

## CO Hydrogenation Catalyzed by Magnesia-Supported Osmium Derived from $\text{Os}_3(\text{CO})_{12}$

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A catalyst prepared by the reaction of  $[\text{Os}_3(\text{CO})_{12}]$  with the surface of magnesia exhibited infrared spectra in the carbonyl region suggestive of the formation of the supported cluster  $[\text{HOs}_3(\text{CO})_{10}\text{OMg}]$ . After oxidation in air, the sample exhibited a spectrum indicative of a mononuclear osmium carbonyl complex. The catalyst, initially present in either the original or oxidized form, was active for CO hydrogenation; the products at low conversions were  $\text{C}_1$ - $\text{C}_4$  paraffins formed at a rate of about  $10^{-3}$  molecules/(Os atom · s) at 300°C and 31.8 atm with a 4:1  $\text{H}_2$ :CO ratio. The infrared spectrum of the used catalyst is suggestive of a trinuclear osmium carbonyl cluster, and we propose that a cluster is the catalytically active species.

### INTRODUCTION

The need for selective catalysts for synthesis gas conversion has focused attention on metal clusters (1, 2). Triosmium (1, 3), triruthenium (3), and tetrairidium (1, 3) carbonyl clusters in solution have been implicated in catalysis of CO hydrogenation to give methane, but the reaction rates were so low and the numbers of turnovers so few that the catalytic species could not be determined. Rhodium clusters have been identified in solutions catalyzing CO hydrogenation at pressures of hundreds of atmospheres to give ethylene glycol and methanol, but mononuclear rhodium complexes were also present and the catalytic species remain undetermined (4). There is still no evidence of a structurally defined metal cluster acting as a synthesis gas conversion catalyst.

Attempts have been made to stabilize metal-cluster catalysts by bonding them to solid supports, thereby minimizing the interactions which occur in solution and often lead to loss of the metal framework integ-

riety. Most of the reported supports are polymers or silica with pendant electron-donor phosphine ligands (5). Only a few authors have reported the stabilization of metal clusters on typical oxide supports such as silica and alumina; most have found that the metal aggregated to give crystallites.

Robertson and Webb (6) brought solutions of  $[\text{Ru}_3(\text{CO})_{12}]$  in contact with silica and inferred that at low temperatures ( $<127^\circ\text{C}$ ) the metal framework structures remained intact on the surface and provided catalytic sites for olefin isomerization; at high temperatures, the clusters decomposed, giving mononuclear Ru complexes. Kuznetsov *et al.* (7) prepared silica- and alumina-supported ruthenium using  $[\text{Ru}_3(\text{CO})_{12}]$ ,  $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ , or  $[\text{Ru}_6\text{C}(\text{CO})_{17}]$  as a starting material. Infrared spectra showed that all the clusters were converted into mononuclear complexes, apparently including the same species observed by Robertson and Webb (6). The alumina- and silica-supported Ru (upon reduction in  $\text{H}_2$  at temperatures  $>400^\circ\text{C}$ ) aggregated and formed crystallites (7).

Several groups have done experiments with  $[\text{Rh}_6(\text{CO})_{16}]$  brought in contact with alumina; the surface chemistry is complex,

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and the structures of the rhodium cluster species remain in doubt (8-11). Tri-iron carbonyl clusters on alumina and on magnesia have been used as precursors of catalysts for CO hydrogenation; the iron aggregated during the catalysis (12). Triosmium clusters have been bonded to oxides by the reaction of  $[\text{Os}_3(\text{CO})_{12}]$  with surface  $-\text{OH}$  groups, giving  $[\text{HOs}_3(\text{CO})_{10}\text{OM}]$ , where M is Si (13-15), Al (13-18), Ti (15), or Zn (15).

The triosmium carbonyls are the best-defined oxide-supported clusters, the structures having been defined by the stoichiometry of the surface attachment (13, 14) infrared spectra in the carbonyl region and their comparison with spectra of known molecular clusters (13-18), EXAFS (14), and Raman spectra indicating the Os-Os bonds (17). Upon heating, the supported triosmium clusters are broken up into mononuclear osmium carbonyl complexes, and infrared spectra of used catalysts have formed the basis for the suggestion that mononuclear osmium complexes were the catalytically active species for hydrogenation of CO and ethylene (15).

Here we report a continuing study of oxide-supported triosmium clusters, now with a basic support (magnesia). The materials have been characterized by infrared spectroscopy and by catalytic activities for CO hydrogenation.

