Catalysis by Osmium Metal Clusters

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Recent studies of catalysis by supported metal cluster compounds have shown that these systems exhibit novel behaviour. Although difficult to characterise, by using a combination of analytical techniques an overall picture can be developed of the cluster nuclearity and the number and type of ligands present. Chemisorption and catalytic studies have both shown behaviour fundamentally different from that obtained with conventional metal catalysts.

Over the last decade the interest in the use of metal cluster compounds, especially the carbonyls, as catalysts has grown steadily (1). This area of research has many attractions, state-of-the-art preparative inorganic chemistry coupled to catalysis using defined molecular species, sounds too good to be true; and it is. The obvious attractions are well balanced initially by often difficult preparations with low yields but may be heavily counter-balanced by the difficulties of characterising the catalytically active species when it is a small metal cluster compound. In the last five years we have been involved in a major study of catalysts prepared from supporting osmium carbonyl cluster compounds on materials such as silica, alumina,

and titania. In this review we will briefly examine the characterisation, chemisorptive behaviour, and catalysis of these systems and give a biased view on where cluster catalysis may go in the future.

Characterisation

Without doubt unequivocal characterisation of supported cluster compounds is a difficult, if not impossible, task. In our attempts to characterise these species we have used infrared and ultraviolet-visible spectroscopies, temperature programmed decomposition, electron microscopy and Extended X-ray Absorption Fine Structure (EXAFS) analyses; none of these techniques on their own was definitive
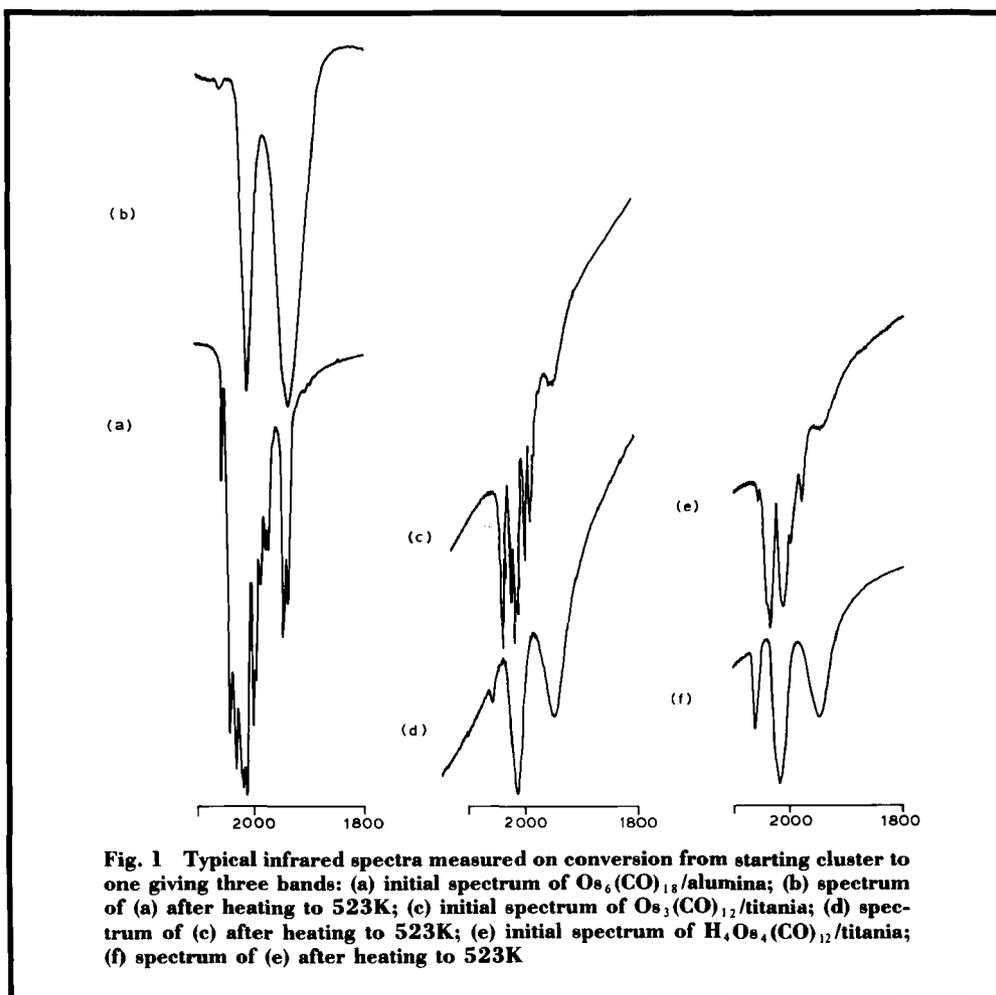
Table I

