

## Observation of Cluster Formation from MgO-supported Mononuclear Ir-Complexes by Aberration-Corrected STEM

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Molecular organometallic precursors that react precisely with supports offer excellent opportunities for synthesis of uniform site-isolated supported catalysts with simple structures. Simple and uniform structures can help in the determination of information towards developing a fundamental understanding of the structure-activity relationship in these essentially molecular catalysts. Aberration-corrected scanning transmission electron microscopy (STEM) is a powerful tool for exploring the structural changes including cluster formation at the atomic level. The formation of extremely small supported metal clusters, starting from the simplest case of essentially molecular, atomically dispersed catalysts –in our case, supported mononuclear iridium complexes, has been recorded by high-resolution STEM imaging at the atomic scale in real time. This investigation is one of the very first atomic-scale investigations of such structural changes, and thus it points the way to determination of significant information about the dependence of catalytic activity on structure of supported catalysts.

The starting material was a MgO-supported mononuclear catalyst containing 1 wt% Ir prepared by the reaction of  $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{acac})$  [acac is  $\text{CH}_3\text{COCHCOCH}_3$ ] with dehydroxylated high-area MgO powder [1]. Individual Ir atoms were observed via high angle annular dark-field (HAADF) STEM imaging. Moreover, the structure was also characterized by extended X-ray absorption fine structure (EXAFS), and infrared (IR) spectroscopies. The results indicate that catalyst initially consisted of mononuclear iridium complexes,  $\text{Ir}(\text{C}_2\text{H}_4)_2$ , on MgO as confirmed by the lack of Ir–Ir contributions in the EXAFS spectra and detection of ethylene ligands in the IR and EXAFS spectra.

To understand the mechanisms of cluster formation from mononuclear complexes on MgO, HAADF-STEM images were recorded using Cs-corrected 200kV JEOL 2200FS and 300kV FEI Titan-S microscopes to determine effects of electron irradiation and temperature. Heating experiments were performed by using Protochips Co. Aduro™ MEMS-based heating technology, which provides highly stable operation at temperature that does not compromise the resolution of the microscope [2]. Figure 2 shows 3 frames selected from a sequence of 47 HAADF images recorded at a nominal 800°C using the Protochips Aduro™ heater in the JEOL 2200FS.

HAADF-STEM imaging has advantages over bright-field TEM imaging for the size measurements of mononuclear and nanocluster catalysts. Because this technique almost eliminates the coherent diffraction contrast contributions from the catalysts and support, and the contrast is roughly proportional to the square of the atomic number (showing the high contrast of heavy metals (e.g. Ir,  $Z = 77$ ) on the low background intensity of a light oxide support (e.g. Mg,  $Z = 12$ )) [3]. Figure 2 shows two examples of Ir/MgO as prepared, recorded at RT in the FEI Titan. The movies, obtained in real time, show cluster formation from the mononuclear complexes and provide valuable information regarding diffusion and cluster formation mechanisms on the MgO surface. Our experiments showed that the Ir atoms always reside on the Mg sites as they are moving on the surface and they diffuse by a hopping mechanism. The diffusion mechanism of iridium atoms and clusters was observed on both (110) (Fig. 2.A) and (100) (Fig. 2.B) surfaces of MgO. These

observations were also confirmed with first-principles calculations. The binding energy of the Ir to the Mg and O site was found as  $-4.97$  and  $-4.19$  eV per iridium atom, respectively. This result confirms that the most favorable configuration of Ir atoms on MgO 110 surface is the Mg site as we observed in STEM Z-contrast images in Figure 2A. This atomic scale understanding will lead to the opportunity of controlling the cluster sizes, which in turn will help in controlling the selectivity and activity of these materials for the catalysts in this class.

## References

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- [3] N. L. Okamoto et al., *J. Phys. Chem. C*, 112(6), (2008) 1759.
- [4] This work was supported in part by NSF grant number CTS-0500511. Research was conducted at ORNL's SHaRE and HTML User Facilities.

