

Dynamic Structural Changes in a Zeolite-Supported Iridium Catalyst for Ethylene Hydrogenation: Reversible Interconversion of Metal Complexes and Clusters Controlled by the Reactant Composition

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Introduction

Molecular organometallic precursors that react precisely with structurally well-defined supports offer excellent opportunities for synthesis of uniform site-isolated supported catalysts that allow precise determinations of catalyst structure-property relationships. With complementary spectroscopic methods, such species can be characterized in the working state and as they undergo structural changes. We now report real-time characterization of such a catalyst, showing the dynamic balance between catalytically active metal complexes and metal clusters. Time-resolved extended X-ray absorption fine structure (EXAFS) data characterizing a zeolite-supported iridium catalyst for ethylene hydrogenation demonstrate the reversible interconversion of mononuclear iridium complexes and Ir₄ clusters, controlled by changes in the feed C₂H₄:H₂ ratio. Further evidence of the structural changes was provided by IR spectra characterizing iridium carbonyls, which distinguish mononuclear complexes from clusters.

Materials and Methods

A zeolite-supported catalyst containing 1.0 wt% Ir was prepared by the reaction of Ir(C₂H₄)₂(acac) [acac is CH₃COCHCOCH₃] with highly dealuminated HY zeolite (DAY) (Zeolyst CBV760). IR and EXAFS measurements were made separately during the catalytic reaction occurring in cells that are flow reactors. Time-resolved EXAFS spectra of the catalyst in various atmospheres were recorded in transmission mode every 2 min at beamline MR-CAT of the Advanced Photon Source at Argonne National Laboratory. Details of the X-ray absorption spectroscopy experiments and data analysis procedures are described elsewhere [1], as is the EXAFS cell/reactor [2]. During the initial treatment of the catalyst in flowing H₂, the temperature was increased to 80°C and then kept constant and the flow of reactant gas started, and the feed composition was subsequently cycled between a C₂H₄-rich mixture (C₂H₄:H₂ = 4, molar), an equimolar mixture, and a H₂-rich mixture (C₂H₄:H₂ = 0.5).

Results and Discussion

Ir₄ clusters formed during treatment of the supported mononuclear iridium complexes in H₂ as the temperature increased to 80°C [1]. Then the flow of the C₂H₄-rich feed started at 80°C, and time-resolved EXAFS spectra showed the breakup of the clusters, indicated by the decreasing Ir–Ir coordination number (from 3 to 0.4 over a period of 20 min) and increasing Ir–low-Z-scatterer contributions (Ir–O and Ir–C) (Figure 1). The data demonstrate the formation of mononuclear iridium complexes, present with clusters. Confirmation of the formation of mononuclear iridium complexes by the cluster breakup under

these conditions was provided by IR spectra of the sample probed with CO, indicating the formation of Ir(CO)₂ species (ν_{CO}: 2108 and 2038 cm⁻¹) following a CO pulse.

The cluster breakup was reversible. Changing the feed from ethylene-rich to equimolar ethylene + H₂ and then H₂-rich led to reconstruction of Ir₄ clusters, shown by an increasing Ir–Ir coordination number, from 0.4 to 3, and a corresponding decrease in the Ir–low-Z-scatterer contributions. IR spectra obtained after a CO pulse indicated iridium carbonyl clusters, Ir₄(CO)₁₂, (ν_{CO}: 2108, 2038, 2022, and 1984 cm⁻¹) [3]. The catalyst was cycled repeatedly between the two states as the gas composition was cycled during the reaction (Figure 1).

Significance

This work illustrates clearly how reactant composition determines catalyst structure; specifically, supported group-8 metal catalysts are readily converted between mononuclear and cluster forms—thus there is a large and important class of catalysts that can exist in various forms that require characterization under working conditions. The data demonstrate the power of a third-generation synchrotron and a beamline equipped with an insertion device for excellent time-resolved EXAFS measurements of working catalysts.

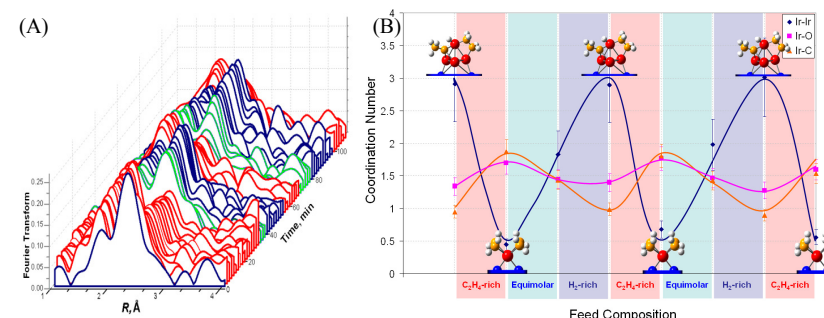


Figure 1. (A) Radial distribution function determined from time-resolved EXAFS measurements of working catalyst formed from Ir(C₂H₄)₂(acac) and dealuminated zeolite Y recorded during changes in the C₂H₄:H₂ ratio: C₂H₄-rich mixture (red), equimolar C₂H₄ + H₂ mixture (green), and H₂-rich mixture (dark blue); (B) EXAFS results characterizing changes in coordination numbers as the reactant composition was cycled (the structural models are simplified).

References

- Uzun, A., Gates, B. C. *Angew. Chem. Int. Ed.* DOI:10.1002/anie.200802140.
- Odzak, J. F., Argo, A. M., Lai, F. S., Gates, B. C. *Rev. Sci. Instrum.* 72, 3943 (2001).
- Argo, A. M., Gates, B. C. *J. Phys. Chem. B* 107, 5519 (2003).