Vapour phase deposition and thermal decarbonylation of $Re_2(CO)_{10}$ on gamma-alumina: infrared studies

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Dirheniumdecacarbonyl vacuum sublimed onto mesoporous γ-alumina forms Lewis type adducts where an axial CO group is coordinated to an Al^{3+} ion at the metal oxide surface, as revealed by IR spectroscopy. Vacuum heating of the surface adduct at 773 K brings about decarbonylation, with intermediate formation of a surface-bound mononuclear tricarbonyl which was completely decarbonylated on prolonged heating at the same temperature. The resulting material strongly chemisorbs CO to yield mainly a surface-bound pentacarbonyl species. This suggests that the supported metal remains primarily in a zero-valent and well dispersed state.

Keywords: gamma-alumina; $Re_2(CO)_{10}$; vapour phase deposition; thermal decarbonylation; IR spectroscopy

1. Introduction

Transition metal carbonyls supported on high-surface-area metal oxides are systems of current interest in catalytic research. They provide a means to heterogenize homogeneous catalysts, and also show potential as convenient precursors of highly dispersed supported metals [1–4]. On dehydroxylated metal oxide supports, many metal carbonyls are molecularly adsorbed forming 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 [5–7]. Ligand re-arrangement and partial decarbonylation [7,8] are processes which can also occur upon carbonyl–support interaction. Infrared spectrometry is a very useful technique to investigate these processes, since both adduct formation and partial decarbonylation affect bond vibrations of the CO ligands which can be used to monitor surface species. In particular, significant lowering (100–300 cm^{-1}) of a ν(C–O) stretching mode is a highly reliable diagnostic feature for adduct formation [7,9,10].

We report on a detailed IR characterization of $Re_2(CO)_{10}$ sublimed onto boeh-

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mite-derived γ-alumina, and on subsequent thermal decarbonylation to generate supported rhenium which was also characterized by IR spectroscopy of adsorbed CO. Interest in $Re_2(CO)_{10}$ as a catalyst precursor arises from the known ability of supported rhenium metal and several rhenium compounds to act as reforming, hydrogenation and olefin metathesis catalysts [11–17]. Previous studies on alumina-supported $Re_2(CO)_{10}$ have been reported by several authors [18–21] who prepared their materials by an impregnation procedure. This usually leads to a weak interaction between the support and the metal carbonyl. Some of us [22] have already described a stronger interaction in a study of vapour deposition on alum-derived active alumina. However, no decarbonylation experiments were performed at that time.

2. Experimental

High-purity dirheniumdecacarbonyl was supplied by Aldrich-Chemie (Steinheim). Synthetic boehmite was prepared following the method described by McIver et al. [23]. This parent material was calcined at 873 K to yield the γ-alumina support used in the present work (structure checked by powder X-ray diffraction). Analysis of the corresponding nitrogen adsorption–desorption isotherm (at 77 K) showed a BET surface area of 160 $m^2\ g^{-1}$, and a mesoporous texture (although a small contribution from microporosity was also present) with a most frequent pore diameter of 4 nm. This allows free diffusion of $Re_2(CO)_{10}$ molecules, which have dimensions of about 1.1 × 0.8 nm [24].

For infrared studies, a portion of the γ-alumina sample was pressed into a self-supporting disc and placed inside a silica cell fitted with NaCl windows which allowed in situ thermal activation and dosification of the metal carbonyl by vacuum sublimation at 330 K. For activation, the γ-alumina wafer was heated at 1073 K for 2 h under a dynamic vacuum of 10^{-4} Torr. Room temperature FTIR transmission spectra were recorded, at 3 cm^{-1} resolution, using a Bruker 66 spectrometer. After dosing with $Re_2(CO)_{10}$ and recording the corresponding spectra, the alumina wafer was heated (inside the IR cell) from room temperature up to 773 K in 50 K intervals in order to achieve thermal decarbonylation. Evolved CO was evacuated by outgassing the IR cell for a few minutes after each heating period. The decarbonylation process was followed by IR spectroscopy. Chemical analysis of the alumina wafer after total decarbonylation was achieved showed a residual rhenium loading of ca. 1 wt%. The original loading of the metal carbonyl was significantly higher, since partial thermal desorption occurred during heating for thermolysis.

