 2. IR spectra of successive doses of $Ru_3(CO)_{12}$ on sample A273.

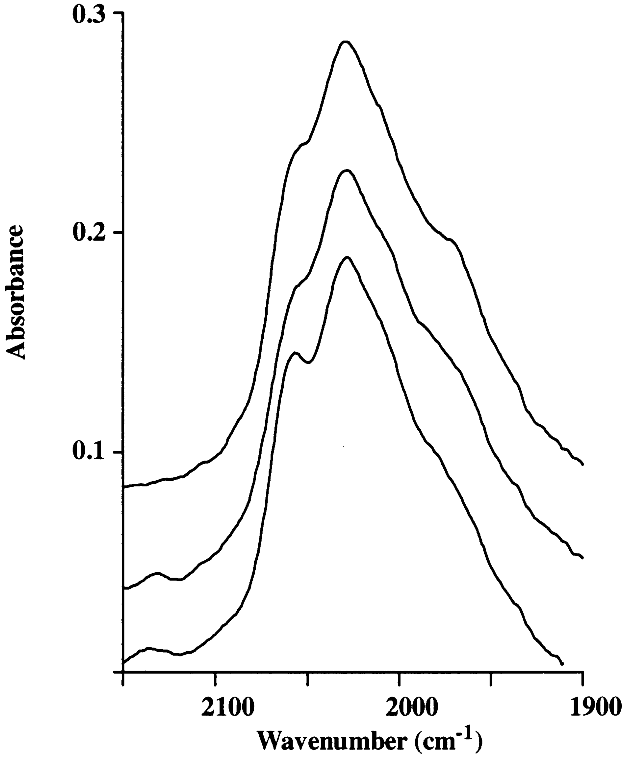


Figure 3. IR spectra of successive doses of $Ru_3(CO)_{12}$ on sample A873.

(s), 2000 (m,sh) and 1969 (m,sh) cm^{-1}. The parallel growth of the different IR bands suggests that they all belong to the same species. The spectra observed in figure 4 (sample A1173) display a set of partially overlapping absorption bands in the 2150–1950 cm^{-1} region with maxima at 2136 (vw), 2086 (w,sh), 2071 (m,sh), 2062 (m,sh), 2032 (s,sh), 2015 (vs) and 1965 cm^{-1} (m,sh), and a broad band in the 1875–1750 cm^{-1} region. Also in this case, all the bands grow in parallel and therefore, they can be assigned to the same surface species. Table 1 summarises the ν(CO) wavenumber values measured on the different IR spectra (figures 2, 3, and 4). For comparison, also the IR absorption wavenumbers for $Ru_3(CO)_{12}$ and some related species are given.

The IR spectra shown in figure 2 are very similar to the IR spectrum of $Ru_3(CO)_{12}$ in CCl_4 solution (table 1), thus indicating that the metal carbonyl is molecularly physisorbed onto the surface of hydrated γ-Al_2O_3 (sample A273). The presence of the weak band at 2119 cm^{-1} is assigned to the Raman active mode at 2127 cm^{-1} (A'_1) [19], which becomes IR active when the metal carbonyl interacts with the alumina surface causing a slight perturbation of the original D_{3d} symmetry. Similar spectra were obtained by supporting $Ru_3(CO)_{12}$ onto SiO_2 and TiO_2 activated at 473 K and were also assigned to the metal carbonyl physisorbed onto the metal oxides [12].

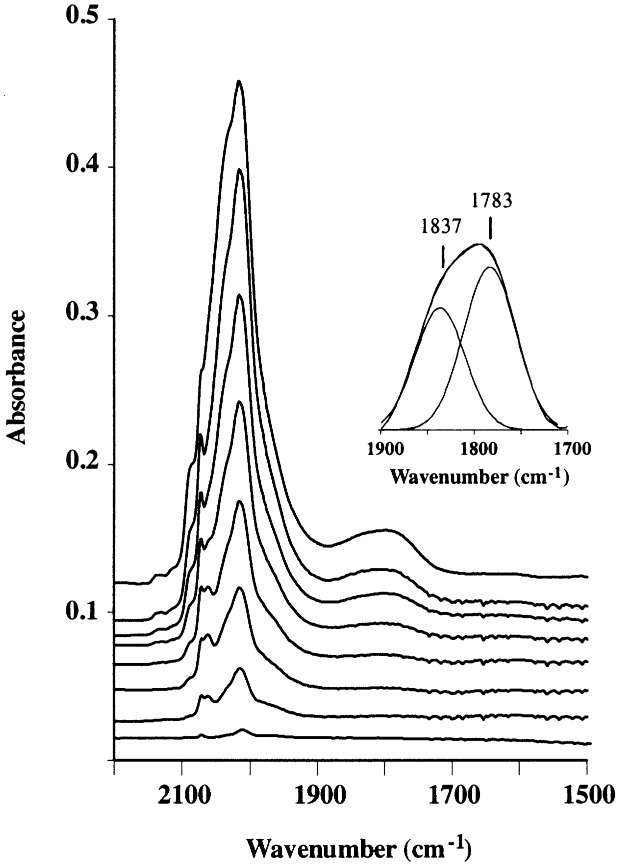
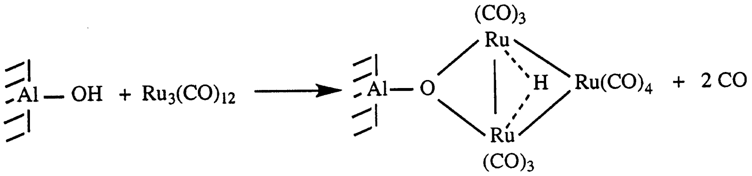


Figure 4. IR spectra of successive doses of $Ru_3(CO)_{12}$ on sample A1173. The inset shows computer deconvolution of the low-frequency band.

