# Nearly Uniform Tri- and Deca-Osmium Clusters Supported on MgO: Complementary Characterization by EXAFS and HAADF-STEM

A. Kulkarni[1], S. Mehraeen[1], N. Okamoto[1], B. Reed[2], N. D. Browning[1, 2] and  B. C. Gates[1]*
*University of California, Davis, California 95616 (USA)*
*Lawrence Livermore National Laboratory, Livermore, California 94550 (USA)*
*bcgates@ucdavis.edu

## Introduction

Determination of the dependence of catalytic properties on structure motivates the synthesis of structurally uniform samples. Two of the dominant techniques for characterization of supported nano-structured catalysts are EXAFS spectroscopy (which provides average information integrated over a sample) and STEM (which provides local information). These techniques are strongly complementary, but there are hardly any results that allow a quantitative comparison of them. Thus, we attempted to prepare nearly uniform supported catalysts that are nearly optimal for characterization by these techniques. We chose osmium clusters on MgO because of the high Z-contrast available in STEM imaging as a consequence of the large difference in mass of Os atoms, on the one hand, and Mg and O atoms, on the other, and, further, because earlier results show that high yields of osmium clusters of various nuclearities (1, 3, 5, 10) can be made on MgO via osmium carbonyls. When clusters on supports are small enough, they are sensitive to the beam in STEM and require low-dose techniques that invariably introduce noise into images. Our goals were to provide a thorough assessment of the two techniques for these samples, including their strengths and limitations.

A specific goal was to prepare supported metal clusters with such a high degree of uniformity that their structures could be determined with unprecedented accuracy by these complementary spectroscopic and microscopic methods and to test the catalytic properties for a simple test reaction occurring under such mild conditions that the structures would be preserved, as checked by EXAFS spectra of catalysts recorded during ethylene hydrogenation.

We used a novel method of quantifying nanocluster sizes (rms radii) and size distributions by HAADF in STEM [1]. Average inter-atomic distances obtained from EXAFS spectra of the supported species and by X-ray diffraction (XRD) crystallography of pure-compound analogues of the supported clusters were used to determine rms radii (XRD data were used with electron elastic-scattering cross sections from the NIST database). The sizes of individual clusters determined by STEM were compared with the average values determined by EXAFS and the XRD data representing the pure clusters in the crystalline state.

## Materials and Methods

The catalysts were synthesized at 298 K from $Os_3(CO)_{12}$ on MgO powder calcined at 673 K. A specially designed TEM sample holder was used to protect the samples, which were handled with rigorous exclusion of air and moisture. The samples, containing 2 wt% Os, were treated in He at for 2 h, followed by treatment in CO for  4 h at 548 K to convert triosmium clusters into $[Os_{10}C(CO)_{24}]^{2-}$.  These clusters were partially decarbonlylated by treatment in $H_2$ for 2 h at 473 K. Samples were tested as catalysts for ethylene hydrogenation in a once-through flow reactor at 298 K and 1 atm  The reaction was slow enough that the influence of  transport phenomena on the rate was negligible, and conversions were differential.

## Results and Discussion

IR spectra characterizing the sample prepared from $Os_3(CO)_{12}$ on MgO indicated formation of $[Os_3(CO)_{11}]^{2-}$ ion-paired with $Mg^{2+}$ sites on the MgO as the principal supported species;  the sample was characterized by EXAFS spectroscopy at the Os $L_{III}$  edge. The Os–Os distance of 2.89 Å agrees well with the XRD value of 2.89 Å for the pure compound. All the EXAFS parameters agree within the expected errors with the crystallographic structure of the triosmium carbonyl clusters.

HAADF-STEM images of the sample containing predominantly $[Os_3(CO)_{11}]^{2-}$ (Fig. 1) includes strong scattering centers of nearly uniform size with diameters of  2.02 Å, indicative of the clusters, along with evidence of the regular MgO  lattice structure. The scattering centers are attributed solely to the triosmium cluster frames. The sizes estimated from the EXAFS data, STEM images and XRD data all match within 0.1 standard deviation (Table 1). $[Os_3(CO)_{11}]^{2-}$/MgO were active for ethylene hydrogenation at  323 K.

Similarly,  $[Os_{10}C(CO)_{24}]^{2-}$ on MgO and partially decarbonylated $[Os_{10}C(CO)_{24}]^{2}$ on MgO were characterized by EXAFS and STEM, and the resulting rms radius from EXAFS, STEM, and XRD (of the pure compound) were found to be in agreement with a discrepancy of 1.8 and 0.9 standard deviations, respectively. The greater discrepancy in the estimates of the radii of the larger clusters relative to the smaller clusters suggests that the Gaussian used in the fitting in the STEM analysis may not be a universal for clusters of all sizes. MgO-supported $[Os_{10}C(CO)_{24}]^{2-}$ were active for ethylene hydrogenation at  323 K..

Decarbonylation of the supported $[Os_{10}C(CO)_{24}]^{2-}$ was carried out by treatment in $H_2$; $v_{CO}$ IR spectra demonstrated the removal of the CO ligands starting at 323 K and becoming nearly complete at 723 K. EXAFS spectra of the completely decarbonylated sample indicate aggregation to form larger clusters, but at temperatures up to 473 K, partial decarbonylation was observed with a reduction of the Os−carbonyl carbon and Os−carbonyl oxygen contributions, an increase in the Os−support oxygen contribution, and retention of the $Os_{10}$ frame. In contrast to MgO-supported $[Os_{10}C(CO)_{24}]^{2-}$, decarbonylated MgO-supported osmium clusters were active for ethylene hydrogenation at 298 K .
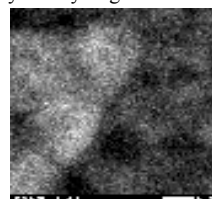


**Figure 1.**  HAADF-STEM image of $[Os_3(CO)_{11}]^{2-}$/MgO

**Table 1.**  rms radii  obtained by XRD, EXAFS, and STEM

| Sample[a] | rms radii (Å) | | |
|---|---|---|---|
| | **XRD** | **EXAFS** | **STEM** |
| A | 2.02 | 2.02 | 2.01± 0.01 |
| B | 2.80 | 2.82 | 3.11± 0.02 |
| C | 2.74 | 2.70 | 3.14± 0.02 |

[a]Sample A: $[Os_3(CO)_{11}]^{2-}$/MgO; B: $[Os_{10}C(CO)_{24}]^{2-}$/MgO; C: partially decarbonylated $[Os_{10}C(CO)_{24}]^{2-}$/MgO.

## Significance

We report the first highly uniform supported metal cluster catalysts characterized by both EXAFS spectroscopy and STEM. We demonstrate for beam-sensitive metal clusters that low-dose STEM techniques combined with image analysis determine cluster sizes in good quantitative agreement with those determined by EXAFS spectroscopy, although questions remain about the analysis of data for the larger clusters.

## References

1.  N. Okamoto, B. Reed, S. Mehraeen, A. Kulkarni, D. Morgan, B. C. Gates, N. D. Browning *J. Phys. Chem. C,* 112 (6), 1759, 2008.