Characteristics of Temperature Programmed Decomposition of Osmium Cluster Catalysts

Catalyst	Loss[a] per cent	Products of T.P.D. per cent			CO-ligands retained per Os
		CO	CO_2	$C_2H_4 + C_2H_6$	
$Os_3(CO)_{12}/Al_2O_3$	40	88	9	3	2.2
$Os_3(CO)_{12}/SiO_2$	27	92	8	0	2.8
$Os_6(CO)_{18}/SiO_2$	5	0	100	0	2.8
$Os_6(CO)_{18}/TiO_2$	27	82	16	2	2.0
$H_4Os_4(CO)_{12}/TiO_2$	18	45	50	5	2.2
$H_4Os_4(CO)_{12}/Al_2O_3$	13	39	60	1	2.4

(a) Total carbon loss expressed as the percentage of CO-ligands converted to products

but taken together a consistent description of the systems can be achieved. Catalysts prepared from $Os_3(CO)_{12}$, $Os_6(CO)_{18}$, $H_4Os_4(CO)_{12}$, and $H_2Os_{10}C(CO)_{24}$ supported on silica, alumina, and titania were characterised after impregnation of the cluster onto the support and after temperature programmed decomposition (heating to 523K) (2). Immediately after impregnation both infrared and ultraviolet-visible spectroscopies indicated that the majority of the starting cluster was intact on the support although bands not attributable to the starting cluster were apparent. On heating the samples both carbon monoxide and carbon dioxide were produced and by 473K the bands

not attributable to the starting cluster were the dominant features in the spectra; by 523K they were the only features of the spectra. Table I and Figure 1 show typical results; there is significant ligand retention and the three band infrared spectrum is common to all the samples. However we needed to know whether the species formed after heating was a cluster. To answer this question we turned to ultraviolet-visible diffuse reflectance spectroscopy and EXAFS. A study by Tyler, Leverson and Gray (3) on the ultraviolet-visible absorbance spectra of $Os_3(CO)_{12}$ assigned bands at 330 and 385nm to $\sigma \rightarrow \sigma^*$ and $\sigma^{*1} \rightarrow \sigma^*$ transitions, that is transitions involving orbitals

Fig. 1 Typical infrared spectra measured on conversion from starting cluster to one giving three bands: (a) initial spectrum of $Os_6(CO)_{18}$/alumina; (b) spectrum of (a) after heating to 523K; (c) initial spectrum of $Os_3(CO)_{12}$/titania; (d) spectrum of (c) after heating to 523K; (e) initial spectrum of $H_4Os_4(CO)_{12}$/titania; (f) spectrum of (e) after heating to 523K

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Table II

Peak Maxima in Ultraviolet/Visible Absorbance and Reflectance Spectra

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Sample		Band maxima (nm)			
$Os_3(CO)_{12}$ [a]	244	289	329	394	
$Os_6(CO)_{18}$ [a]	209,242	296		355,394	442,463,530,595
$Os_3(CO)_{12}/Al_2O_3$ [b]	223,233	273,286	320	394	540,613,870
$H_4Os_4(CO)_{12}/SiO_2$ [b]	220	279		352,397	476 597,869
$Os_6(CO)_{18}/Al_2O_3$ [b]	226,231	269,283	317	394	540,613
	M.L.C.T. [c]	Unassigned	$\sigma \rightarrow \sigma^*$ and $\sigma^{*\,1} \rightarrow \sigma^*$ transitions		Unassigned

