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FTIR characterisation of $Re_2(CO)_{10}$ adsorbed on sulfated zirconium dioxide

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Abstract—The interaction of $Re_2(CO)_{10}$ with highly dehydroxylated sulfated zirconia has been studied by *in situ* FTIR spectroscopy. Adsorption at room temperature leads to the formation of O-bonded surface adducts, where an axial CO ligand of the metal carbonyl is coordinated to a Zr^{4+} ion at the oxide surface. Two sets of IR absorption bands were observed in the carbonyl stretching region. These were assigned to $Re_2(CO)_{10}$ interacting with two types of surface sites of different Lewis acid strength. In addition, physically adsorbed $Re_2(CO)_{10}$ was also observed. Upon heating at 373 K, the carbonyl (both physically and chemically adsorbed) moves to surface sites with higher Lewis acid strength. © 1997 Elsevier Science Ltd

Interest in metal carbonyls supported on high-surface-area inorganic materials stems from their potential use in catalysis. These systems are expected to combine advantages of both homogeneous and heterogeneous catalysis [1–6]. On the other hand, they also provide convenient precursors of finely dispersed metals in low oxidation state [7–11]. In both cases, it is important to understand first of all the interaction between the metal carbonyl and the support.

We report here on a detailed characterisation by infrared (IR) spectrometry of $Re_2(CO)_{10}$ sublimed onto highly dehydroxylated sulfated-ZrO_2. Interest in $Re_2(CO)_{10}$ arises from the known ability of supported rhenium metal and metal compounds to act as reforming, hydrogenation and olefin metathesis catalysts [12–15].

Sulfated-ZrO_2 has been widely investigated in the last years because of its enhanced surface acidity [16–24]. It can easily be prepared in the high surface area form [16–22,25], and it shows good thermal stability and resistance to chemical attack, which are desirable properties for a catalyst support. Group 6 metal carbonyls supported on sulfated zirconia have previously been studied by IR spectroscopy [26]. The metal carbonyls were found to adsorb molecularly onto zirconia forming Lewis-type (donor-acceptor) σ-adducts, where the basic oxygen atom of a CO ligand

interacts with a coordinatively unsaturated cation at the oxide surface. Adduct formation strongly affects bond vibrations of the CO ligands, and hence infrared spectrometry can be used to monitor surface species. In particular, significant lowering of a $\nu(CO)$ stretching mode is a reliable diagnostic feature [5,27–29] for adduct formation (100–150 and 200–400 cm^{-1} shifts are expected for linear and bridging CO groups, respectively [5,29]). Related work on $Re_2(CO)_{10}$ supported on active alumina [11,30], on Na–Y zeolite [31], and on high-surface area spinels [32] has been reported by several workers.

EXPERIMENTAL

High purity $Re_2(CO)_{10}$ was supplied by Aldrich Chemie. Sulfated-ZrO_2 with a BET surface area of 90 m^2 g^{-1} and a more frequent pore radius of 8 nm was prepared by thermolysis at 1000 K of $Zr(SO_4)_2 \cdot 4H_2O$ (BDH, analytical grade). Powder X-ray diffraction showed the material to be mainly in the monoclinic form (although a small proportion of the tetragonal phase was also observed). Chemical analysis showed a residual sulfur content of 1.1%. IR spectrometry of CO adsorbed at 77 K on sulfated-ZrO_2 activated at 873 K [24] showed the presence at the oxide surface of several types of Lewis acid centres (coordinatively unsaturated Zr^{4+} ions). Further details on the prep-

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aration and characterisation of this material were given elsewhere [23–25].

For IR studies a quartz cell fitted with NaCl windows was used [33], which allowed *in situ* activation of the sulfated zirconia sample and dosing of the metal carbonyl by vacuum sublimation at 373 K. For activation, a self-supporting wafer of sulfated zirconia was fired for 60 min at 873 K under a dynamic vacuum (residual pressure *ca* 0.01 Pa). Room temperature FTIR transmission spectra were recorded at 3 cm^{-1} resolution by using a Bruker IFS66 spectrometer.

RESULTS AND DISCUSSION

IR spectra (in the CO stretching region) of increasing doses of $Re_2(CO)_{10}$ adsorbed onto the sulfated zirconia wafer are presented in Fig. 1. It has been observed that the final spectrum does not change with time. The blank IR spectrum of the sulfated zirconia shows very weak O—H stretching bands at 3755 and 3650 cm^{-1} (see inset in Fig. 1), thus indicating that a high degree of dehydroxylation was achieved during thermal activation. Bands in the 1450–850 cm^{-1} region (not shown) were assigned, as previously [23,24] to disulfate and monosulfate species having one S=O bond per sulfur atom. Upon dosing with $Re_2(CO)_{10}$, no significant spectral changes were observed in the O—H, S—O and S=O stretching regions. The same behaviour was observed in the case of Group 6 hexacarbonyls [26].

