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THE ANCHORING OF [$HFeCo_3(CO)_{12}$] TO OXIDE SUPPORTS

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Summary

The interaction of [$HFeCo_3(CO)_{12}$] (**1**) with oxide supports gives a variety of surface metal carbonyl species, as revealed by IR spectroscopy. Vapour phase adsorption on SiO_2 leaves the starting compound unchanged, whereas on partially hydrated Al_2O_3 and MgO, impregnated in solution, deprotonation of **1** occurs, to give the anion $[FeCo_3(CO)_{12}]^-$ (**2**) linked to the surface. Adsorption of **1** from the vapour phase onto fully dehydrated Al_2O_3 and MgO leads subsequently to cluster decomposition, with the loss of carbon monoxide. The results indicate that the nature of the support and the method of preparation of the supported complex play an important role in forming the surface species.

Introduction

Transition metal clusters have been tested as homogeneous catalysts for a number of reactions [1], but technological problems connected with homogeneous system (especially separation of the catalyst from the reaction products) have turned attention to clusters which are anchored to organic or inorganic supports [2]. In the anchoring process the cluster should ideally maintain its integrity, to give a material with known metal particle size. Two deceptively simple routes have generally been employed for grafting clusters onto inorganic supports (especially oxides): (i) direct interaction of the molecular cluster with the hydroxyl groups of oxides; and (ii) interaction of the molecular cluster with ligand-functionalized oxides or, conversely, interaction of the bridging ligands of the cluster with unmodified oxides.

For instance, in the case of $Os_3(CO)_{12}$ on silica, route (i) gives the surface species [$HOs_3(CO)_{10}(O{-}Si{\equiv})$] through an oxidative addition of the surface silanol groups to Os–Os bonds, as has been elegantly demostrated by IR and Raman spectroscopy, EXAFS and by comparison with well-defined molecular analogues [3,4]. Route (ii)

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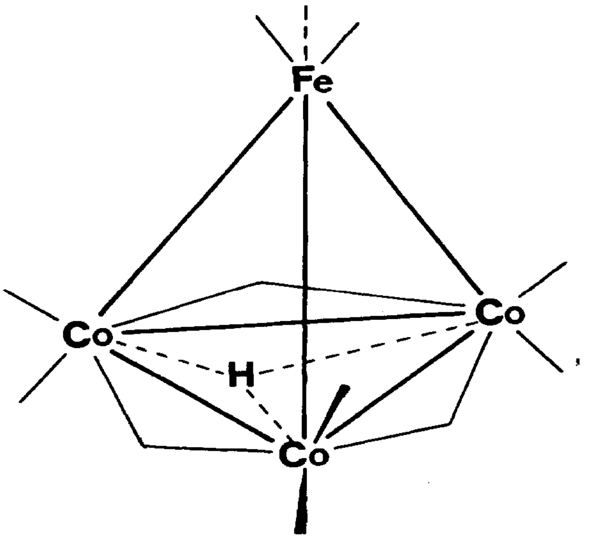

Fig. 1. Structure of $[HFeCo_3(CO)_{12}]$.

has been used to produce cobalt, iridium, ruthenium and osmium clusters grafted to inorganic supports through phosphinated or thiolated chains [5,6].

Simple alternative anchoring route involves the acid-base interaction between hydrido clusters and basic oxides [7,8]. Transition metal hydrides can generally act as Brønsted acids in solution and although few measurements of their pK_a have been reported, general trends have been noted [9]: hydrides of the lighter transition metals are more acidic than those of the heavier ones and bridging hydrides are more acidic than terminal ones. The $[HFeCo_3(CO)_{12}]$ complex (**1**), synthesized by Chini et al. in 1960 [10], fulfils these requirements for strong acidity. Its structure can be inferred from the results of the neutron diffraction study of $[HFeCo_3(CO)_9(P(OMe)_3)_3]$ [11], the hydrogen being located outside the metal cluster in a face-bridging position and 0.987 Å from the Co_3 plane (see Fig. 1). A considerable polarization of the Fe–H bond in the sense $Fe(\delta^-)$–$H(\delta^+)$ has been suggested on the basis of IR studies [12], and the strong acidity shown experimentally by potentiometric titrations [10].