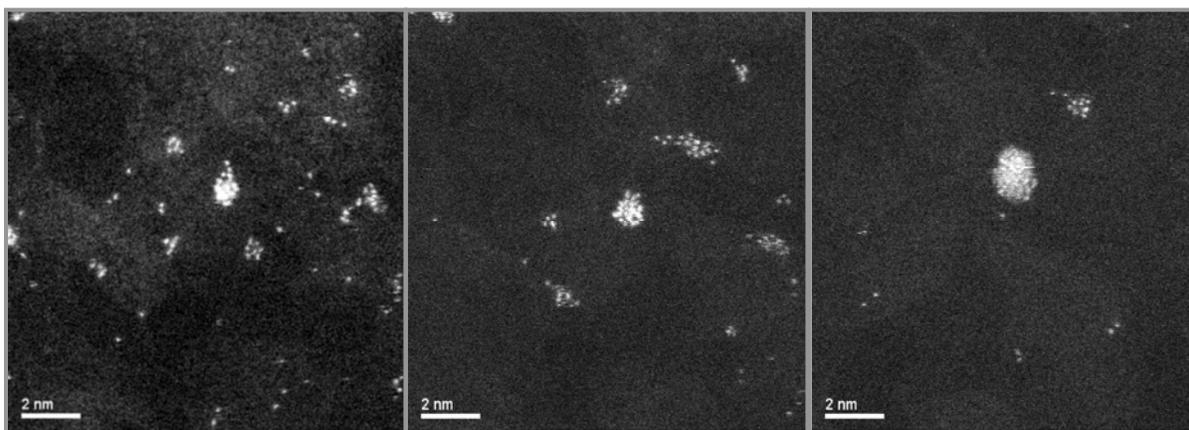


Fig. 1. HAADF-STEM images of single atoms and small clusters of Ir on MgO at 800 °C.

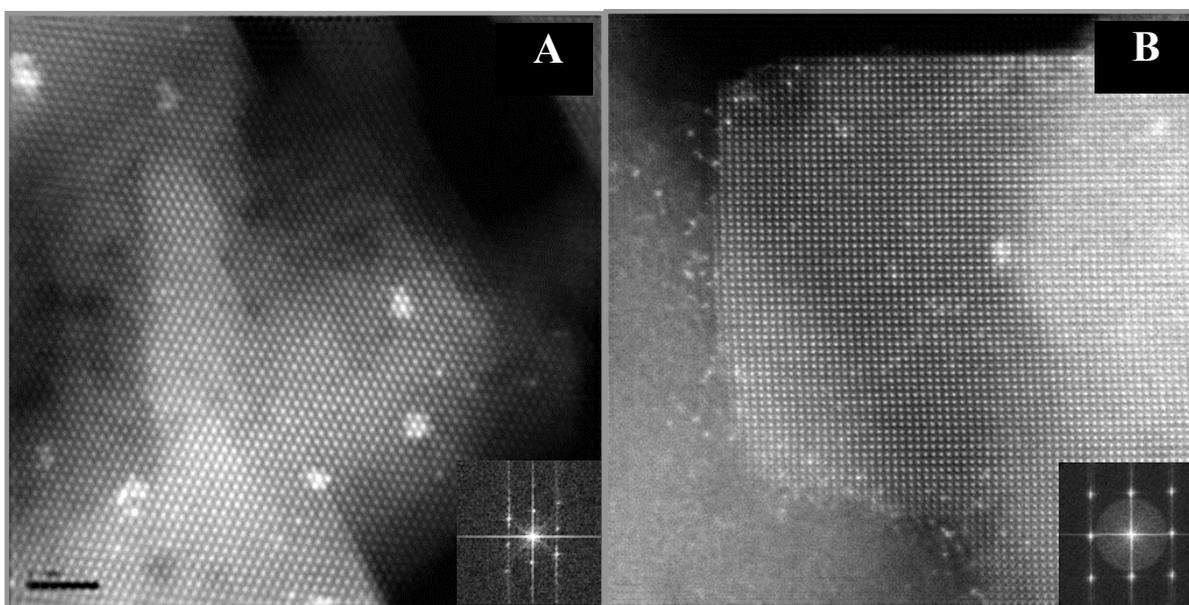


Fig. 2. HAADF-STEM images of Ir atoms on MgO. A. Ir atoms on MgO(110) surface. B. Ir atoms on MgO(100) surface.