

Atomic Level Characterization of Transition-Metal Catalytic Clusters and Nanoparticles on MgAl₂O₄ Substrate

L. Kovarik*, R. Dagle**, H. Wan**, J.H. Kwak**, B. Kabius*, C.M. Wang*, S. Thevuthasan* S.C.H.F. Peden**

* Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352

** Institute for Interfacial Catalysis, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352

Transition metals supported by MgAl₂O₄ represent a prevalent group of heterogeneous catalysts used in a variety of reforming reactions. The relationship between the atomic level microstructure and property of these catalytic systems remains a subject of a wide research effort. This is especially the case for systems prepared in the form of small clusters due to their intriguing catalytic properties. In this work we will report a recent progress in the study of Pt, Pd, Rh, Ir clusters/nanoparticles supported by MgAl₂O₄. These catalysts are currently being developed for tar and methane reforming for the cleanup of biomass-derived syngas utilized for thermochemical conversions to fuels and chemicals.

The aim of this work is to develop a detail structural understanding of the metallic clusters/nanoparticles and the way they are anchored to substrate matrix. Complimentary imaging techniques, such as STEM HAADF and HRTEM together with image simulation were employed. The electron microscopy observations were performed on FEI Titan 80-300 equipped with CEOS C_s-probe corrector operated at 300kV.

Figure 1a shows a representative bright field image of the MgAl₂O₄ crystals supporting Ir reduced at 850°C. A large portion of the freshly reduced Ir clusters/nanoparticles are in the size range of 1-2nm. The Rh, Pd and Pt clusters/nanoparticles exhibit a similar size distribution. Detailed HRTEM work reveals that many of the nanoparticles assume their bulk FCC crystal structure and that they are preferentially attached to the (110) MgAl₂O₄ facets. These nanoparticles are epitaxially related to the substrate, and the relationship can be described as (110)_{MgAl₂O₄}//(110)_{TM} and [200]_{MgAl₂O₄}//[200]_{TM}, as shown in Fig.2b. The epitaxial relationship can be well-rationalized based on the structural compatibility at (110) metal/oxide interface.

Aberration corrected STEM HAADF imaging provides further insight about the structural nature of the clusters/nanoparticles and the way they are anchored to the MgAl₂O₄ substrate. Figure 1c shows an example of Ir nanoparticle and several other Ir clusters populating the (110) MgAl₂O₄ surface. This HAADF image directly reveals the position of the oxide crystallographic lattice planes with respect to the Ir atoms and the lattice planes of the nanoparticle. Please note that the characteristic spinel periodicity of (111) planes is not detected in this image, suggesting a possible disordering of the Mg tetrahedral and Al octahedral sites in this thin section. The other important feature in this HAADF image is the intensity at the position of the Ir atoms/atomic columns. Analysis of the image intensities and the lattice correspondence enables us to propose a full 3D model of the nanoparticle, as shown in Fig.1d. The assumption used in the structural and morphological derivation together with a complimentary STEM HAADF imaging simulations will be presented.

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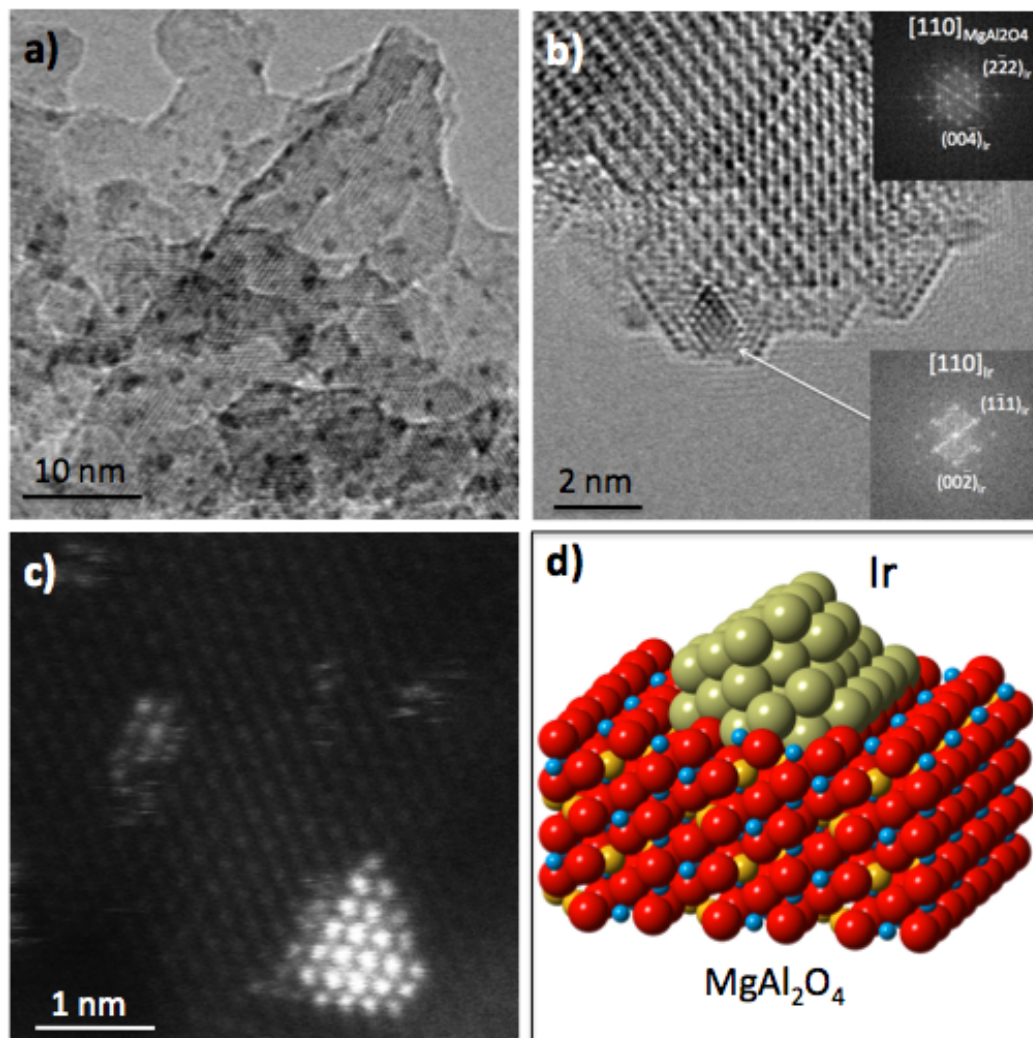


Fig.1 a) Representative bright field image of the MgAl_2O_4 crystals supporting Ir clusters/nanoparticles. b) HRTEM image of Ir nanoparticle attached to the (110) surface of the MgAl_2O_4 . c) STEM HAADF detail view of the Ir clusters and nanoparticles on the support oxide. d) Atomic model of the Ir nanoparticle anchored to the oxide support as derived on the basis of the HAADF observations.