The results of attempts to anchor the cluster **1** onto inorganic oxides, such as SiO_2, Al_2O_3 and MgO, by both liquid and vapour phase impregnation techniques are reported below.

Experimental

(a) Preparation of the complexes

$[HFeCo_3(CO)_{12}]$ and $[FeCo_3(CO)_{12}]^-$ were prepared according to the published procedure [8]. Their purity was checked by IR and mass spectroscopy.

(b) Activation of the supports

"The oxide" SiO_2 (Aerosil, surface area 380 m^2 g^{-1}) was activated by heating in vacuo (1×10^{-5} Torr) at 500°C for 2 h, which left only free surface hydroxyls, with a strong and narrow band at 3750 cm^{-1}.

The aluminium oxide η-Al_2O_3 (surface area 110 m^2 g^{-1}) was heated for 4 h at 600°C, when its IR spectrum showed bands in the 3600–3800 cm^{-1} range assigned to residual surface OH groups [13].

The oxide MgO (surface area 120 m^2 g^{-1}) was prepared by heating $Mg(OH)_2$ at 800°C for 2 h in vacuo. This treatment eliminates all the OH groups and the surface is active towards CO adsorption [14].

(c) Preparation of the supported complex by reactions in solution

All the manipulations were carried out in a glove-box filled with dry nitrogen because of the air-sensitivity of the supported complex.

The activated support (ca. 1 g) was introduced into a 2 × 10 cm chromatographic column and small volume (5–6 ml) of an approximately saturated solution of **1** in $CHCl_3$ was allowed to percolate slowly through it. The column was washed carefully with n-pentane until the solvent remained colorless, and the impregnated support was the evaporated to dryness. IR spectra were taken on disks prepared by pressing the dried support, or on the Nujol mulls. All the samples show increased ν(OH) absorptions, compared with the activated supports, indicating that traces of water had been adsorbed during the handling in spite of careful drying.

(d) Preparation of the supported complex via deposition from the vapour phase

Wafers of the oxides were prepared and activated in a vacuum IR cell, and impregnated by slow sublimation of the complex at room temperature over ca. 1 day: this temperature ensured a reasonably rapid process and avoided any decompostion of the complex.

(e) Apparatus

The IR spectra were obtained on a Perkin–Elmer 580B IR spectrophotometer with data station, using gas-tight IR cells with NaCl windows.

Results and discussion

(1) Heterogenization of the complex 1 on the oxides via the liquid phase

The IR spectra of the supported complexes prepared by solution/support interaction are reported in Fig. 2 and are indicative of the markedly different effect of the supports.

When SiO_2 is used as the support it seems to be unable to adsorb the solute and it remains practically colorless after the percolation of the solution: its IR spectrum reveals only a weak broad band, centered at ca. 2004 cm^{-1}, which is indicative of the presence of trace of complex **2** (vide infra). The percolated solution is apparently unchanged.

When the solution is passed through Al_2O_3 a significant change is observed. Part of the solute is adsorbed onto the support and its colour changes from violet (complex **1**) to dark-brown (complex **2**). The IR spectrum (Fig. 2) shows a striking similarity with that of **2** in solution, small frequency shifts and band broadenings being ascribed to the effect of the support. On the other hand, the absence of any IR bands between 2050 and 2060 cm^{-1} clearly indicates that **1** is completely converted into **2** by the support, as depicted in eq. 1, in which the support S acts as a Brønsted

$$[(\mu_3\text{-H})FeCo_3(CO)_{12}] + S \rightarrow H^+ \ldots S + [FeCo_3(CO)_{12}]^- \qquad (1)$$

base in deprotonating the complex **1**. A closer examination of Fig. 2 shows small differences between the spectra of complex **2** in solution and on Al_2O_3 in the lower frequency range: the medium-strong band at ca. 1813 cm^{-1} (curve **A**) is shifted to 1827 cm^{-1} in the curve **B** in which a new weak band appears at ca. 1860 cm^{-1}. As these bands are readily assigned to the stretching modes of the bridging CO groups, it is plausible to assume that the interaction of **2** with the support can markedly affect the bridging CO groups which lies in the Co_3 plane [9], giving rise to significant frequency shifts or intensity changes of their stretching modes.