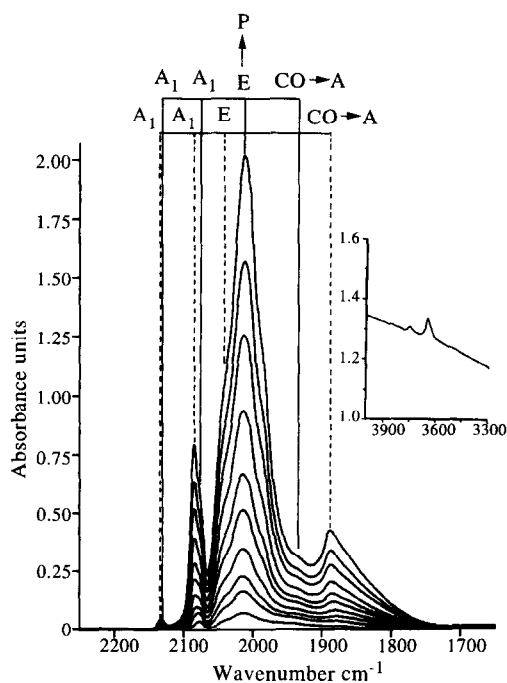IR spectra of the adsorbed metal carbonyl (Fig. 1)

Fig. 1. IR spectra of successive doses of $Re_2(CO)_{10}$ on sulfated-ZrO$_2$. The zirconia blank has been subtracted from each spectrum. Inset shows the blank IR spectrum of the zirconium oxide wafer in the O—H stretching region.

show band maxima at 2135 (w), 2133 (sh), 2084 (m), 2076 (sh), 2044 (sh), 2013 (vs), 1981 (sh), 1933 (w) and 1888 (m). All of these bands grow in parallel when the amount of adsorbed $Re_2(CO)_{10}$ is increased. Dissociation to give free CO ligands was not observed; it would give rise to bands around 2200 cm^{-1} (due to adsorbed CO) as seen for Mo(CO)$_6$ [26], which slightly decarbonylates upon adsorption on sulfated zirconia. This fact provides evidence that $Re_2(CO)_{10}$ is molecularly adsorbed (without decomposition). Interpretation of the complex IR spectra in Fig. 1 requires some brief theoretical considerations.

Free $Re_2(CO)_{10}$ has point symmetry D_{4d} and a CO stretching representation $\Gamma_{CO} = 2A_1 + E_2 + E_3 + 2B_2 + E_1$, where the $2B_2 + E_1$ modes are IR active [34]. The Raman-active modes may become IR-active (although showing very weak intensity) when the molecular symmetry is slightly perturbed: $Re_2(CO)_{10}$ in solution or physisorbed (see Fig. 2) [35]. In cyclohexane solution, the initially IR-active modes were observed [35] at 2070 (B_2), 2014 (E_1) and 1976 (B_2) cm^{-1}. Coordination to a Lewis acid site through an axial CO ligand results in considerable lowering of the stretching frequency of the involved CO, which is decoupled from the remaining nine ligands. For an axially perturbed $Re_2(CO)_{10}$ molecule, with point symmetry C_{4v}, the C—O streching representation is $\Gamma_{C-O} = 2E + B_1 + B_2 + 4A_1$, where the IR active modes of the unperturbed CO ligands are $2E + 3A_1$, as shown in Fig. 2. Thus, the similar compound ax-Mn$_2$(CO)$_9^{13}$CO, where the ^{13}CO group is decoupled from the remaining CO ligands, was reported [36] to give IR absorption bands at 2110 (w, A_1), 2037 (m, A_1), 2013 (vs, E), 1990 (w, A_1) and 1979 (sh, E) cm^{-1}, assigned to the ^{12}CO ligands, and at 1950 cm^{-1}, assigned to the ^{13}CO ligand.