An independent experiment was carried out to obtain the IR spectrum of CO adsorbed at liquid nitrogen temperature on a γ-alumina wafer previously activated under the same conditions as described above. This allowed to probe surface Lewis acid sites of the metal oxide.

3. Results and discussion

Fig. 1 shows the spectra (in the C–O stretching region) of carbon monoxide adsorbed at 77 K on the γ-alumina sample. A similar spectrum, with lower intensity, was observed at room temperature. Two IR absorption maxima are seen, which for small CO doses are centred at 2220 and at 2203 cm^{-1}. It is well known [25–28] that interaction of CO (via the carbon end) with coordinatively unsaturated cations at the surface of oxides and halides shifts the C–O stretching vibration upwards from the 2143 cm^{-1} value corresponding to the free molecule. Thus, the spectra in fig. 1 show the presence (at the γ-alumina surface) of two types of coordinatively unsaturated Al^{3+} ions (Lewis acid centres). This is in agreement with reported studies on the surface chemistry of γ-alumina. The band at 2220 cm^{-1}, which saturates at low CO doses, has been assigned [29,30] to Al^{3+} ions on edges, steps and other singularities due to surface roughness. IR absorption at 2203 cm^{-1} corresponds to CO absorbed on trigonal Al^{3+} ions at more regular surface sites [29,30]. Notice that (i) the broadness of the IR absorption bands reveals surface het-

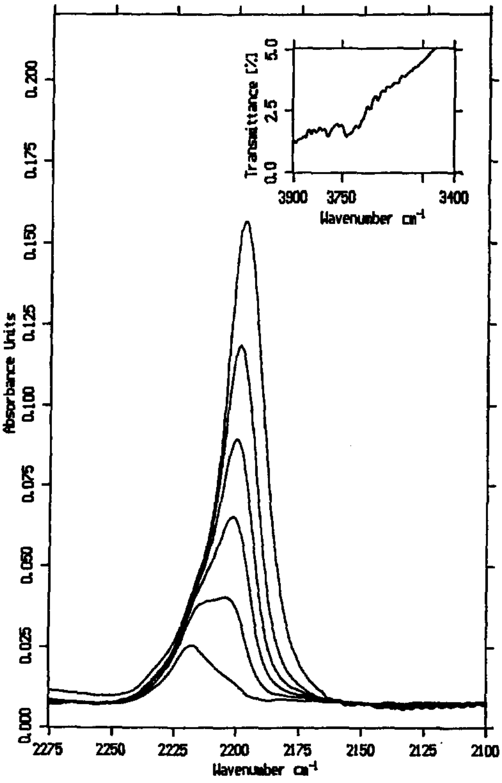


Fig. 1. IR spectra of CO adsorbed (at 77 K) on the γ-alumina sample. Equilibrium pressure from 10^{-2} up to 10 Torr (1 Torr = 133.33 Pa). Inset shows the blank IR spectrum of the alumina wafer in the O–H stretching region.

erogeneity, and (ii) the shift towards lower wavenumbers with increasing CO equilibrium pressure (particularly clear for the 2203 cm^{-1} band) is a consequence of progressive building up of adsorbate–adsorbate interactions [26,30].

The inset in fig. 1 shows the blank IR spectrum of the alumina wafer in the 3900–3400 cm^{-1} region. Only faint IR absorption due to O–H stretching was observed, thus proving that the oxide support was highly dehydroxylated during thermal activation. No significant spectral changes were observed in the O–H stretching region upon dosing with $Re_2(CO)_{10}$ and subsequent thermal decarbonylation.