MgO has a substantially similar behaviour, but two points must be emphasized. Firstly, the solution-substrate interaction is greater than in the case of Al_2O_3 (the percolated solution was completely colorless); secondly, some chemical changes have begun to occur in the structure of the adsorbed **2**, as indicated by the greater complexity in the low wavenumber range of its IR spectrum (Fig. 2, curve **C**).

Elution by polar solvents, such as methanol or THF, gives complete recovery of the anion $[FeCo_3(CO)_{12}]^-$ which had been adsorbed on the support (Al_2O_3 or MgO), as shown by the IR spectrum of the eluted solution.

(2) Heterogenization of the complex 1 on the oxides by deposition from the vapour phase

The adsorption of **1** in the vapour phase onto SiO_2 is clearly a physisorption

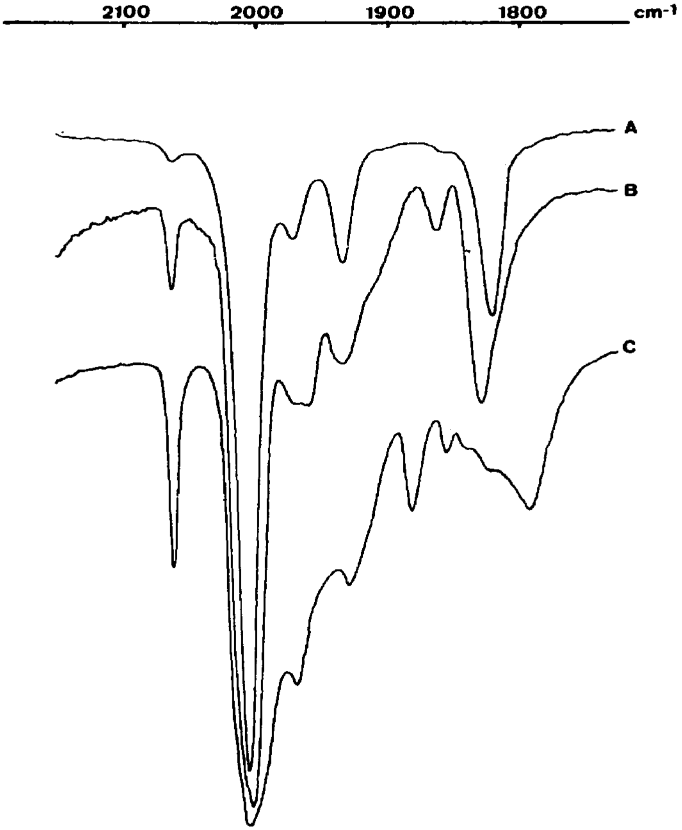

Fig. 2. Spectra of $[FeCo_3(CO)_{12}]^-$ in acetone solution (**A**), and adsorbed (via liquid chromatography) on Al_2O_3 (**B**) and on MgO (**C**).

process, as underlined by the identity of the IR spectra of the supported complex and of the complex in solution (Fig. 3). Heating at ca. 80°C causes a completely irreversible decomposition of the adsorbate.

When **1** is adsorbed on Al_2O_3, more dramatic chemical changes occur, as shown by the IR spectrum (Fig. 4). Even at low coverages (2–4 h of contact), the appearance of a weak band at 2240 cm^{-1}, commonly assigned to the CO group adsorbed on Al^{3+}(cus) sites in tetrahedral coordination [15], is an indication of decomposition of the compound, with CO evolution. The previous experiment with SiO_2 indicates that the decomposition of the complex is not the result of the high vacuum sublimation but clearly occurs because of the interaction with the support. The ν(CO) pattern due to the adsorbed metal carbonyl species is strongly modified compared with the spectrum of **1**, or even of the anionic cluster **2**, and suggests the presence of one or more new $Fe_yCo_x(CO)_z$ species. As the broad ν(OH) adsorption (3600–3800 cm^{-1}) is still present in the strongly dehydrated alumina, it cannot be used to check on the possible transfer of H from the cluster, with hydroxyl formation.