(a) In solution in cyclohexane
(b) Reflectance spectra after samples had been heated to 523K
(c) M.L.C.T. = metal-ligand charge transfer

associated with Os-Os bonds. Table II shows the bands in this region of the spectrum for various clusters and catalysts, clearly the bands are present on the samples after heating, indicating a retention of Os-Os bonding. However a more definitive answer was given by EXAFS. Figure 2 shows the EXAFS spectra of $Os_6(CO)_{18}$/alumina after heating to 523K (4) and that of a conventional osmium/silica catalyst; clearly interpretation of the spectra is not simple, but the important points are (i) Os-Os bonding was retained, (ii) the cluster species did not have the same spectra as bulk metal, and (iii) the average co-ordination number for nearest neighbour osmium atoms was 4. Therefore the species on the support was a cluster. A full analysis of an $H_2Os_{10}C(CO)_{24}$/alumina catalyst has shown that the tetra-capped octahedral skeleton is intact after activation (5).

The infrared spectra obtained exhibited three bands, shown in Figure 1. The band at $2030cm^{-1}$ is typical of carbon monoxide linearly bonded to zero valent osmium, while we have assigned the low frequency band to carbon monoxide linearly bonded to osmium in a δ-negative valence state and the high frequency band to carbon monoxide bonded to osmium in a δ-positive valence state.

From the temperature programmed decomposition experiments, the number of carbonyl ligands retained during the heating process was known; however for catalysis to occur some degree of co-ordinative unsaturation must be present. We investigated this via the chemisorption behaviour of the cluster catalysts.

Chemisorption

The chemisorptive properties of the supported osmium clusters were investigated using carbon monoxide and oxygen as adsorbates (6). Typical adsorption isotherms are shown in Figure 3. Although the carbon monoxide isotherms are typical for the cluster catalysts they are not typical for carbon monoxide adsorption on conventional metal catalysts; the difference lies in the slowly rising part of the isotherm above 0.2 Torr. Below 0.2 Torr there is rapid adsorption of the gas on free metal sites, above there is slow adsorption on sites which have been produced during the thermal activation. These sites we have designated "ligand-C"; they are produced when two carbonyl ligands react to give carbon dioxide, $2CO \rightarrow CO_2 + C$. The adsorption on ligand-C by carbon monoxide is reversible at 293K whereas adsorption on the metal is not. The carbon monoxide can be desorbed from the metal sites by heating to 523K. By this method the adsorption/desorption cycle can be repeated time and time again. When carbon monoxide is adsorbed, carbonyl ligands are still present on the cluster and by adsorbing labelled [^{18}O] carbon monoxide it was possible to show that only
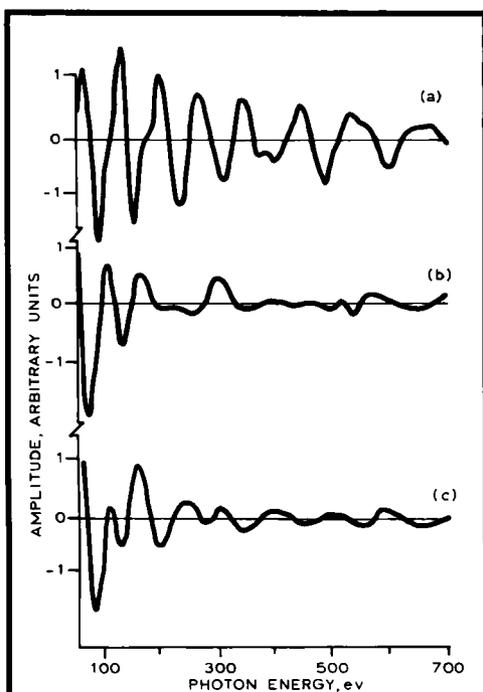
Fig. 2 EXAFS spectra of (a) a conventional silica-supported osmium catalyst prepared from the trichloride; (b) an $Os_6(CO)_{18}$/alumina catalyst after heating to 523K; (c) freshly impregnated $Os_6(CO)_{18}$/alumina
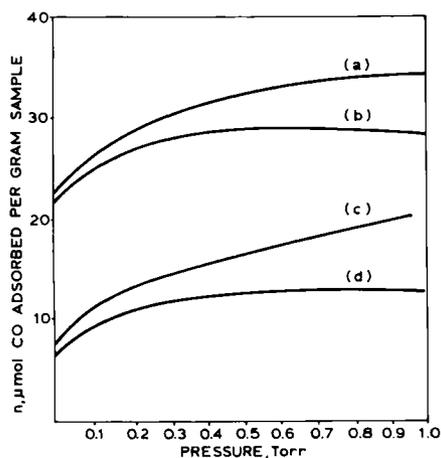
Fig. 3 Carbon monoxide and oxygen adsorption isotherms:
(a) CO adsorption on $H_4Os_4(CO)_{12}$/titania;
(b) O_2 adsorption on $H_4Os_4(CO)_{12}$/titania;
(c) CO adsorption on $Os_6(CO)_{18}$/alumina;
(d) O_2 adsorption on $Os_6(CO)_{18}$/alumina

