

Supporting Information

Migration of Single Iridium Atoms and Tri-iridium Clusters on MgO Surfaces: Aberration-Corrected STEM Imaging and ab-initio Calculations

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The MgO support was obtained from EM Science. A paste was obtained by adding deionized water to the MgO, and dried overnight in air at 120 °C. The resultant solid was ground and treated in flowing O₂ as the temperature was ramped linearly at a heating rate of 3 °C/min from room temperature to 700 °C and then held for 2 h in O₂ flow following by evacuation for 14 h at 700 °C, resulting in a high degree of dihydroxylation.¹ The resultant calcined MgO was then cooled to room temperature under vacuum and transferred to an argon-filled glove box (< 1 ppm O₂ and < 1 ppm H₂O). The surface area of final calcined MgO is approximately 100 m²/g. The precursor, Ir(C₂H₄)₂(acac), was synthesized as described before,² and stored in an argon-filled glove box. To prepare the supported catalyst containing 1.0 wt% Ir, 54 mg of Ir(C₂H₄)₂(acac) and 2.946 g of calcined MgO were slurried in dried and deoxygenated *n*-pentane (Fisher, HPLC grade, dried and purified by a Grubbs apparatus, MBraun SPS, in the presence of argon) that was initially at dry-ice temperature. The slurry was mixed for two days at dry-ice temperature, and thereafter the solvent was removed by evacuation for a day. The resultant supported iridium sample was light gray in color. It was stored in an argon-filled glove box.

To transfer the supported iridium sample to the TEM facility, it was first packed in small vials and wrapped with paraffin film under argon atmosphere. Then, the vials were placed in a 10-cm vacuum tube sealed with vacuum flanges from both sides. The sealed vacuum tube was then shipped to the TEM facility.

At the TEM facility, the sealed vacuum tube containing the samples were transferred into a glove bag filled with ultrahigh-purity argon. In there, the tube was opened and the samples were loaded into a lacey carbon grid, which was inserted in a TEM holder under

argon. The glove bag was next moved to the microscope and briefly opened, whereupon the TEM holder was transferred quickly to the microscope. The turbo-molecular pump used to evacuate the microscope chamber was switched on several minutes before insertion of the sample to allow the attainment of its operational speed. The pumping on the airlock was begun immediately after the specimen was inserted into the microscope. We estimate that the time period during which trace contaminants of air might have intruded into the sample holder prior to its insertion into the airlock and re-establishment of the vacuum was less than 5 s.

The fast-scan high-angle annular dark-field (HAADF) STEM imaging experiments were performed at 300 kV using an FEI TitanS 80-300 electron microscope at the Center for Nanophase Materials Sciences, Oak Ridge National Laboratory. This microscope was equipped with a high brightness XFEG field emission gun and a CEOS dodecapole probe (STEM) aberration corrector. The images were captured by a HAADF detector with a probe convergence angle of 27.5 mrad and with collection angle from 50 to 200 mrad. Intensities of atomic columns in the sequential Z-contrast images were quantified using the ImageJ software³.

To investigate the relative stability of the different adsorption configurations of Ir(1-3) clusters on both (110) and (100) MgO surfaces, calculations were performed using Density Functional Theory (DFT) as implemented in the Vienna *ab-initio* Simulations Package VASP^{4,5} with Perdew-Wang exchange-correlation functionals⁶. We have used the projector augmented wave (PAW)⁷ potentials with cutoff of 400 eV. The atomic positions were relaxed until the Hellmann-Feynman forces were less than 4×10^{-3} eV/Å. Brillouin zone integrations during the structural optimization are based on a (3x3x1) grid

of Monkhorst-Pack points⁸. MgO (110) surfaces were modeled using periodic symmetric seven-layer slabs, and a vacuum region of 19.16 Å, while MgO (100) were modeled using asymmetric four-layer slabs and a vacuum region of 11.26 Å. The middle/bottom layers were fixed at the calculated bulk lattice constant 4.207 Å, in the case of symmetric/asymmetric slabs, respectively. The calculated lattice constant is in agreement with previous *ab-initio* pseudopotential calculations (4.16 Å)⁹ and experimental measurements (4.207 Å at 19.8 K)¹⁰. The extent of the vacuum region was chosen larger for the (110) surface to accommodate the Ir₃ clusters adsorbed on both faces of the slabs, to ensure minimum interaction between the images. We used (2ax2a) and (2ax2a√2) surface cells to describe the (100) and (110) surfaces, respectively, where a is the lattice parameter.

References

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