The heating at 50°C completely eliminates the CO adsorbed on Al^{3+}(cus) sites and strongly weakens and modifies the ν(CO) bands in the 2100–1800 cm^{-1} region.

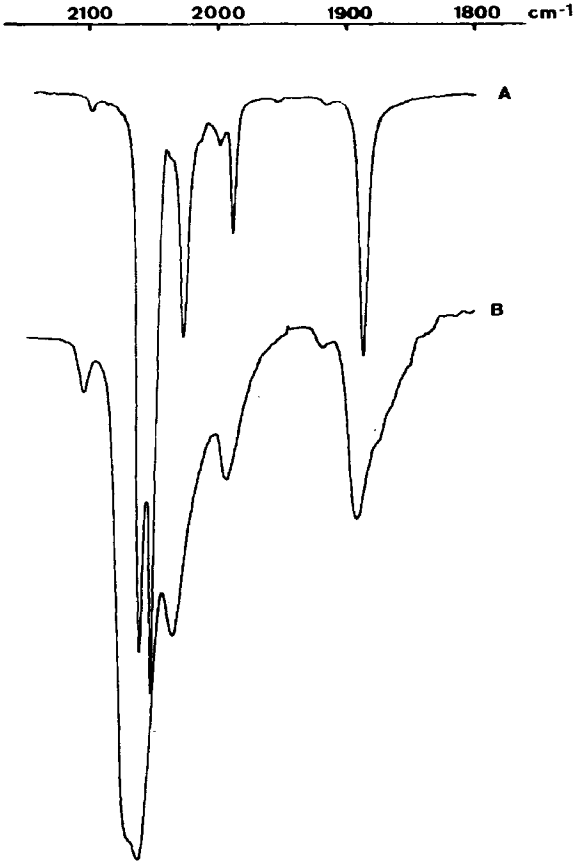

Fig. 3. Spectra of $[HFeCo_3(CO)_{12}]$ in n-heptane solution (A) and adsorbed (by deposition from the gas phase) on SiO_2 (B).

At 80°C the ν(CO) bands disappear completely and are not reformed by increasing the CO pressure; probably a considerable change of the initial $FeCo_3$ cluster has occurred with agglomeration into large clusters [16].

An experiment using hydrated Al_2O_3 (η-Al_2O_3 outgassed at room temperature) gave material with an IR spectrum in the CO stretching region closely similar to that of **2** in solution or adsorbed onto Al_2O_3 by liquid chromatography, but with the bands of CO adsorbed on Al^{3+}(cus) sites absent.

The process of adsorption on MgO is in many instances similar to that on Al_2O_3 and basically consists in a partial fragmentation of **1** with the loss of H and of CO and the formation of new metal carbonyl species. The IR spectrum indicates the presence of new OH groups (a weak band at ca. 3700 cm^{-1}) and of CO adsorbed onto MgO (weak bands at 1630, 1380, 1330 cm^{-1}) [14], together with the ν(CO) pattern in the range 2100–1800 cm^{-1} very similar to that shown by Al_2O_3. As reported above for the supports impregnated in the liquid phase, the MgO spectrum shows broad and strong bands in the low wavenumber CO region which are indicative of an interaction process which is more complex than that which occurs on Al_2O_3, probably because of the more basic character of the support.

