

A Supported Triosmium Cluster Catalyst: Evidence for Metal-Metal Bonds from Laser Raman Spectroscopy

The opportunities for determining the dependence of catalytic activity on the structure of supported-metal catalysts have motivated the preparation of a variety of metal clusters bonded to solids through pendant ligands such as phosphines (1). Extensions have been made to unfunctionalized supports, including triosmium on SiO₂ (2-4), Al₂O₃ (3, 4), TiO₂ (3), and MgO (5) and tri-iron on Al₂O₃ and MgO (6). All these supported clusters have been characterized by comparison of their infrared spectra in the carbonyl region with the spectra of analogous molecular clusters. Further structural characterization is needed. In this report we present the first evidence of the structure of a supported-metal species determined by Raman spectroscopy.

A distinctive characteristic of a metal cluster is its metal-metal bonds. Raman spectroscopy has been used to demonstrate metal-metal bonding in a wide range of molecular metal clusters (7), and the Raman technique is potentially valuable for determining the structures of supported-metal clusters; in particular, it may determine when the clusters have broken up into mononuclear metal complexes or aggregated to form crystallites.

The low intensity of the Raman scattering from many clusters and the interference of fluorescence by many supports make these Raman studies difficult. The availability of tunable lasers for resonance Raman spectroscopy and the interfacing of spectrometers with computers, however, now make the technique more generally applicable to supported catalysts.

The Raman spectral results reported here provide a direct indication of Os-Os bond-

ing in alumina-supported hydridotriosmium clusters. The spectra also suggest that, upon heating of the cluster on the surface, the Os-Os bonds are broken and atomically dispersed osmium species are formed.

Supported osmium clusters were prepared (3) by contacting a refluxing *n*-octane solution containing [Os₃(CO)₁₂] under N₂ with γ -Al₂O₃ (Ketjen, surface area = 415 m²/g, partially dehydroxylated by treatment with flowing O₂ at 400°C followed by N₂ at 400°C). The sample was filtered and washed with CH₂Cl₂ until no more [Os₃(CO)₁₂] was desorbed. Following heat treatment in CO for 4 hr at 130°C, the sample was pressed into a pellet for acquisition of the spectra.

Spectra in the visible region were obtained with a Cary 219 spectrophotometer with a Cary diffuse reflectance accessory. The sample was in the powdered form. Raman spectra were obtained with a Spex Ramalog spectrometer with a triple monochromator. Excitation of the sample was accomplished by using the 488.0-nm line of a Spectra Physics model 164 argon ion laser. A standard Spex solid sample rotator was used to prevent thermal or photochemical decomposition. The laser power was about 100 mW (measured at the source). The spectra were recorded with a resolution of about 4 cm⁻¹. The instrument was interfaced to a Nicolet 1180 data system controlling both the scan and the data acquisition. About 50 scans had to be averaged to provide a suitable signal-to-noise ratio. The frequencies reported are accurate to within ± 2 cm⁻¹.

Figure 1 shows the Raman spectrum of the osmium species on alumina in the region from 100 to 500 cm⁻¹. Figure 2 is the

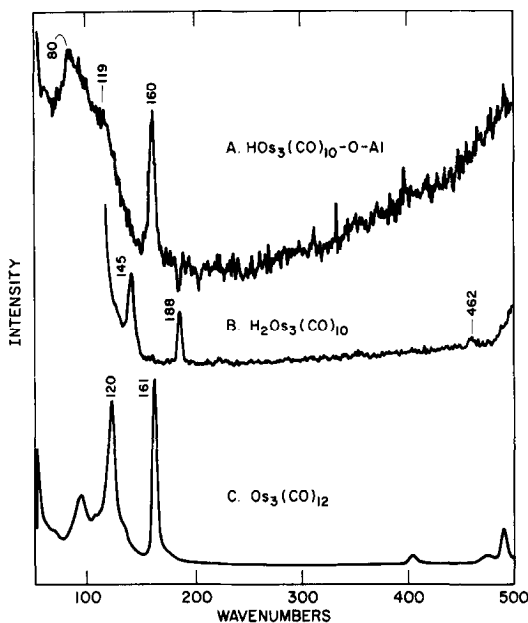


FIG. 1. Raman spectra of the solid phase of (A) alumina-supported triosmium cluster, (B) $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$, and (C) $[\text{Os}_3(\text{CO})_{12}]$ from 50 to 500 cm^{-1} .

visible spectrum of the same material. Since the 488.0-nm excitation line falls within the electronic absorption band, we suggest that the spectrum in Fig. 1 may be due to resonance Raman enhancement.