The IR spectra obtained by interaction of the metal carbonyl with sample A873 (figure 3) are very different from those of $Ru_3(CO)_{12}$ in CCl_4 solution (table 1). However, they closely resemble those of $[Ru_3(CO)_{10}(\mu$-$H)(\mu$-$SC_2H_5)]$ [18] and $[Ru_3(CO)_{10}(\mu$-$H)(\mu$-$OSi)]$ [20],

Table 1
Summary of C–O IR stretching bands (cm^{-1})

Carbonyl	ν(CO) (terminal)	ν(CO) (–CO–Al)	Ref.
$Ru_3(CO)_{12}$ in CCl_4 solution	2061 (s), 2032 (s), 2015 (m)		[17]
$[Ru_3(CO)_{10}(\mu$-$H)(\mu$-$SC_2H_5)]$	2105 (m), 2064 (s), 2056 (s), 2025 (s), 2012 (m), 2008 (s), 1994 (m)		[18]
$[Ru_3(CO)_{10}(\mu$-$H)(\mu$-$OAl)]$	2130 (w), 2100 (m), 2075 (s), 2030 (s), 2000 (sh)		[12]
$Ru_3(CO)_{12}$/A273	2119 (vw), 2063 (s), 2029 (s), 2014 (m,sh)		this work
$Ru_3(CO)_{12}$/A873	2131 (vw), 2090 (w,sh), 2057 (m), 2028 (s), 2000 (m,sh), 1969 (m,sh)		this work
$Ru_3(CO)_{12}$/A1173	2136 (vw), 2086 (w,sh), 2071 (m,sh), 2062 (m,sh), 2032 (s,sh), 2015 (vs), 1965 (m,sh)	1875–1750 (m)	this work



Scheme 1.

indicating the formation of $[Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OAl)]$ by reaction of $Ru_3(CO)_{12}$ with OH groups on the surface of hydroxylated alumina (sample A873). In this surface complex, the metal carbonyl retains the triangular Ru_3 structure, but it undergoes oxidative addition of a surface OH group with the attendant release of two CO ligands (see scheme 1). This conclusion has been previously achieved by Zecchina et al. [11] and by Asakura et al. [12], who thoroughly investigated the interaction of $Ru_3(CO)_{12}$ with hydroxylated alumina by IR [11,12] and EXAFS spectroscopy [12]. Due to the close similarity between our spectra and those previously reported [11,12] for the same surface complex, no more comments are needed on this system.

IR spectra of $Ru_3(CO)_{12}$ interacting with dehydroxylated alumina (figure 4) clearly differ from those obtained on samples A273 and A873 (figures 2 and 3). One of the main differences is the presence of a broad band in the 1875–1750 cm^{-1} region. As already stated in section 1, previous studies have shown that many metal carbonyls are molecularly adsorbed onto highly dehydroxylated alumina [21–24] forming Lewis-type (donor–acceptor) σ-adducts, where the basic oxygen atom of a CO ligand interacts with an Al^{3+} cation at the oxide surface. Adduct formation strongly affects bond vibrations of the CO ligands, and hence infrared spectroscopy has been used to monitor surface species. In particular, the stretching mode of the carbonyl group directly involved in bond formation is strongly perturbed: bathochromic shifts of 100–150 cm^{-1} and 200–400 cm^{-1} being typically observed for linear and bridging CO groups respectively [4].

Shriver et al. [25,26] have shown that under homogeneous conditions, interaction of $Ru_3(CO)_{12}$ with the Lewis acid $AlBr_3$ induces a terminal-to-bridge CO shift. The μ-CO ligand is coordinated to the aluminium, and is responsible for an IR band at 1535 cm^{-1}. Recently, Otero Areán and Mas Carbonell [27] have observed a similar behaviour when $Ru_3(CO)_{12}$ is adsorbed onto highly dehydroxylated spinel. In this case, the implied μ-CO ligand is responsible for a band at 1604 cm^{-1}. Looking at the IR spectra shown in figure 4, terminal-to-bridge CO shift can be discarded because no bands are observed in the 1525–1625 cm^{-1} region. However, the broad band at 1875–1750 cm^{-1} strongly suggests the formation of Lewis type adducts where terminal CO groups are coordinated to coordinatively unsaturated Al^{3+} ions at the surface of the dehydroxylated $\gamma\text{-}Al_2O_3$. The remaining CO ligands, those not involved in adduct formation, are responsible for the complex IR absorption observed in the 2135–1965 cm^{-1} range. From the present IR investigation, it is not possible to establish whether the metal carbonyl is anchored to the surface through an axial or a radial CO group.

The broad band in the 1875–1750 cm^{-1} range can be resolved into two components with maxima at 1837 and 1783 cm^{-1}, as shown in the inset of figure 4. We tentatively propose that these maxima correspond to two sets of chemisorbed metal carbonyl species. It is worth noticing in this context that there are two types of coordinatively unsaturated Al^{3+} ions (Lewis acid centres having different strengths) [24] on the surface of $\gamma\text{-}Al_2O_3$, and previous IR studies on group VI metal carbonyls [21] and on dirheniumdecacarbonyl [24] adsorbed onto dehydroxylated $\gamma\text{-}Al_2O_3$ have shown the presence of two sets of chemisorbed metal carbonyls associated with the two types of Lewis acid centres.

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