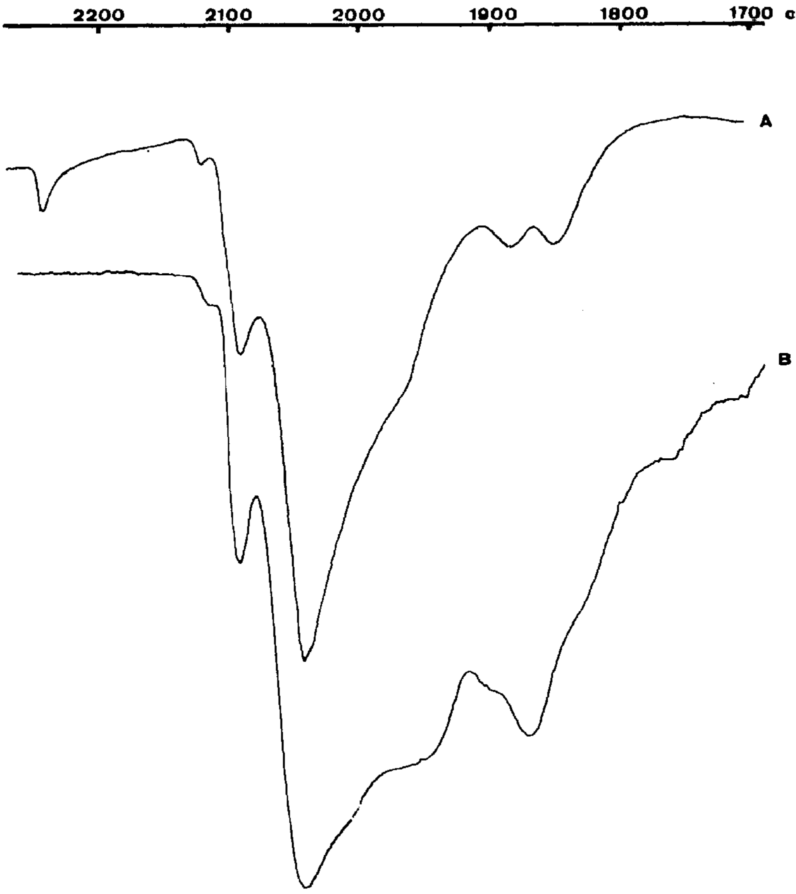

Fig. 4. Spectra of [$HFeCo_3(CO)_{12}$] adsorbed (by deposition from the gas phase) on Al_2O_3 (A) and on MgO (B).

The decarbonylation process under vacuum is nearly complete and irreversible at 80°C: partial readsorption of CO gives material with a different weak ν(CO) band pattern, indicative of destruction of the original $FeCo_3$ framework and of the formation of larger metal agglomerates.

Conclusion

The results are only of a preliminary nature and do not allow final conclusions to be made about the interaction between $[HFeCo_3(CO)_{12}]$ and the various supports. Nevertheless, an attempt to rationalize the experimental data can be made and the following points asserted with some confidence.

(1) At least under some experimental conditions, the interaction of $[HFeCo_3(CO)_{12}]$ with the support is an acid-base reaction, in which the cluster transfers a proton to a basic site on the support, probably an highly activated O^{2-} species. The dissociation of the proton gives rise to the formation of the anionic cluster **2** (eq. 1), which is linked to the surface as the ionic pair $[FeCo_3(CO)_{12}]^-$ M^+, in which M^+ is $Al(O-)^+{}_x$ or $Mg(O-)^+{}_y$. This reaction is an example of the interaction of an hydrido metal carbonyl cluster with an inorganic support in which the stoichiometry of the interaction is clearly established and suggests that an hydrido metal cluster could be initially adsorbed on a basic support as a deprotonated anionic species [7,8]. Because of the strongly acidic character of $HFeCo_3(CO)_{12}$ [10], medium strength bases, such as hydrated Al_2O_3 and MgO [17], are basic enough to give complete deprotonation; the same result has been obtained by using as a basic support silica which has been modified by amino donor functions [18].

(2) The process of adsorption of $[HFeCo_3(CO)_{12}]$ onto stronger bases (fully dehydrated Al_2O_3 or MgO) is more complex and, at present its chemistry has not been ascertained. Deprotonation occurs here also, but it is accompanied by other cluster-support interactions which involve the loss of coordinated CO [19]. We have not obtained evidence as to the nature of the surface species, but the pattern of their IR spectra suggests that they could be chemically well defined and not greatly different from the parent cluster. Undefined larger metal aggregates are formed at moderately increased temperatures.

(3) The support itself and the method of preparation of the supported complex have been shown to play an important role in forming the metal carbonyl surface species. A comparison of the experimental data obtained by different techniques indicates that, when impregnating solutions are used, solvent molecules and/or traces of water may deactivate the most basic centres of the support, substantially changing its properties and, consequently, its interaction with the complex.

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