#### EXPERIMENTAL METHODS

##### Materials

Cyclohexane (Fisher spectroanalyzed) was dried and redistilled before use.  $[\text{Os}_3(\text{CO})_{12}]$  (Strem) was used without further purification. Magnesia powder (MCB MX65, surface area  $\approx 30 \text{ m}^2/\text{g}$ ) was treated for 2 hr in flowing oxygen at  $200^\circ\text{C}$  then purged with nitrogen. The materials were routinely handled under nitrogen to minimize contamination by air.

##### Catalyst Preparation

The supported osmium catalyst was prepared by stirring the magnesia overnight in

a saturated solution of  $[\text{Os}_3(\text{CO})_{12}]$  in cyclohexane at room temperature; the procedure was similar to that used previously with  $\text{SiO}_2$ ,  $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{ZnO}$  (15). The mixture was allowed to settle, the supernatant liquid drawn off, and the solid washed three times with  $\text{CH}_2\text{Cl}_2$  which had been freshly distilled from  $\text{P}_2\text{O}_5$ . The light-yellow solid was dried by gentle warming and stored under nitrogen.

##### Equipment and Procedures

Infrared spectra of catalyst wafers (1  $\text{cm}^2$ , pressed at 7000 psi) were measured with a Nicolet 7000 Fourier transform infrared spectrophotometer. The cell was glass with NaCl windows and a Teflon sample holder mounted at a ground glass joint. Samples were placed in the cell under nitrogen in a glove bag.

Catalytic reaction experiments were done in a flow microreactor interfaced to a gas chromatograph (GLC). The system allowed metering of CO and  $\text{H}_2$  (purified by flow through traps to remove traces of metal carbonyls and water) to a thermostated packed-bed reactor, which was copper lined to prevent metal carbonyl formation. Details of the system are to be presented elsewhere (19).

About 0.5 g of catalyst powder was dispersed between layers of glass wool and loaded into the tubular flow reactor, which was packed at the top and bottom with glass wool plugs. The reactor was placed in the flow system and purged with ultrahigh-purity helium at 1 atm. The system was brought to 31.8 atm with the helium flowing at a purge rate of about  $20 \text{ cm}^3$  (STP)/min. The reactor was then heated for about 15 min to bring the temperature to  $300^\circ\text{C}$ , and the helium flow was stopped and the reactant flow started at  $120.5 \text{ cm}^3$  (STP)/min of  $\text{H}_2$  and  $30.5 \text{ cm}^3$  (STP)/min of CO. The start of reactant flow was defined as zero on-stream time.

One catalyst sample contacted air for  $>24$  hr before charging to the reactor. Another was charged to the reactor in a glove

box with a valving and purge arrangement assuring that it experienced virtually no exposure to air before being brought on stream.

During a catalysis experiment, the reactor temperature, pressure, and feed flow rates were held constant and the product stream (maintained in the vapor phase in a heated exit line) was intercepted periodically with a gas sampling valve on the GLC (an Antek 300), which was equipped with a flame-ionization detector and a  $\frac{1}{8}$ -in.  $\times$  13-ft column packed with *n*-octane on Porasil-C. The helium carrier gas flow rate was 7.5  $\text{cm}^3/\text{min}$ . Temperature programming of the column involved an initial 4-min hold at 65°C, heating at 4°C/min to 135°C, then a 4-min hold at 135°C. The GLC was calibrated with the following known compounds to determine response factors and elution times: methane, ethane, ethylene, propane, propylene, and *n*-butane. Products were identified by their elution times.

### Catalyst Analysis

The catalysts were analyzed for osmium by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

## RESULTS AND DISCUSSION

### Infrared Spectra

The infrared spectrum of the magnesia-supported osmium in its originally prepared form (Fig. 1) shows five peaks in the carbonyl region, apparently superimposed on a broad band.<sup>3</sup> The peak locations (Table 1) are close to those of similarly prepared osmium carbonyl species on  $\text{SiO}_2$  (13–15),  $\text{Al}_2\text{O}_3$  (13–18),  $\text{TiO}_2$  (15), and  $\text{ZnO}$  (15), and they are close to those of the triosmium clusters formed by reaction of  $[\text{Os}_3(\text{CO})_{12}]$  with water, alcohols, thiols, or amines (Ta-

<sup>3</sup> These carbonyl spectra and those mentioned subsequently are clearly different from the spectrum indicating CO adsorbed on osmium metal [which has broad bands at 2010 and 1860  $\text{cm}^{-1}$  (20)] and clearly different from the spectrum of  $[\text{Os}_3(\text{CO})_{12}]$  physically adsorbed on  $\text{Al}_2\text{O}_3$  [2069vs, 2035vs, 2015m, 2000m] (15).

