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Mononuclear and Trinuclear Osmium Carbonyl Catalysts Supported on SiO_2, Al_2O_3, TiO_2, and ZnO

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Most supported-metal catalysts consist of a variety of metal aggregates with poorly defined structures. Structurally defined supported metals have been prepared by bonding metal clusters to supports through pendant surface ligands like phosphines (*1*), but these are expected to lack the stability required for most catalytic applications.

Preparation of discrete metal clusters on supports like SiO_2 and Al_2O_3 without the pendant ligands has been attempted, but most investigators have formed species with undetermined structures. Robertson and Webb (*2*), however, brought solutions of $[Ru_3(CO)_{12}]$ in contact with silica and found that at temperatures $<127°C$, the trinuclear cluster framework was apparently supported intact; the solid was catalytically active for isomerization of 1-butene. As temperature was increased, the activity decreased, and a new carbonyl spectrum was formed; Robertson and Webb speculated that mononuclear ruthenium formed, and a comparison of the infrared spectrum (*2*) with the spectra of complexes $[Ru(CO)_2X_2]$ (X = Cl, Br, or I) (*3*) substantiates the identification. In related studies, the presence of the following supported clusters was inferred: hexarhodium on Al_2O_3 (*4–6*), triosmium on SiO_2 and η-Al_2O_3 (*7*), and tri-iron on Al_2O_3 and MgO (*8*).

In the work reported here, mononuclear and trinuclear osmium complexes were brought in contact with surfaces of SiO_2, Al_2O_3, TiO_2, ZnO, and the resulting surface species were characterized by carbonyl infrared spectroscopy. The spectra indicate the formation of either atomically dispersed or trinuclear supported osmium, the former being stable at 400°C and catalytically active for hydrogenation of ethylene and hydrogenation of CO to give methane.

Supported-osmium catalysts were prepared by contacting a refluxing *n*-octane solution containing $[Os_3(CO)_{12}]$ with γ-Al_2O_3 (Ketjen), TiO_2 (anatase) (prepared in this laboratory by Gajardo, Saito, and Katzer), SiO_2 (Ketjen), or ZnO (Kadox 15) having surface areas of 185, 120, 382, and 20 m^2/g, respectively. The supports had been partially dehydroxylated by treatment with flowing nitrogen at 300°C. The samples were pressed into wafers and placed in conventional cells (under N_2). Their spectra were determined with a Nicolet 7000 Fourier transform infrared spectrometer. The spectra of the surface-bound osmium (Fig. 1, Table 1) are nearly identical to those of the molecular clusters formed by reaction of $[Os_3(CO)_{12}]$ with water, alcohols, phenols, thiols, or amines (Table 1).[2] These comparisons strongly suggest that the surface osmium species were formed by reaction of $[Os_3(CO)_{12}]$ with surface M–OH groups to give CO and the following sur-

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[2] These spectra are clearly different from those of $[Os_3(CO)_{12}]$ physically adsorbed on silica, which was prepared by contacting the solid with a solution of $[Os_3(CO)_{12}]$ in *n*-octane at room temperature (Table 1).

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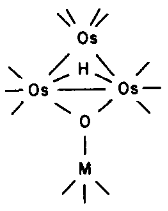
TABLE 1

Infrared Characterization of Molecular and Surface-Bound Triosmium Clusters

Cluster	ν_{CO} (cm^{-1})	Ref.
Molecular		
$[\mathrm{Os_3(CO)_{12}}]$	2069vs, 2035vs, 2015m, 2000m	This work
$[\mathrm{HOs_3(CO)_{10}OCH(CH_3)_2}]$	2110w, 2070s, 2059ms, 2023vs, 1998m, 1988	(*9*)
$[\mathrm{HOs_3(CO)_{10}OH}]$	2110w, 2072s, 2060m, 2027vs, 2025sh, 2006m	(*11*)
$[\mathrm{HOs_3(CO)_{10}SC_6H_5}]$	2106m, 2067vs, 2057s, 2024vs, 2018s, 2000s, 1980m	(*10*)
$[\mathrm{HOs_3(CO)_{10}(HN\text{-}}n\mathrm{\text{-}Bu)}]$	2103w, 2065s, 2050m, 2021s, 2002s, 1989m	(*12*)
$[\mathrm{HOs_3(CO)_{10}{-}O{-}Si(Ph)_3}]$	2107w, 2069s, 2055s, 2017s, 1997m, 1980m, 1907w, 1887w	(*7*)
Physically adsorbed		
$\mathrm{Os_3(CO)_{12}/\gamma\text{-}Al_2O_3}$	2069vs, 2035vs, 2015m, 2000m	This work
Surface-bound		
$\mathrm{HOs_3(CO)_{10}{-}O{-}Al}\begin{smallmatrix}/\\-\\\backslash\end{smallmatrix}$	2107w, 2068s, 2056s, 2023vs, 2005m	This work
$\mathrm{HOs_3(CO)_{10}{-}O{-}Al}\begin{smallmatrix}/\\-\\\backslash\end{smallmatrix}$	2109w, 2070m(sh), 2058s, 2030vs, 2018s, 2012s, 2000ms, 1990m(sh)	(*7*)
$\mathrm{HOs_3(CO)_{10}{-}O{-}Ti}\begin{smallmatrix}/\\-\\\backslash\end{smallmatrix}$	2107mw, 2067s, 2055s, 2026s,b, 2010m, 2000sh	This work
$\mathrm{HOs_3(CO)_{10}{-}O{-}Zn}\begin{smallmatrix}/\\-\\\backslash\end{smallmatrix}$	2107m, 2067s, 2050s, 2030vs, 2006m, 2000sh	This work
$\mathrm{HOs_3(CO)_{10}{-}O{-}Si}\begin{smallmatrix}/\\-\\\backslash\end{smallmatrix}$	2115m, 2080s, 2067s, 2031s, 2013sh, 1995sh	This work
$\mathrm{HOs_3(CO)_{10}{-}O{-}Si}\begin{smallmatrix}/\\-\\\backslash\end{smallmatrix}$	2122w, 2088s, 2075s, 2037vs(br), 1955w(sh)	(*7*)

