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Interaction of $Os_3(CO)_{12}$ with Silica and Lanthanum Oxide Supports

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Abstract

Interaction of $Os_3(CO)_{12}$ has been studied with SiO_2 and La_2O_3. On SiO_2, a hydridotriosmiumcarbonyl is formed at 50 °C. The cluster breaks up at 250 °C. On La_2O_3 the osmium cluster breaks up at room temperature forming mononuclear tri- and dicarbonyl osmium species. At 250 °C, only the dicarbonyl survives but the tricarbonyl can be regenerated by treatment with CO.

Introduction

Interaction of metal carbonyl cluster compounds with various supports has been studied extensively in recent years. This is important, first of all. owing to the fact that many of the metal carbonyl clusters are good homogeneous catalysts for a variety of reactions; interaction with the support will heterogenise them, possibly retaining at the same time the high selectivity of the homogeneous catalysts. Besides, partial decarbonylation of the supported clusters may lead to coordinative unsaturation, which is very much necessary for catalysis Finally, complete decarbonylation of the supported carbonyl clusters under milder conditions may lead to the formation of highly dispersed supported metal catalysts.

Most metal clusters, however, break up on interaction with the support. From this point the carbonyl clusters of osmium offer a better possibility because of the presence of strong osmium–osmium bonds, and extensive studies on the interaction of $Os_3(CO)_{12}$ have been made with supports like SiO_2, Al_2O_3, ZnO and MgO [1–5]. On decarbonylation at lower temperature, a surface bound cluster $Os_3(H)(CO)_{10}(OM)$, where M is Si, Al, Zn or Mg, is formed. On further heating at higher temperature, the cluster breaks down to form Os(II) tri- and di-carbonyl species. Collier *et al.* [6], on the other hand, suggest the formation of species $Os_n(CO)_{xn}C_{yn}$ where n can be as high as 12. In this paper we report the interaction of $Os_3(CO)_{12}$ with La_2O_3. Interaction with SiO_2 has also been studied to check whether the cluster breaking as proposed by various authors [1–3, 8] occurs, or the view expressed by Collier *et al.* [6] is correct.

Experimental

The compound $Os_3(CO)_{12}$ was obtained from Strem chemicals. The supports were silica (Davison grade 979; specific surface 280 m^2/g) and La_2O_3 (99.9% purity; specific surface 12 m^2/g). The supports were heated at 400 °C for 4 h and stored in a dessicator. $Os_3(CO)_{12}$ was dissolved in dry HPLC grade hexane and added to the support kept in a flask through which dry helium gas was passed. The mixture was stirred in helium for 4 h. The supernatant colorless solvent was then evaporated by slow heating to obtain a dry mass that was kept under helium. The metal loading was 1% by weight.

A small amount of the sample was quickly transferred into a tube, evacuated to 10^{-4} torr and heated at various temperatures for 2 h, and the spectra were recorded in nujol using a Fourier transform spectrometer Nicolet-170 SX at a resolution 1 cm^{-1}. Infrared spectra were also recorded in a high vacuum IR cell using a thin self-supporting wafer of the sample (~20 mg/cm^2) that could be heated *in situ.*

Diffuse reflectance spectra were recorded on a UV–Vis spectrophotometer (Shimadzu UV-260) using the pure support as the reference.

Results and Discussions

The solution spectrum of $Os_3(CO)_{12}$ showed four infrared bands (2086, 2036, 2016 and 2004 cm^{-1}) in agreement with the literature [7]. The solid state spectrum in nujol shows some extra bands; this finding is very similar to that reported by Collier *et al.* [6]. The spectrum of freshly prepared $Os_3(CO)_{12}/SiO_2$ shows that $Os_3(CO)_{12}$ has remained intact, possibly physisorbed on silica (Fig. 1). Spectra 1C and 1D are obtained by heating $Os_3(CO)_{12}/SiO_2$ at 50 and 125 °C, respectively, under vacuum. These spectra are identical with that reported for $Os_3(H)(CO)_{10}O{-}Si{<}$ [3, 5, 8]. Our results show that the

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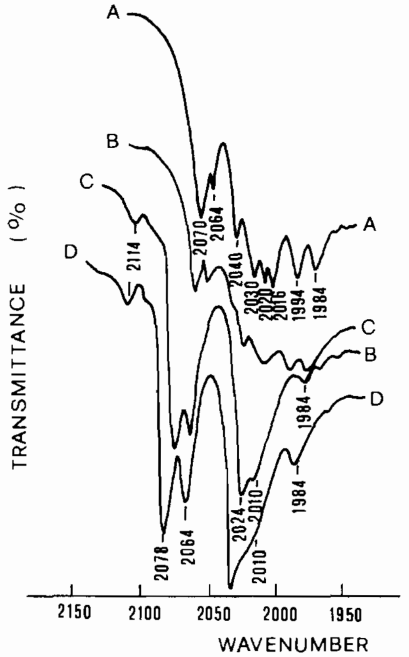

Fig. 1. Infrared spectra in nujol: (a) $Os_3(CO)_{12}$, (b) $Os_3(CO)_{12}/SiO_2$, (c) and (d) are sample (b) after thermoevacuation for 2 h at 50 and 125 °C, respectively.