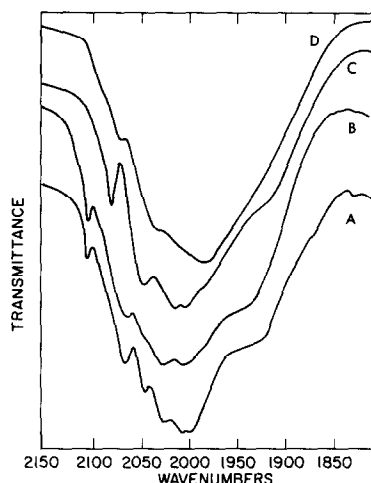
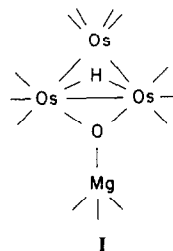


FIG. 1. Infrared spectra of supported osmium carbonyls: (A) supported on magnesia and prepared from  $[\text{Os}_3(\text{CO})_{12}]$  at 25°C; (B) after heating in CO at 1 atm and 125°C; (C) after heating in CO at 1 atm and 250°C; and (D) after heating in CO at 1 atm and 350°C.

ble 1). These comparisons suggest that the synthesis of surface-bound triosmium clusters resulting when  $[\text{Os}_3(\text{CO})_{12}]$  reacts with the surface  $-\text{OH}$  groups of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{ZnO}$  {which has been inferred to be analogous to the synthesis of  $[\text{HOs}_3(\text{CO})_{10}\text{OR}]$  from  $[\text{Os}_3(\text{CO})_{12}]$  and  $\text{ROH}$  (13–18)} also pertains when the surface  $-\text{OH}$  groups are present on magnesia. Consequently, the structure of the supported osmium carbonyl species (referred to as I) is suggested to be



Alternatively, a comparison of the spectrum of I with that of  $[\text{Os}_3(\text{CO})_{10}(\text{OCH}_3)_2]$  (Table 1) suggests that the structure of I might be  $[\text{Os}_3(\text{CO})_{10}(\text{OMg}\leftarrow)_2]$ ; we lack sufficient data to determine the exact structure of the supported triosmium carbonyl.

TABLE 1  
Infrared Characterization of Molecular and Surface-Bound Triosmium Clusters

	Molecular cluster	$\nu_{\text{CO}}$ ( $\text{cm}^{-1}$ )	Ref.
	$[\text{HOs}_3(\text{CO})_{10}\text{OCH}(\text{CH}_3)_2]$	2110w, 2070s, 2059ms, 2033vs, 1998m, 1988m	(21)
	$[\text{HOs}_3(\text{CO})_{10}(\text{OH})]$	2110vw, 2072s, 2060m, 2027vs, 2025sh, 2006m, 1989w	(22)
	$[\text{HOs}_3(\text{CO})_{10}(n\text{-BuNH})]$	2103w, 2063s, 2050m, 2021s, 2002, 2989m	(23)
	$[\text{HOs}_3(\text{CO})_{10}\text{OSiPh}_3]$	2107w, 2069s, 2055s, 2017s, 1997m, 1980m, 1907w, 1887w	(13)
	$[\text{HOs}_3(\text{CO})_9\text{CCSi}(\text{OC}_2\text{H}_5)_3]$	2102.5w, 2077vs, 2054vs, 2020vs, 2016.5sh, 1983sh, 1981m	(24)
	$[\text{Os}_3(\text{CO})_{10}(\text{OCH}_3)_2]$	2107m, 2071vs, 2056s, 2016vs, 1989s, 1979m, 1951w	(22)
	Surface-bound cluster		
	$[\text{HOs}_3(\text{CO})_9\text{CCSiL}]$	2078s, 2054s, 2022s, 2014s, 1983m	(24)
	$[\text{H}_2\text{Os}_3(\text{CO})_9\text{PPH}_2\text{C}_2\text{H}_4\text{SiL}]$	2095m, 2063sh, 2053s, 2034sh, 2015vs, 1979sh	(24)
Surface-bound species	Suggested structure of surface-bound cluster		
I	$[\text{HOs}_3(\text{CO})_{10}\text{OMg}\leftarrow]$	2105m, 2064s, 2047s, 2028vs, 2005s, 1930sh	This work
II	$[\text{HOs}_3(\text{CO})_9\text{OMg}\leftarrow]$	2085m, 2053s, 2022s, 2009s, 1990sh	This work
IV	$[\text{H}_2\text{Os}_3(\text{CO})_9\text{OMg}\leftarrow]$	2080m, 2048sh, 2039s, 2010sh, 1986vs, 1950sh	This work