labelled carbon monoxide was desorbed; no isotopic scrambling took place even at a temperature of 523K (6, 7).

Oxygen adsorption looked at first sight similar to adsorption on conventional metal catalysts, however the energetics of the adsorption were fundamentally different from conventional metal catalysts. On heating to 523K all the oxygen was desorbed from the surface without any reaction with the carbonyl ligands. This weak bonding (for oxygen) was found to have interesting consequences when the catalytic behaviour of these systems was subjected to a thorough examination.

Catalysis

Four reactions were studied in detail over the osmium cluster catalysts; the hydrogenation of ethene, carbon monoxide and carbon dioxide, and the hydrogenolysis of ethane (7, 8). We will consider each of the reactions in turn and compare them with results from conventional catalysts. However certain aspects of the catalysis were common to all the reactions and their implications will be considered first.

One aspect of the novel chemistry encountered with cluster catalysts, which was common to all, was their insensitivity to poisoning by air/oxygen (9). An active cluster catalyst could be removed from a reactor, exposed to air, replaced in the reactor and reaction continued at the same rate as before without any induction period. The process was repeatable and the length of time the catalyst was exposed to air made no difference (Table III). The reason for this insensitivity is related to the strength of oxygen adsorption on the osmium clusters. Because the osmium is already engaged in bonding to the carbonyl ligands, to other osmium, to the support, and to ligand-C, the bonding to adsorbed oxygen is weak. As a consequence oxygen does not dissociate on adsorption, contrary to the behaviour on osmium metal. Another general aspect of the catalytic chemistry of these systems was the non steady-state. When any of the reactant mixtures were passed over the catalysts there occurred a period of non steady-state behaviour (8). The

Table III

### Activities of Cluster-Derived Catalysts Before and After Exposure to Air at 293K [a]

Catalyst	Initial rate before exposure to air[b]	Duration of exposure, hours	Initial rate after exposure to air
$Os_3(CO)_{12}/Al_2O_3$	1.1	0.2	1.1
		2.0	1.1
		24.0	1.1
$Os_6(CO)_{18}/TiO_2$	2.8	0.2	2.8

(a) Reaction, $C_2H_4 + H_2 \rightarrow C_2H_6$ at 435K and a pressure of 100Torr
(b) Rates μmol/min/g catalyst