Also shown in Fig. 1 are the Raman spectra of solid samples of two molecular

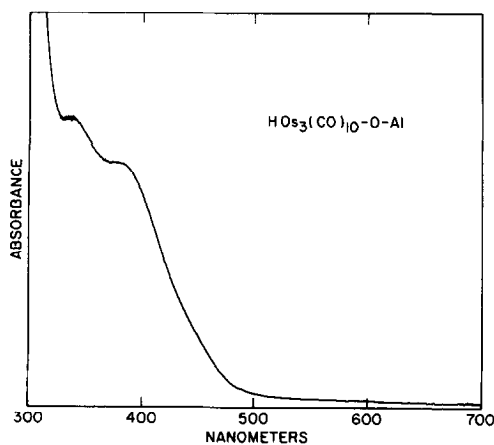


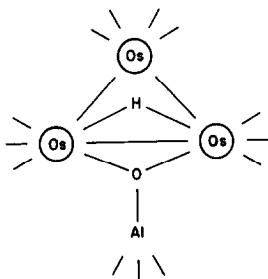
FIG. 2. Diffuse reflectance spectrum of alumina-supported triosmium cluster from 320 to 700 nm. The spectrum was obtained through a Pyrex window.

clusters, $[\text{Os}_3(\text{CO})_{12}]$ (Strem) and $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$, synthesized by the method of Knox *et al.* (8). A strong band for the supported osmium species was observed at 160 cm^{-1} , with a broad band and shoulder appearing at lower frequencies; this band has maxima at approximately 80 and 119 cm^{-1} . At frequencies less than 500 cm^{-1} , several vibrations are expected to be active in the Raman spectra of the metal clusters. The strongest of these are expected to be the Os–Os, Os–C, and Os–O stretching modes. Of these vibrations, only the Os–Os stretching modes are expected at such low frequencies as those observed, and the 160- cm^{-1} band is therefore assigned to this mode. This assignment is in agreement with that of the parent compound, $[\text{Os}_3(\text{CO})_{12}]$, for which the A'_1 Os–Os stretching mode is assigned to a band at 160 cm^{-1} and the E'_1 Os–Os stretching mode is assigned to a band at 119 cm^{-1} (9, 10). Upon interaction with the surface, the symmetry of the cluster is expected to be lowered from D_{3h} to C_s , with splitting of the E'_1 mode into A' and A'' modes. These would be expected at about the same frequency as the E'_1 mode in $[\text{Os}_3(\text{CO})_{12}]$. The Raman spectrum of the other molecular cluster, $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$, also has two sharp bands in this region, at 145 and 188 cm^{-1} . These are presumably the two A' modes expected from its C_s symmetry.

In summary, the spectra of Fig. 1 demonstrate that an osmium species with metal-metal bonds was present on the surface, and the comparison with the spectra of the molecular triosmium clusters is consistent with the identification of the surface species as a triosmium cluster.

Infrared spectra in the carbonyl region have been reported (3) for the surface-bound osmium species and have provided the basis for its identification as a hydrido-triosmium cluster, the bands being nearly identical to those of the molecular clusters formed by reaction of $[\text{Os}_3(\text{CO})_{12}]$ with phenols, thiols, or amines. We conclude that the Raman data indicating Os–Os bonds

confirm the conclusion that the surface osmium species were formed by reaction of $[\text{Os}_3(\text{CO})_{12}]$ with surface hydroxyl groups to give the following species:



The structure of this cluster (3) and the analogous silica-supported cluster (2) had already been inferred from the infrared spectra.

The alumina-supported triosmium was characterized briefly as a catalyst for isomerization of 1.5 ml of 1-hexene in 1.5 ml of C_6D_6 at 76°C and 1 atm. A batch reactor contained particles of catalyst suspended in the reactant under a N_2 atmosphere. Liquid products were drawn periodically and analyzed by gas chromatography. Internal olefins were formed, the conversion after 16 hr being about 5% with 0.20 g of catalyst containing about 0.4 wt% Os. The catalytic activity observed in this experiment is comparable to that of triosmium clusters in solution (11, 12) and of triosmium clusters bonded to phosphine-functionalized silica supports (13, 14).

In a separate experiment, the surface-bound osmium cluster was heated under CO at 400°C , and a new species was formed, as evidenced by the infrared spectrum (3). This species had three carbonyl bands, similar to those observed for the complex $[\text{Os}(\text{CO})_2\text{I}_2]$ (which is presumably oligomeric) (3). It was inferred that the osmium in this species was highly dispersed and present as divalent osmium in a mononuclear surface-bound complex. The Raman spectrum of this species showed no bands in the low-frequency region, a result that is consistent with the absence of Os-

Os bonds in the structure. The distinct structure of the supported osmium in this form was confirmed by a catalytic activity measurement—it showed immeasurably low conversion of 1-hexene after 48 hr at 82°C under the conditions described above.

In summary, the Raman results provide the first vibrational spectrum indicating metal-metal bonds in a supported-metal catalyst. In combination with the previously reported infrared spectra, the Raman spectra are strong evidence for the presence of triosmium clusters. These are catalytically distinct from the highly dispersed osmium in the structures formed upon decomposition of the clusters. The Raman technique is uniquely suited to provide information about metal-metal bonds in supported-metal catalysts. The applicability of this technique to other supported metals depends on the intensity of Raman scattering from the metal species; the technique is expected to be most useful for supported clusters with discrete, simple structures.

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