When the magnesia incorporating I was heated to 250°C under CO in the infrared cell, the carbonyl bands in the spectrum disappeared and a new set appeared [Fig. 1C]. The new spectrum is also suggestive of a triosmium carbonyl (designated II), being similar to the spectrum of  $[\text{HOs}_3(\text{CO})_9\text{CCSi}(\text{OEt})_3]$  (formed from  $[\text{Os}_3(\text{CO})_{12}]$  and vinyltriethoxysilane) and of the analogous hydridotriosmium cluster anchored to silica (and formed by the reaction of  $[\text{HOs}_3(\text{CO})_9\text{CCSi}(\text{OEt})_3]$  with silica) ( $[\text{HOs}_3(\text{CO})_9\text{CCSiL}]$ ) (Table 1) (24). We speculate that the structure of II is  $[\text{HOs}_3(\text{CO})_9\text{OMg}\leftarrow]$ , but other triosmium carbonyl structures are not ruled out.

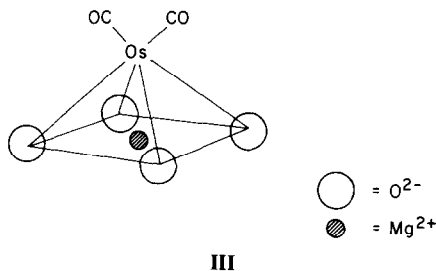
Magnesia's basicity evidently sets it apart from the other oxide supports—structures analogous to I formed on  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZnO}$ , and  $\text{TiO}_2$  (15), but are not stable in

CO at temperatures exceeding roughly 150–200°C, being broken up into mononuclear surface carbonyl complexes (25). No spectrum like that observed for II on MgO was observed with the other oxides (13–18).

When the magnesia-supported osmium species I was left in air at 25°C for 12 hr, the carbonyl bands disappeared and still another set appeared (Fig. 2). The spectrum showed that the new carbonyl species (designated III) was stable in He at temperatures up to about 400°C. The spectrum is clearly distinct from those mentioned above and is similar to those of the divalent osmium complexes  $[\text{Os}(\text{CO})_2\text{X}_4]^{2-}$  (where X = Cl, Br, or I) (26), which have  $C_{2v}$  symmetry (Table 2). We infer that the supported Os was present in mononuclear complexes in this sample.

Mononuclear osmium complexes formed

on the other aforementioned oxides also, with the metal evidently being strongly bonded to surface oxygen ions (13–18), possibly two of them. Since magnesia may expose (100) surface faces with four oxygen atoms in a square planar array (27), we postulate the following structure to account for the spectrum and the stability of III:



When magnesia incorporating structure III was heated to 100°C under CO, its carbonyl spectrum underwent only a small change (Fig. 2). But when the sample was heated to 200–300°C under CO, another new set of carbonyl bands replaced those of III (Fig. 2, Table 1). This spectrum is similar to that of II. The result suggests that a tris-osmium carbonyl cluster was reconstituted from the mononuclear Os(II) complexes on the surface. Presuming the correctness of this suggestion, we infer that the Os(II) ions on the surface formed by breakup of the tris-osmium clusters had been so strongly bonded to the oxygen ions that they had nearly retained their initial positions and could therefore be easily reunited into trinuclear clusters upon carbonylation. A similar reversible breakup and reconsti-

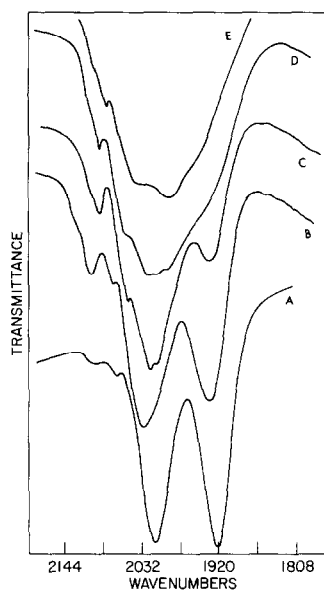


FIG. 2. Infrared spectra of (A) supported osmium species after exposure to air and presumed oxidation to mononuclear complexes; (B) after heating in CO at 1 atm and 100°C; (C) after heating in CO at 1 atm and 200°C; (D) after heating in CO at 1 atm and 300°C; (E) after heating in CO at 1 atm and 400°C.

tution of rhodium clusters on alumina had been suggested earlier (8–11).