form this behaviour took is shown in Figure 4; initially the activity increased to a maximum then decreased to the steady-state value. During this behaviour carbonaceous material was deposited on the catalyst and the maximum in activity was reached when the amount deposited was equal to the number of sites. Our interpretation of this behaviour is that the deposited material acts as a hydrogen-transfer agent which is more efficient for hydrogen transfer than the osmium metal sites. As the amount deposited increases so does the rate until every site has a deposit, at this point a maximum is reached. The decrease in activity is due to site blocking effects and steric hindrance as deposition continues. One other general aspect of the catalytic behaviour of these osmium cluster catalysts, which is specific to them, was the variation in activity which follows the shift in frequency of the low frequency infrared band (Figure 5). The variation in position of this band is caused by differing amounts of electron-density being transferred from the support to the osmium. Therefore when there is the largest transfer of electron-density the Os-C bond is strengthened and the C=O bond weakened due to increased back-bonding from the osmium into the anti-bonding orbitals of the carbon monoxide. The effect this has on the catalytic activity can be explained by changes in the strength of adsorption brought about by the varying electron-density. When there is a large amount of transfer the chemisorptive bond is strong and hence activity low; as the amount transferred decreases the activity increases with
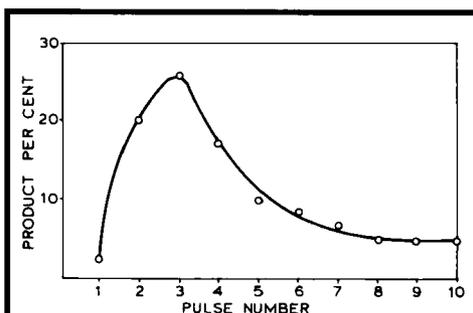
Fig. 4 Typical non-steady state behaviour, showing an increase in rate to a maximum followed by a decrease to the steady state value. Carbon monoxide hydrogenation to methane over an $Os_3(CO)_{12}/silica$ catalyst
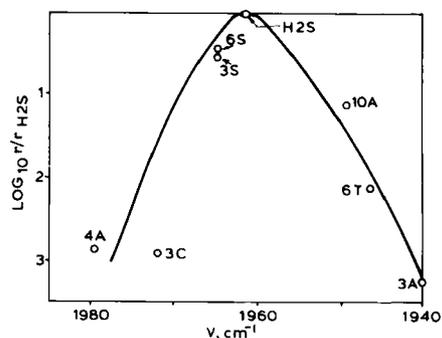
Fig. 5 Volcano relationship for CO hydrogenation. Rates, r (mol/s/g) divided by that for $H_2Os_3(CO)_{10}/silica$ (H2S). Codes, 3 = $Os_3(CO)_{12}$, 4 = $H_4Os_4(CO)_{12}$, 6 = $Os_6(CO)_{18}$, 10 = $H_2Os_{10}C(CO)_{24}$, H2 = $H_2Os_3(CO)_{10}$, S = silica, A = alumina, T = titania, C = ceria

Catalyst	Reaction			
	$C_2H_4 + H_2 \rightarrow C_2H_6$ [c]		$CO + 3H_2 \rightarrow CH_4 + H_2O$ [d]	
	Ea	$\log_{10}r_{390}$	Ea	$\log_{10}r_{605}$
$H_2Os_3(CO)_{10}/SiO_2$	42(378–406K)	0.25	114(485–561K)	0.03
$Os_3(CO)_{12}/Al_2O_3$	50(390–500K)	–1.65	95(540–645K)	–3.21
$Os_3(CO)_{12}/TiO_2$	44(355–390K)	–0.15	93(485–570K)	–0.62
$Os_6(CO)_{18}/SiO_2$	41(385–425K)	–0.09	73(590–665K)	–0.32
$Os_6(CO)_{18}/TiO_2$	45(325–425K)	–0.54	80(465–605K)	–2.00
$H_2Os_{10}C(CO)_{24}/Al_2O_3$	53(520–590K)	–2.25	122(520–590K)	–1.07
Os/Al_2O_3	35(290–320K)	[e]	119(500–560K)	–0.09 [f]

reducing strength of adsorption until a maximum is reached. Further reduction in the strength of adsorption causes a reduction in the concentration of reactive species and a subsequent reduction in activity.

The hydrogenation of ethene over the osmium cluster catalysts required a significantly higher temperature than that required over a conventional metal catalyst, similarly the activation energies were also higher than those found with a conventional osmium catalyst (Table IV). Positive orders of reaction in ethene for the cluster catalysts compared with zero order for conventional catalysts suggested that ethene adsorption on the cluster catalysts is weak. Hence higher temperatures are required to obtain measurable rates from low steady-state concentrations of adsorbed ethene. Therefore for this reaction the behaviour of the cluster catalyst is similar to that of a carbon monoxide poisoned conventional osmium catalyst.