face-bound hydridotriosmium clusters:



I M = Si, Al, Ti, or Zn

The structure of the silica-supported cluster has recently been suggested in a communication by Smith *et al.* (*7*), whose results showed that about two molecules of CO were evolved per supported cluster, while no significant H_2 or CO_2 evolution was detected. Smith *et al.* also observed infrared bands of the surface cluster similar to those of the aforementioned molecular clusters (Table 1).

When the surface-bound triosmium clusters were heated to temperatures between 100 and 400°C under He, H_2, or CO at atmospheric pressure, CO and CH_4 were evolved (as determined by glc analysis of the effluent gas), the carbonyl bands disappeared, and a new set of bands simultaneously formed (Fig. 1).[3] Evidently a new surface osmium carbonyl species (designated **II**) was formed. The spectra showed

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[3] TiO_2-supported **I** was air sensitive, the infrared spectra showing that its structure changed (in an uncharacterized way) upon contacting O_2. Samples were handled appropriately, and we infer from infrared spectra that none of the samples was oxidized by air in our experiments.

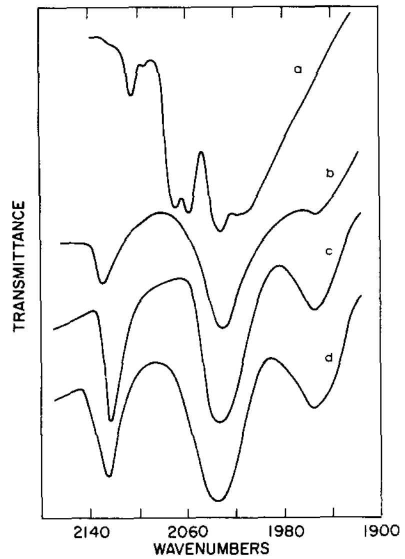
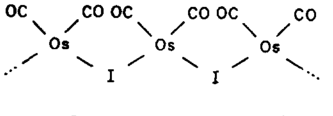


FIG. 1. Infrared spectra of osmium carbonyls: (a) supported on Al_2O_3 prepared from $[Os_3(CO)_{12}]$ at 125°C; (b) after heating in CO at 300°C; (c) supported on TiO_2 prepared from $[Os_3(CO)_{12}]$ treated under CO at 200°C; (d) supported on TiO_2 prepared from $[H_2Os_3(CO)_{10}]$ at 125°C.

that it was stable under vacuum or He at temperatures up to 400°C. It underwent decarbonylation in contact with H_2 at 400°C, and the spectrum of species **II** was regenerated when the decarbonylated sample was brought in contact with CO at 1 atm and 25°C.

The infrared bands of the new osmium carbonyl species **II** on Al_2O_3 were located at 2118, 2040, and 1955 cm^{-1}, and those for the species on TiO_2 were located at 2120, 2045, and 1960 cm^{-1}. These bands are similar to those observed for the complex $[Os(CO)_2I_2]$ (2119, 2045, and 1988 cm^{-1}), which is presumably polymeric, with iodide ligands bridging the divalent osmium ions (*13*). We infer that the surface osmium species had a structure analogous to that of the complex



The change from supported-trinuclear to atomically dispersed osmium can be envisioned as occurring during formation of Os–O bonds with breaking of Os–Os bonds in structure **I**. Confirmation of this suggestion is provided by the following preliminary results: (i) when phenol in solution with *n*-dodecane was refluxed with $[Os_3(CO)_{12}]$, a number of still-uncharacterized compounds were formed, one of them evidencing a carbonyl infrared spectrum almost identical to that of species **II**; (ii) when SiO_2 was brought in contact with a refluxing solution of *n*-decane and $[Os_3(CO)_{12}]$, a surface species was formed with an infrared spectrum indistinguishable from that of species **II**.[4]

When the unsaturated cluster $[H_2Os_3(CO)_{10}]$ in cyclohexane solution was brought in contact at 25°C with γ-Al_2O_3 or TiO_2 (dehydroxylated at either 300 or 400°C), the infrared spectrum indicative of surface species **II** was again observed (Fig. 1). Evidently, the reactivity of $[H_2Os_3(CO)_{10}]$ in the presence of surface M–OH groups was sufficient for the breaking of Os–Os bonds and the formation of Os–O bonds.