#### Catalytic Hydrogenation of CO

The organic reaction products observed in the catalytic hydrogenation of CO at low conversion (<0.1% of the CO) are methane, ethane, propane, and (traces of) butane; olefins were not observed. Rates of reaction, calculated assuming that the con-

TABLE 2

Infrared Characterization of Molecular and Surface-Bound Mononuclear Osmium Complexes

	Molecular complex	$\nu_{\text{CO}}$ (cm <sup>-1</sup> )	Ref.
	[Os(CO) <sub>2</sub> Cl <sub>4</sub> ] <sup>2-</sup>	2003vs, 1905vs	(26)
	[Os(CO) <sub>2</sub> Br <sub>4</sub> ] <sup>2-</sup>	2008vs, 1918vs	(26)
	[Os(CO) <sub>2</sub> I <sub>4</sub> ] <sup>2-</sup>	2008vs, 1926vs	(26)
Surface-bound species III	Suggested structure of surface-bound complex [Os(CO) <sub>2</sub> (O<) <sub>4</sub> ]	2013vs, 1920vs	This work

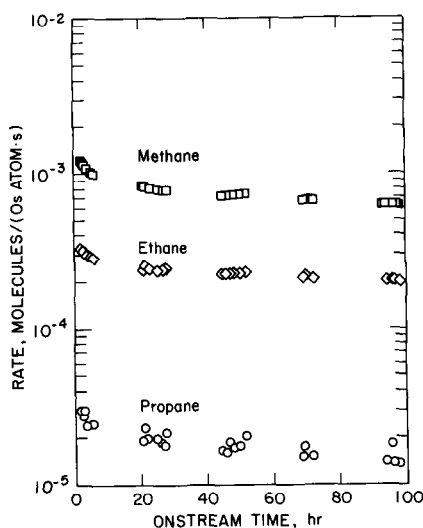


FIG. 3. Rates of paraffin formation from CO + H<sub>2</sub> at 300°C and 31.8 atm. The flow rates of H<sub>2</sub> and CO were 120.5 and 30.5 std cm<sup>3</sup>/min, respectively. The catalyst (0.530 g, initially containing 0.36 wt% Os with structure I) was not allowed to come in contact with air.

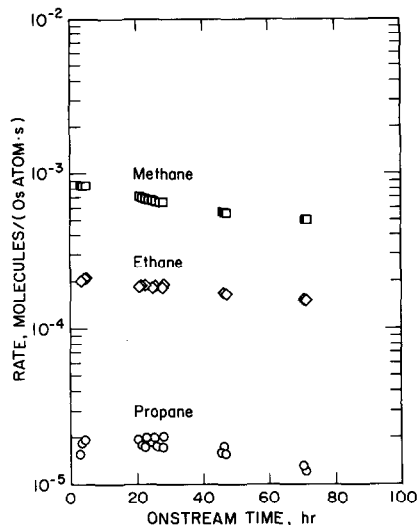


FIG. 4. Rates of paraffin formation from CO + H<sub>2</sub> at 300°C and 31.8 atm. The flow rates of H<sub>2</sub> and CO were 120.5 and 30.5 std cm<sup>3</sup>/min, respectively. The catalyst (0.551 g, initially containing 0.36 wt% Os) was brought in contact with air before operation.

versions were differential, are summarized in Figs. 3 and 4. During the initial period, the observed products were characteristic of structural changes in the osmium species and not necessarily of catalysis;<sup>4</sup> later there was a slow loss of catalytic activity. The sample which was not allowed to come in contact with air (and which incorporated triosmium clusters I at the start of the experiment) apparently underwent a more rapid change during the initial period than the sample which had been oxidized prior to the catalysis experiment. After a few hours on stream, the two catalyst samples attained nearly equal activities and selectivities (Figs. 3 and 4). This comparison indicates that the osmium species in each sample were the same after the short initial period.