According to the foregoing considerations, the IR absorption maxima in Fig. 1 are assigned in terms of two families of $Re_2(CO)_{10}$ molecules axially anchored to surface Lewis acid sites of different strength (Zr^{4+} ions with different degree of coordinative unsaturation). The bands observed at 1933 and 1888 cm^{-1} are assigned to the anchoring CO ligands, whilst the remaining bands are assigned as shown in Table 1. It is well known [28] that the downward shift of the O-bonded CO increases with increasing strength of the Lewis acid centre, and the same applies to the upward shift of the stretching frequency of the remaining CO ligands. This allowed a correlation to be made between the two low frequency bands and the corresponding high-frequency ones as shown in Fig. 1 and in Table 1. Maxima corresponding to the modes $(A_1 + E)$ associated to the 1888 cm^{-1} band are probably shadowed by the very intense absorption at 2013 cm^{-1}, which dominates the last spectrum of Fig. 1. In fact, the high intensity of the 2013 cm^{-1} band, when compared to the intensity of the related absorption at 1933 cm^{-1}, cannot be explained only in terms of the formation of an acid-base adduct between the metal
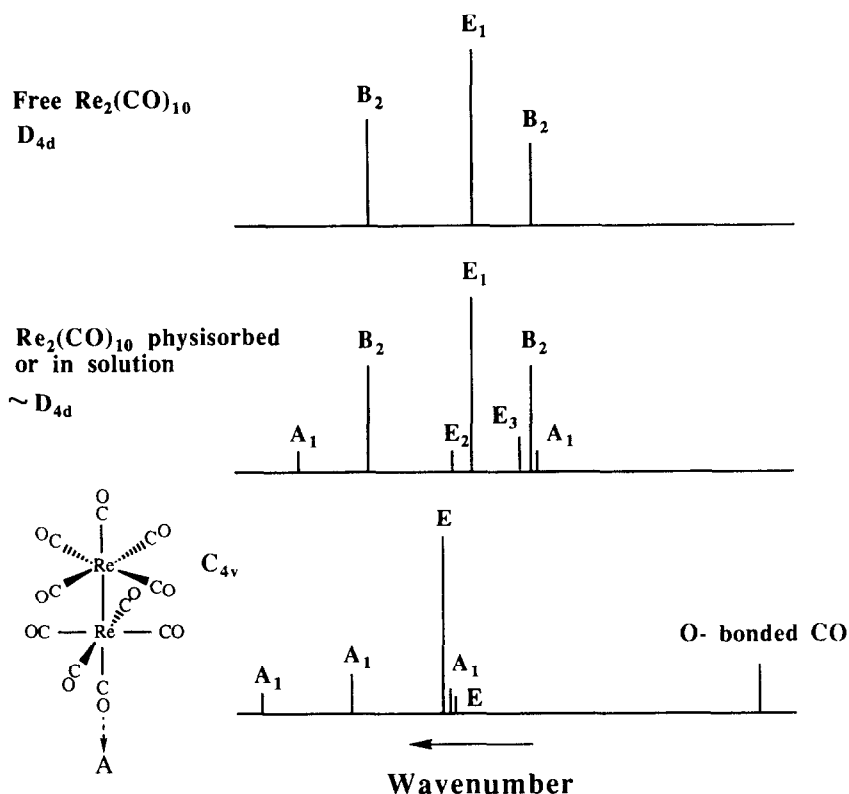
Fig. 2. Scheme showing the IR absorption modes of free and adsorbed $Re_2(CO)_{10}$.

Table 1. Summary of C—O stretching bands

Assignment	v (CO) (cm^{-1})	
A_1	2135	2133
A_1	2084	2076
E	2044	2013
$(A_1 + E)$	—	1981
$CO \rightarrow A$	1888	1933

carbonyl and a Zr^{4+} ion from the surface. The 2013 cm^{-1} band is also assigned to the E_1 mode of slightly perturbed (physisorbed) $Re_2(CO)_{10}$ molecules. The expected weaker B_2 modes (at 1976 and at 2070 cm^{-1}) are very likely to be obscured by other absorption bands in this region of the spectra. 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 $Re_2(CO)_{10}$. It is relevant to add that parallel experiments carried out on a non-sulfated zirconia showed a similar anchoring of the $Re_2(CO)_{10}$ molecules (through an axial CO ligand).

After the last dose of metal carbonyl (spectrum 1 in Fig. 3), the sample wafer was heated inside the IR cell for 5 min at 373 K, allowed to cool down at room temperature and then outgassed for a few minutes.
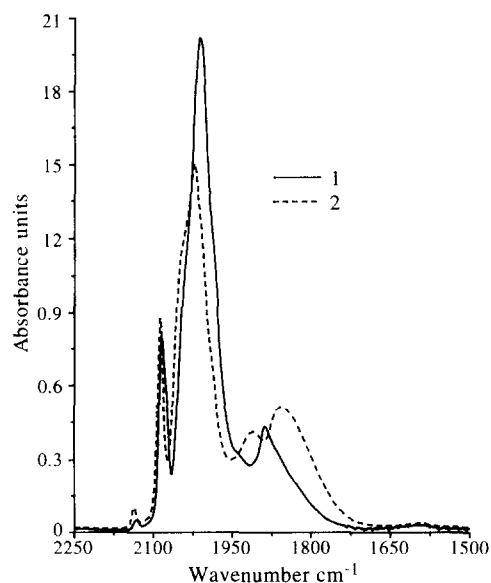

Fig. 3. IR spectra of $Re_2(CO)_{10}$ on sulfated-ZrO_2 immediately after the last dose (1), and after heating 5 min at 373 K (2). The zirconia blank has been subtracted from each spectrum.

The corresponding IR spectrum: number 2 in Fig. 3, shows bands at 2137 (w), 2132 (sh), 2087 (m), 2048 (sh), 2023 (s), 1989 (sh), 1911 (m) and 1856 cm^{-1} (m). It is clearly seen that after the heat treatment at 373

K the bands assigned to the anchoring CO ligand grow and shift to lower wavenumbers. The remaining bands also grow, but shift to higher wavenumbers, except for the 2013 cm^{-1} band, whose intensity decreases. This is consistent with the previous assignment of this band (in part) to a physisorbed species, which would diffuse into the oxide wafer when heated at 373 K causing the carbonyl to chemisorb onto surface available Zr^{4+} ions. The observed frequency shifts suggest that upon mild heating, surface adsorbed Re$_2$(CO)$_{10}$ molecules gain enough energy to diffuse and reach stronger Lewis acid sites, presumably situated inside pores of the solid support.

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