Fig. 2 shows the IR spectra of $Re_2(CO)_{10}$ adsorbed (at increasing doses) on a γ-alumina wafer. A broad IR absorption band is observed in the 1800 cm^{-1} region, which can be resolved into two components centred respectively at 1780 and at 1830 cm^{-1}. As stated in the Introduction, bands in this region can be assigned to a CO ligand anchored to the metal oxide support. The presence of two bands correlates with results from CO adsorption, which evidenced two types of Lewis acid sites. The remaining nine CO groups in $Re_2(CO)_{10}$ give the complex IR absorption observed in the 1950–2150 cm^{-1} region. Interpretation of this complex spectrum requires some brief theoretical considerations.

Free $Re_2(CO)_{10}$ (point symmetry D_{4d}) has a CO stretching representation $\Gamma_{CO} = 2A_1 + E_2 + E_3 + 2B_2 + E_1$, where $2B_2 + E_1$ are IR active. In cyclohexane

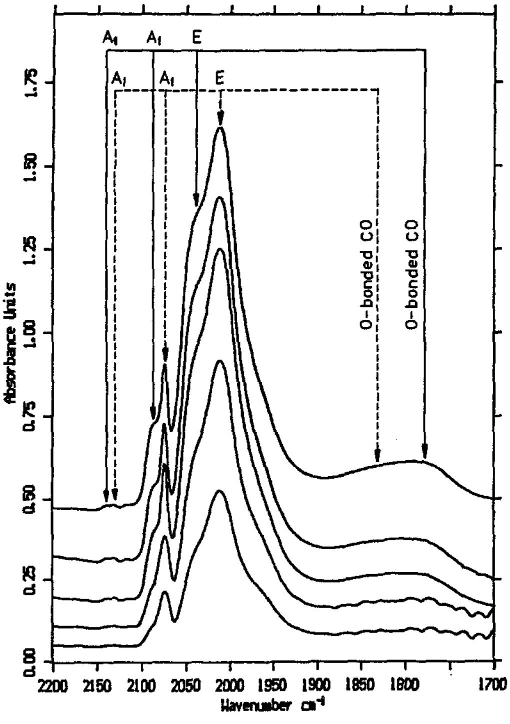
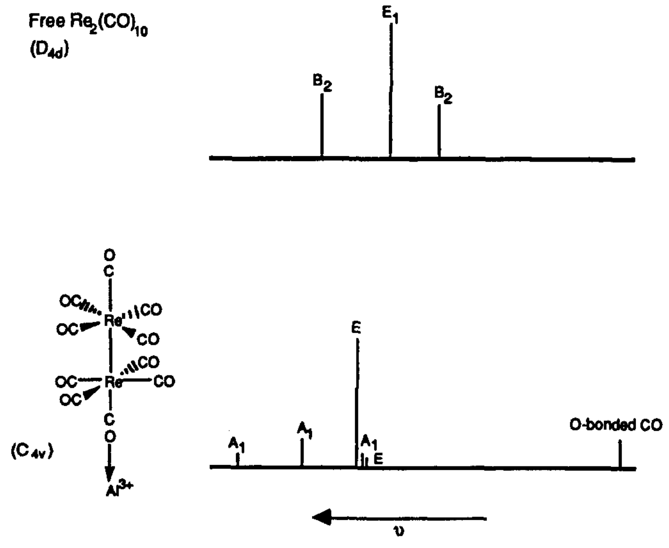


Fig. 2. IR spectra of successive doses (ca. 10^{-2} Torr) of $Re_2(CO)_{10}$ on γ-alumina.