The observed rates of hydrocarbon formation [about 10<sup>-3</sup> molecules/(Os atom · s)] fall within the three-order-of-magnitude range observed by Vannice (29)

<sup>4</sup> A stoichiometric reaction of [HOs<sub>3</sub>(CO)<sub>10</sub>OAl] in helium, hydrogen, or CO gives CH<sub>4</sub> and traces of higher hydrocarbons (13, 15, 28).

with group VIII metal crystallites supported on alumina at 275°C and 1 atm, with a 1 : 1 H<sub>2</sub> : CO ratio. Vannice did not investigate osmium, but it has long been recognized as a Fischer-Tropsch catalyst (30, 31), although its activity on a unit surface area basis is still not reported.

A sample which had been prepared in nearly the same manner as that described above was exposed to air for 4 hr, giving an infrared spectrum indicative of III. It was then tested as a catalyst in apparatus similar to that described above, with the product analysis by GLC being carried out only qualitatively with a relatively insensitive thermal conductivity detector. Consistent with the results mentioned above, methane and water were observed as catalytic reaction products formed at about 300°C and 7 atm, and the catalyst underwent only little deactivation in 20 hr of operation in the flow reactor. Upon removal from the reactor, the catalyst powder was pressed into a wafer and characterized spectroscopically, with all the handling being done under nitrogen in a glove bag. The spectrum (Fig. 5) indicates that yet an-

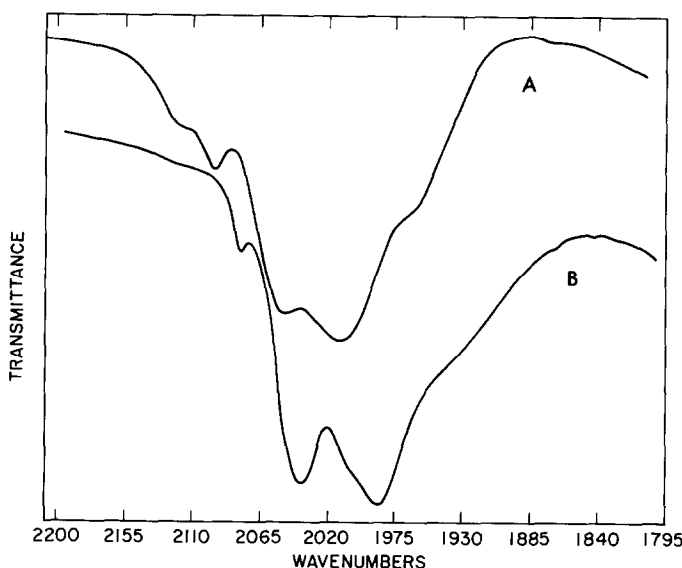


FIG. 5. Infrared spectra of (A)  $[\text{H}_2\text{Os}_3(\text{CO})_9\text{PPh}_2\text{C}_2\text{H}_4\text{SIL}]$  [prepared according to the procedure of Brown and Evans (24)]; (B) catalyst initially incorporating structure III after  $\text{CO} + \text{H}_2$  reaction at approximately  $400^\circ\text{C}$  for 20 hr.

other surface osmium carbonyl species (designated IV) had formed during the catalysis. The carbonyl band positions are nearly the same as those observed for a dihydridotriosmium cluster anchored to silica,  $[\text{H}_2\text{Os}_3(\text{CO})_9\text{PPh}_2\text{C}_2\text{H}_4\text{SIL}]$  (Fig. 5, Table 1), except that they are shifted to a 15- to  $25\text{-cm}^{-1}$  lower frequency. Since the phosphine is a better donor ligand than a surface oxygen ion, we suggest that structure IV may be  $[\text{H}_2\text{Os}_3(\text{CO})_9\text{OMg}\llcorner]$ . This suggestion is speculative.

The important result of this experiment is the indication that during catalysis an osmium carbonyl cluster formed on the surface. We suggest that the catalyst might have incorporated unique triosmium species and that it might, therefore, be recognized as a prototype supported-metal catalyst, one simple enough to be subject to rigorous structural definition and stable enough to be characterized under the conditions required for technologically important reactions of  $\text{CO}$  and  $\text{H}_2$ . When, instead of magnesia, alumina was used as a support for triosmium clusters, the spectrum of the used catalyst indicated mononuclear os-

mium carbonyl species and not clusters (15). The difference suggests the importance of the basic character of the magnesia in stabilizing the clusters.

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