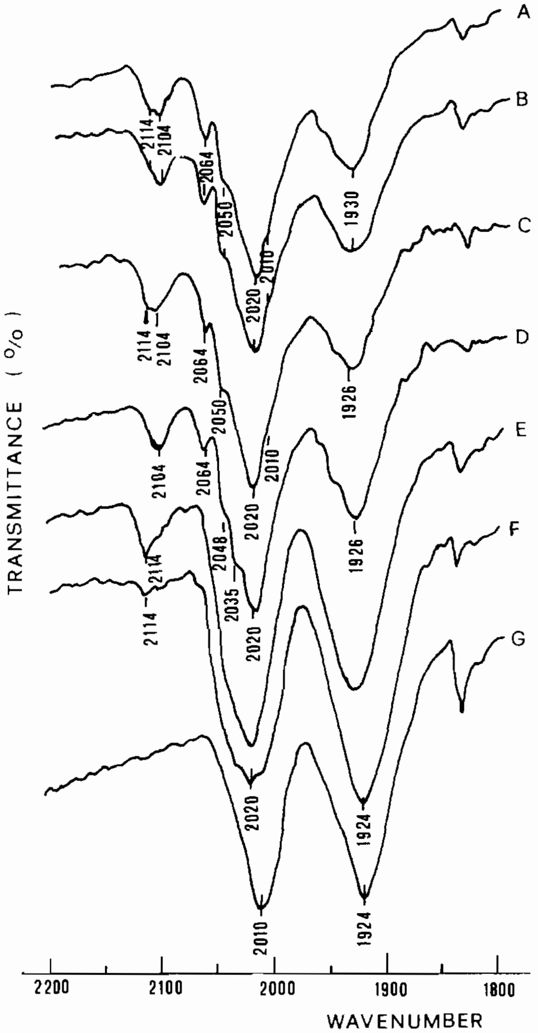

Fig. 2. Infrared spectra in nujol: (a) $Os_3(CO)_{12}/La_2O_3$; (b), (c), (d), (e) and (f) are sample (a) thermoevacuated at 50, 75, 100, 150, 250 and 300 °C, respectively, for 2 h.

surface-bound hydridotriosmium carbonyl species is formed at a much lower temperature than reported earlier and is stable under atmospheric conditions. Hence, it can be used as a heterogenised homogeneous catalyst. The spectra recorded for the wafers in the vacuum cell were very similar to those recorded in nujol. However, on heating the wafer at 250 °C in the vacuum cell, we obtained a three-band spectrum (2130, 2044 and 1964 cm^{-1}) reported by previous authors, but this spectrum was not seen in nujol. This makes it clear that the species responsible for the three-band spectrum on the SiO_2 support are unstable in atmospheric conditions.

The spectrum shown by $Os_3(CO)_{12}$ supported on La_2O_3 is altogether different from those reported so far on other supports (Fig. 2a). The nature of the spectrum remains the same irrespective of whether it is recorded as a wafer in the vacuum cell or as nujol mull. It has three major bands (2114, 2020 and 1930 cm^{-1}), the other bands being at 2064, 2050, 2010 cm^{-1}. On heating to 150 °C, it becomes a clear three-band spectrum; the band at 2114 cm^{-1} completely disappears at 250 °C. Decarbonylation is complete at 300 °C; the band 1830 cm^{-1} is due to La_2O_3. We believe that the minor infrared bands observed on fresh $O_3(CO)_{12}/La_2O_3$ are due to a small amount of $Os_3(CO)_{12}$, and the three major bands are either due to $Os(II)(CO)_3$ and $Os(II)(CO)_2$ as suggested by Gates [1, 2] and others [3, 8] or due to $Os_n(CO)_{xn}(C)_{yn}$ as suggested by Collier *et al.* [6] in the case of silica supported samples. In the case of La_2O_3, the bands are shifted to lower frequencies by about 20 cm^{-1}. Whatever the species may be, they are formed on La_2O_3 at preparation temperature and not at 250 °C as in the case of SiO_2. Figure 3 shows the spectra when recorded in the vacuum cell as wafers. The band at 2114 cm^{-1} disappears at 250 °C, but reappears again on treatment with CO at that temperature, showing the reversible nature of the interaction.