Particles of the oxide-supported osmium species **II**, prepared by all the above-mentioned routes, were introduced into a conventional flow-reactor system. The reactants, purified to remove traces of water and oxygen, flowed through a tubular reactor and to the sampling valve of a gas chromatograph. All the samples catalyzed the conversion of CO + H_2 into CH_4 and H_2O at 7 atm and 225 to 450°C, afterward evidencing unchanged carbonyl infrared spectra. The samples were also active for ethylene hydrogenation at 70 to 100°C, afterward evidencing unchanged carbonyl infrared spectra.

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[4] Supporting evidence is provided by the results of Smith *et al.* with $[Os_3(CO)_{12}]$ and η-Al_2O_3, showing the evolution of three molecules of H_2 per cluster; this result is consistent with the reaction of a surface $\mathrm{HOs_3(CO)_{10}OAl{<}}$ with five surface –OH groups to give three $\mathrm{Os(CO)_2(OAl{<})_2}$ species (*7*).

Osmium supported on γ-Al_2O_3 was also prepared by contacting an aqueous solution of $[H_2OsCl_6]$ with γ-Al_2O_3, according to a method similar to that of Prestridge *et al.* (*14*). The catalyst samples were washed with water, dried, and reduced in flowing H_2 at 400°C. When CO was brought in contact with a sample containing 1 wt% Os, carbonyl infrared bands formed which strongly resemble those of complex **II** (Fig. 2, curve a). In contrast, a sample containing 4 wt% Os showed a different spectrum after similar treatment (Fig. 2, curve b). Spectrum b appears to include all the carbonyl bands of spectrum a. Treatment of the sample containing 4% Os with CO followed by He at 200°C led to the formation of spectrum d, which resembles spectrum a. This result substantiates the suggestion that spectrum a is obscured under spectrum b.

The near equality of the carbonyl spectrum of species **II** prepared from the cluster and the spectrum (curve a, Fig. 2) of the sample prepared by the contacting of $[H_2OsCl_6]$ with γ-Al_2O_3 provides strong evidence that equivalent surface osmium complexes were formed in each case. Their stability at high temperatures (400°C) implies a strong interaction of osmium with the supports, possibly, we suggest, through two O–M groups, where M = Al, Si, or Ti. The behavior of Os is significantly different from that of other group VIII metals, which have much less stable surface-bound carbonyls.

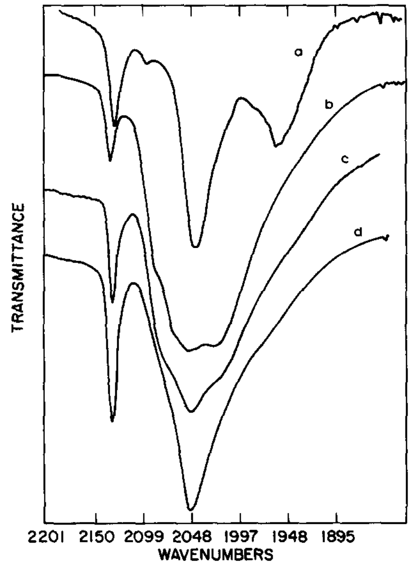

FIG. 2. Infrared spectra of CO adsorbed on supported osmium prepared with $[H_2OsCl_6]$: (a) Os on Al_2O_3 containing 1 wt% Os at 25°C; (b) Os on Al_2O_3 containing 4 wt% Os at 25°C; (c) Os on Al_2O_3 containing 4 wt% Os after heating in CO followed by He at 100°C; (d) Os on Al_2O_3 containing 4 wt% Os after heating in CO followed by He at 200°C.

There are some parallels between the foregoing results and the results of Sinfelt and co-workers (*14–16*), who studied 1-wt% Os on silica prepared with $[H_2OsCl_6]$. Chemisorption of H_2 and CO (*15*) suggested a dispersion of unity in Sinfelt's catalysts H : Os = 1.2 and CO : Os = 1.0). Electron microscopy (*14*) confirmed the high dispersion and showed that the osmium was present as "rafts," apparently monolayers with an average width of about 12 Å. EXAFS (*16*) showed that the average Os–Os distance was the same as that in metal films or clusters (2.78 Å).

The tendency of the osmium to exist in a highly dispersed state on the oxide surface sets it uniquely apart from other metals (e.g., Ru) and is evidence of its strong interaction with the support. Assuming that our samples having Os in low concentration supported on γ-Al_2O_3, TiO_2, or SiO_2 were closely similar to the silica-supported osmium prepared in nearly the same way by Sinfelt and co-workers (*14–16*), we suggest that the "rafts" of osmium, when carbonylated, can be described as osmium complexes like **II** and that the osmium in the rafts is strongly bonded to the support through Os–O–M bonds (where M = Si, Al, or Ti).

ACKNOWLEDGMENT

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