Carbon monoxide hydrogenation over the cluster catalysts was, for the most part, similar to carbon monoxide hydrogenation over conventional catalysts: the activation energies were similar and the products (methane and carbon dioxide) were similar. However, generally the cluster catalysts were significantly less active than their conventional counterparts, although some (notably the silica supported) were as active (Table IV). As the carbonyl ligands are re-

tained throughout the hydrogenation reaction these results may suggest that on a conventional catalyst there is a significant proportion of
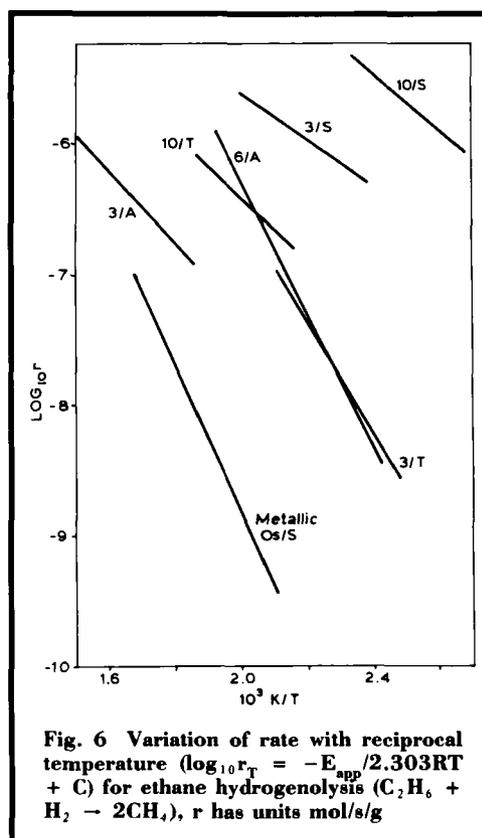
Fig. 6 Variation of rate with reciprocal temperature $(\log_{10}r_T = -E_{app}/2.303RT + C)$ **for ethane hydrogenolysis** $(C_2H_6 + H_2 \rightarrow 2CH_4)$, **r has units mol/s/g**

inactive carbon monoxide present on the surface during hydrogenation.

The hydrogenolysis of ethane to methane was the one structure sensitive reaction studied and again there were differences between the cluster catalysts and conventional catalysts. For this reaction the activation energies were lower and the activities significantly higher than conventional osmium catalyst, see Figure 6. This was the first indication that cluster catalysts could outperform conventional systems. The reason for this superior activity comes about, we believe, due to a change in reaction mechanism when osmium cluster catalysts are used. Because the cluster has a limited number of sites the ethane may not fully dissociate (that is $C_2H_6 \rightarrow$ C-C + 6H), as is the case with conventional osmium catalysts, but retains most of its hydrogen prior to C-C bond rupture.

The Future

Research is continuing and will continue into heterogeneous catalysis by supported metal cluster compounds but the era of them being the "great white hope" for catalysis, if it ever existed, is now dead. These catalysts should be studied for their own sake and for the insight they can give into conventional catalysis but not as the wonder catalysts of the future. Only in the area of structure sensitive reactions do cluster catalysts hold any promise in terms of "applied catalysis" and even here the activity and/or selectivity enhancement would have to be spectacular to overcome the negative aspect of cluster production on a large scale. Even so, cluster catalysts do exhibit novel behaviour, an understanding of which may lead to a questioning of long held beliefs in catalysis or greater insight into areas which are ill understood. Support interactions is one area where we believe cluster catalysts may give us information not readily available from conventional catalysts. Site interactions, which are exceedingly difficult to study in conventional catalysts, are far more open for study when the number of atoms in a cluster is limited, the ligands specified and the geometry known. None of these answers will be easy to obtain but the possibilities are there for using cluster catalysts to help our understanding of fundamental aspects of catalytic chemistry.

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Transparent Platinum Films

When prepared by a conventional evaporation technique, a film of platinum 33 nanometres thick will transmit only about 3 per cent of light. However, workers at two Bell establishments in Murray Hill, New Jersey have reported that the same thickness of film prepared by photoelectrodeposition onto indium phosphide can transmit as much as 92 per cent of light at wavelengths between 210 and 750 nm (A. Heller, D. E. Aspnes, J. D. Porter, T. T. Sheng and R. G. Vadimsky, *J. Phys. Chem.*, 1985, **89**, (21), 4444–4452).

Although this high transparency is due partially to porosity in the film, it is achieved mainly by controlling the microstructure of the deposit so that the particles which make up the film are small, compared with the wavelength of the light, and are not well connected.

The work reported may lead to several new areas of research.