Next we shall take up the question of cluster breaking on interaction of $Os_3(CO)_{12}$ with the support. The reflectance spectra of the samples are shown in Fig. 4. Based on the work of Tyler *et al* [9], the two bands at 324 and 394 nm for fresh $Os_3(CO)_{12}/SiO_2$ may be assigned to transitions within the triangular osmium frame. On heating to 125 °C in vacuum, an additional band appears at 358 nm. One can conclude that the osmium cluster is intact at this

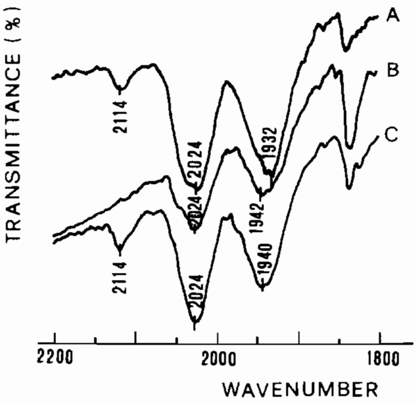

Fig. 3. Infrared spectra of $Os_3(CO)_{12}/La_2O_3$ in vacuum cell. (a) and (b) are thermoevacuated at 150 and 250 °C; (c) sample (b) after treatment with CO at 250 °C and 50 torr.

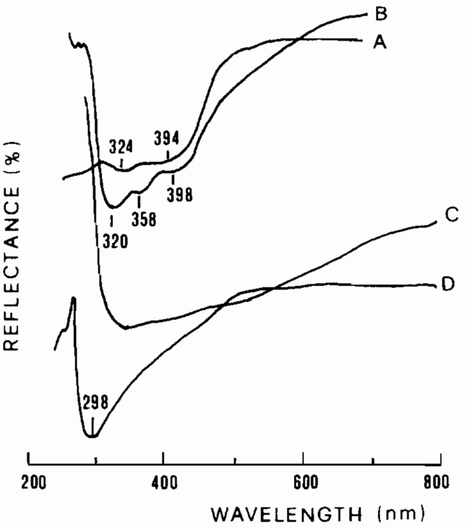

Fig. 4. Reflectance spectra: (a) $Os_3(CO)_{12}/SiO_2$; (b) and (c) are sample (a) heated in vacuum at 125 and 250 °C; (d) $Os_3(CO)_{12}/La_2O_3$.

temperature. On heating to 250 °C, the electronic transitions due to the osmium ring disappear, indicating breaking up of the cluster. In the case of $Os_3(CO)_{12}/La_2O_3$, even the fresh sample does not show any transitions due to the osmium ring. The three-band infrared spectrum for the silica and La_2O_3 supported material, then, should be assigned to mononuclear osmium carbonyls. Thus, it appears that the cluster actually breaks down, and further growth of the cluster as suggested by Collier *et al.* [6] is not occurring.

Figure 3 shows that when $Os_3(CO)_{12}/La_2O_3$ is heated to 250 °C, the band at 2114 cm^{-1} disappears and that at 2024 cm^{-1} is appreciably weakened. Further loss of CO is apparent from the loss of intensity of the carbonyl bands. On treatment with CO at 250 °C, the original spectrum reappears. Knözinger and Zhao [4] argued that $Os(II)(CO)_3$ and $Os(II)(CO)_2$ each should give rise to a two-band spectrum. The three-band spectrum, then, can be taken as a superimposition of these due to the two species. This assignment gains support from the fact when the two-band spectrum changes back to the three-band one on treatment with CO, the relative intensity of the 2024 cm^{-1} band increases, suggesting that it is a composite peak. At 250 °C, only the dicarbonyl species survives, but the tri-carbonyl species can be regenerated by treatment with CO.

When $Os_3(CO)_{12}/La_2O_3$ is heated at 300 °C, decarbonylation is complete. By treating the resulting sample with CO at 300 °C, the carbonyl spectrum can not be regenerated.

Conclusions

On silica support, $Os_3(CO)_{12}$ forms a surface-bound hydridotriosmiumcarbonyl that is stable in the atmosphere. On heating at 250 °C, the cluster breaks up. On La_2O_3 support, the cluster breaks up at the preparation stage, possibly forming a mixture of mononuclear carbonyl species. At 250 °C, only the dicarbonyl is stable, but the tricarbonyl can be regenerated by treatment with CO.

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