

MgO-Supported Decaosmium Cluster Catalyst for Ethylene Hydrogenation: Characterization by EXAFS and TEM

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Introduction

When metal clusters on supports are small enough, their catalytic properties are cluster-size dependent, even for structure-insensitive reactions.¹ The dependence of catalytic activity on cluster size can be demonstrated best in experiments with samples incorporating clusters of essentially uniform sizes, which can be prepared from molecular metal clusters such as $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$, which can be formed on some supports (e.g., MgO) and then decarbonylated to give structures approximated as Os_{10} .² We now report the preparation of such samples and their characterization by X-ray absorption spectroscopy (XAS) and transmission electron microscopy (TEM); we have characterized these supported clusters for a simple test reaction occurring under mild conditions that preserve the cluster structure, ethylene hydrogenation.

Materials and Methods

The catalyst was synthesized from $\text{Os}_3(\text{CO})_{12}$ at 298 K on MgO powder that had been calcined at 673 K. The synthesis and sample handling were done with exclusion of air and moisture. A specially designed TEM sample holder was used to protect the samples. The resultant sample had an Os content of 2 wt%. The sample was treated in He for 2 h and CO for 4 h at 548 K to form the cluster $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ and then decarbonylated in He for 2 h at 733 K. Samples were characterized by IR, EXAFS, and TEM and tested as catalysts for ethylene hydrogenation in a once-through flow reactor at 298 K and 1 atm.

Results and Discussion

Electron diffraction data characterizing the MgO support showed it to be polycrystalline. IR spectra characterizing the sample prepared from $\text{Os}_3(\text{CO})_{12}$ on MgO indicated formation of $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ as the principal supported species; this was characterized by EXAFS spectroscopy at the Os L_{III} edge. The Os-Os bond distance of 2.86 Å agrees well with the XRD value of 2.87 Å for the pure compound. All the EXAFS parameters agree well with the crystallographic structure of $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ within the expected errors.

These supported clusters were imaged by TEM in bright field and in dark field. A micrograph of the sample containing predominantly $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ includes strong scattering centers of nearly uniform size with diameters in the range 8–9 Å, indicative of the clusters, in addition to evidence of the regular lattice structure characteristic of the support. The scattering centers are attributed solely to the decaosmium cluster frames. The sizes estimated from the EXAFS data and the TEM images match, indicating a successful synthesis of uniform supported molecular clusters. The metal-support interaction was investigated by EELS, and EELS spectrum imaging was performed.

Decarbonylation of the supported $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ was carried out by treatment in He. ν_{CO} IR spectra demonstrated the removal of the CO ligands starting at 573 K and being nearly complete at 723 K. EXAFS spectra of the decarbonylated sample indicated the absence of contributions from carbonyl carbon and oxygen atoms. The first-shell Os–Os contribution

indicates retention of the Os_{10} metal frame; the Os–Os distance is less than that characterizing $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ by 0.17 Å. EDX analysis confirmed the presence of osmium in the sample. The data give evidence of an increased interaction between the clusters and MgO as a result of the decarbonylation, as indicated by two Os–support oxygen contributions at distances of 2.15 and 1.73 Å (but we emphasize that identification of the latter contribution is only tentative). The decarbonylated clusters were also characterized by TEM, again giving images consistent with Os_{10} . A difference in the features of the oxygen K edge between the supported sample and the MgO support is consistent with the inference that the osmium clusters were bonded to the support through surface oxygen atoms, in agreement with the EXAFS results indicating Os–O contributions.

The decarbonylated MgO-supported osmium clusters were found to be active for ethylene hydrogenation at 298 K. Calculations with standard methods show that the reaction was slow enough that the influence of transport phenomena on the rate was negligible and conversions were differential. The catalytic activity of MgO-supported $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ was negligible, consistent with the poisoning influence of the CO ligands. The decarbonylated Os_{10} clusters are among the simplest and best-defined supported metal cluster catalysts.

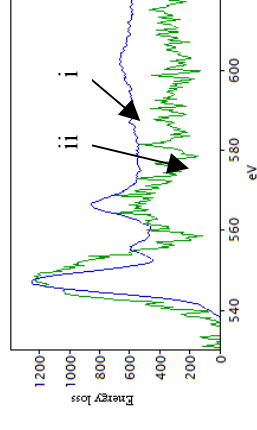


Figure 1. EELS comparison of oxygen K edge of (i) MgO and (ii) $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}/\text{MgO}$.

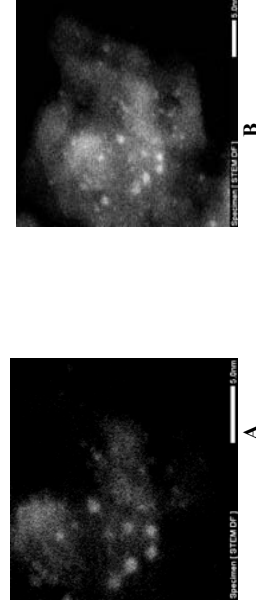


Figure 2. Z-contrast Dark field TEM images A) $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}/\text{MgO}$ B) Decarbonylated sample Os_{10}C metal frame

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References

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