solution, these modes are observed [31] at 2070 (B_2), 2014 (E_1) and 1976 cm^{-1} (B_2). For an axially perturbed (C_{4v}) $Re_2(CO)_{10}$ molecule, the CO stretching representation is $\Gamma_{CO} = 2E + B_1 + B_2 + 3A_1$ where the IR-active modes are $2E + 3A_1$, as shown in scheme 1. The most similar compound found in the literature is ax-$Mn_2(CO)_9{}^{13}CO$, where the ^{13}CO group is decoupled from the remaining CO ligands. Reported [32] C–O stretching frequencies for this compound (in cm^{-1}) are, 2110 w (A_1), 2037 m (A_1), 2014 vs (E), 1990 w (A_1) and 1979 sh (E). For $Re_2(CO)_{10}$, formation of surface adducts with Lewis acid sites (as depicted in scheme 1) would result in electron density withdrawal from rhenium atoms. This decreases π back-donation and increases frequencies of the CO ligands not involved in adduct formation [10]. The effect is expected to increase with increasing acidity of the Lewis surface site, i.e. with decreasing ν(CO) for the corresponding surface anchored CO ligand.

The foregoing considerations led to assignment of the spectra of adsorbed metal carbonyl in terms of two families of $Re_2(CO)_{10}$ molecules axially anchored to surface Lewis acid sites of different strength, as shown in fig. 2. Notice that anchoring of the metal carbonyl through equatorial CO ligands would not explain the observed IR spectra. Further evidence for molecular chemisorption comes from the absence of evolved CO, which would give a band around 2200 cm^{-1}. Table 1 summarizes the most distinctive frequencies observed for the surface adducts. They are in agreement with reported results [22] for $Re_2(CO)_{10}$ sublimed onto alum-derived active alumina. The broad shoulder at about 1965 cm^{-1} is likely to have a contribution from weakly adsorbed (physisorbed) $Re_2(CO)_{10}$, thus precluding accurate determination of frequencies for the weak $A_1 + E$ modes expected in this region of the spectra (fig. 2 and scheme 1).



Scheme 1.

Table 1
Infrared spectra of Re–carbonyl complexes

Rhenium complex	ν(CO) (cm^{-1})	Ref.
γ-alumina supported $Re_2(CO)_{10}$ (strong Lewis-acid sites)	2138(vw), 2087(m), 2040(s), 1780 [a]	this work
γ-alumina supported $Re_2(CO)_{10}$ (weak Lewis-acid sites)	2130(vw), 2073(m), 2011(s), 1830 [a]	this work
$Re_2(CO)_{10}$ supported on alum-derived active alumina	2140, 2090, 2045, 1775 [a]; and 2120, 2075, 2020, 1845 [a]	[22]
$Re(CO)_3(PPh_3)_2I$	2020(s), 1924(s), 1887(s)	[36]
$Re(CO)_3(H_2O)Br$	2020(s), 1940(s)	[36]
$Re(CO)_3$ on γ-alumina	2043(s), 1937(s)	this work
$Re(CO)_5Cl$	2156(w), 2045(s), 2016(w), 1982(m)	[37]
$Re(CO)_5Br$	2150(w), 2045(s), 2016(w), 1984(m)	[37]
$Re(CO)_5I$	2145(w), 2042(s), 2013(w), 1987(m)	[37]
$Re(CO)_5$ on γ-alumina	2153(vw), 2040(s), 2012(s), 1978(sh)	this work

[a] Surface anchored CO ligand.

Fig. 2 shows that relative intensities of IR absorption maxima are approximately independent of surface coverage. This suggests that interaction between the metal carbonyl and the γ-alumina support is sufficiently strong to preclude significant surface migration at room temperature. The fact that the IR spectra do not show any evidence for interaction involving two equatorial CO ligands, even at low coverage, might reflect an inductive effect from the trans-$Re(CO)_5$ group of axially anchored $Re_2(CO)_{10}$.

After the last spectrum in fig. 2 was obtained, the sample was heated in vacuum (inside the IR cell) to achieve decarbonylation of the surface adduct. The first signs of partial decarbonylation appeared after heating for 10 min at 423 K. The corresponding IR spectrum (not shown) was very complex and significantly different from the original one, thus proving the onset of decarbonylation with concomitant formation of a complex subcarbonyl species. After 10 min at 773 K, spectrum B in fig. 3 was obtained. This spectrum which shows broad bands at 1937 and 2043 cm^{-1} can readily be assigned to a mononuclear rhenium tricarbonyl. Table 1 shows comparison with corresponding data for mononuclear Re(I) complexes of the type $Re(CO)_3L_2X$, where X = halogen and L = donor ligand. Surface-bound rhenium tricarbonyl species are well documented [33] for materials prepared by mild reduction in hydrogen of alumina-supported $H_3Re_3(CO)_{12}$. The corresponding IR spectrum is very similar (main bands at 1925 and 2037 cm^{-1}) to that shown in fig. 3 (B).

Additional heating at 773 K for a further 15 min led to an IR spectrum (C, in fig. 3) where no infrared absorption was observed in the carbonyl stretching region, proving that the rhenium surface species had been completely decarbonylated. To gather information on the remaining material, CO was dosed (at room temperature) in the IR cell to a final equilibrium pressure of 10 Torr, and the corresponding

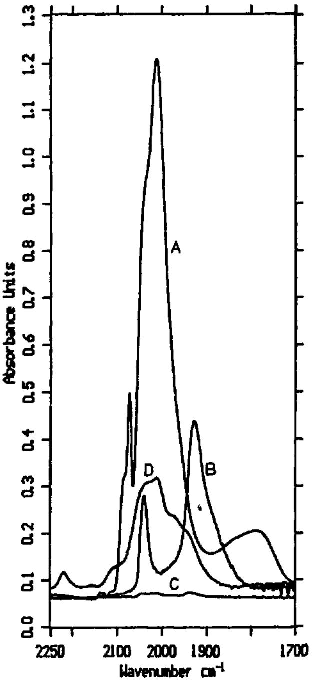


Fig. 3. (A) Alumina-supported $Re_2(CO)_{10}$ (cf. fig. 2); (B) IR spectrum after heating for 10 min at 773 K; (C) after further heating for 15 min at the same temperature; (D) after dosing with CO (10 Torr). Spectra B and D have been multiplied by a factor 2. For clarity, spectrum D was offset on the vertical scale.

IR spectrum was obtained. This is shown in fig. 3 (D). The observed IR absorption maxima at 2153 (w), 2040 (s), 2012 (s) and 1978 (sh) cm^{-1} can be assigned to a mononuclear rhenium pentacarbonyl. Excellent agreement is obtained, both in band number and frequency, when comparison is made (see table 1) with Re(I) molecular species of the type $Re(CO)_5X$ (X = halogen). These results provide clear evidence that alumina-supported rhenium remains primarily in a zero-valent (or at least low-oxidation) state. Additional bands in spectrum D are observed at 1938 and 2200 cm^{-1}, together with a weak broad shoulder in the 2100 cm^{-1} region. The 1938 cm^{-1} band can be assigned to a tricarbonyl species (as stated above) which would have a high frequency partner (2043 cm^{-1}) coincident with one of the bands from the pentacarbonyl. The IR absorption present at 2200 cm^{-1} clearly corresponds to CO adsorbed on the γ-alumina wafer, it was found to disappear on evacuation of the IR cell.

It remains to discuss the weak IR absorption observed in the 2100 cm^{-1} region. We tentatively propose that this corresponds to CO adsorbed on cationic Re^{n+} species, where $n > 1$. It is worth noticing in this context that oxidized rhenium species (most typically Re^{4+}) are known [33] to be very stable on metal oxide supports. CO could have acted as the oxidizing agent. Although non-dissociative CO adsorption is (at room temperature) the dominant process on rhenium, this transition metal is known [34,35] to be in the borderline between those metals which dissociatively chemisorb CO and those which only show molecular adsorption.

The overall intensity of spectrum D in fig. 3 is quite comparable with that of spectrum B, although much smaller than that of A. The intensity loss was mainly due to thermal desorption of the metal carbonyl during thermolysis and evacuation of evolved CO. In fact, the well-developed pentacarbonyl spectrum strongly suggests that the alumina-supported metal is in a highly dispersed state.

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