

Time-Resolved X-ray Absorption Spectra Characterizing Formation and Breakup of Zeolite-Supported Iridium Cluster Catalysts

Alper Uzun¹, Philip W. Kletnieks², James F. Haw², and Bruce C. Gates^{1,*}

¹Dept. of Chemical Engineering and Materials Science, University of California, Davis, CA 95616 (USA)

²Department of Chemistry, University of Southern California, Los Angeles, CA 90089-1661 (USA)

*Corresponding author: bcgates@ucdavis.edu

Introduction

Molecular organometallic precursors that react simply with supports offer excellent opportunities for synthesis of structurally uniform site-isolated mononuclear transition metal complex catalysts. We now report the synthesis of an iridium complex with reactive ethylene ligands bonded to DAY zeolite cages and its characterization by time-resolved EXAFS spectroscopy. The data demonstrate aggregation of the iridium to form extremely small clusters and de-aggregation of the clusters in ethylene to regenerate mononuclear iridium sites; under conditions of catalytic ethylene hydrogenation, EXAFS and IR spectra identify mononuclear iridium complexes as the catalytically active species.

Materials and Methods

A zeolite-supported catalyst containing 1 wt% Ir was prepared by bringing $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{acac})$ [acac is $\text{CH}_3\text{COCHCOCH}_3$] in contact with highly dealuminated HY zeolite (DAY) (Zeolyst CBV760). Measurements of the catalytic activity for ethylene hydrogenation were carried out with a conventional once-through tubular reactor operated at atmospheric pressure and room temperature,¹ and IR and EXAFS measurements were also made during the catalytic hydrogenation of ethylene. Time-resolved EXAFS spectra of the catalyst in various atmospheres were recorded in transmission mode every 3 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,² as is the EXAFS cell that served as a flow reactor.³ During the initial treatment of the catalyst in flowing H_2 , the temperature was increased to 80°C and then kept constant as the gas flow was subsequently cycled between H_2 and C_2H_4 .

Results and Discussion

Time-resolved EXAFS results obtained during heating of the initial supported iridium complex in H_2 show that iridium clusters started to form (as Ir–Ir contributions appeared in the EXAFS spectrum) at about 75°C. When a similar experiment was performed with He instead of H_2 flow, no Ir–Ir contribution was observed, even at 120°C. This comparison shows that H_2 plays an important role for the formation of the iridium clusters. The first data obtained at 80°C under H_2 flow indicate clusters with an Ir–Ir first-shell coordination number of approximately 4, on average, with an Ir–Ir bonding distance of 2.63 Å; thus, the clusters are approximated as Ir_6 octahedra.

When the H_2 flow was replaced by C_2H_4 at 80°C, the Ir–Ir contributions decreased and disappeared gradually in about 20 min; again site-isolated mononuclear iridium complexes formed. The data determine the rates of these cluster formation and de-aggregation processes. The sample in the presence of mixtures of H_2 and ethylene was found to be active for the catalytic formation of ethane, with a turnover frequency of 0.07 s^{-1} at room temperature in the presence of flowing H_2 at 30 Torr and C_2H_4 at 30 Torr. EXAFS spectra of the functioning supported catalyst demonstrate the presence of mononuclear iridium complexes, with no detectable clusters. The Ir atoms in the samples consisting of the disassembled clusters were spaced at an average distance of 3.2 Å, consistent with nearby single-Ir atom fragments and the reversibility of the cluster formation-aggregation process, which was demonstrated by repeated cycling of the catalyst between H_2 and C_2H_4 flows. Thus, the EXAFS results indicate that the catalytically active species are mononuclear iridium complexes and not clusters under these conditions, and that ethylene bonds strongly enough to the iridium to fragment small clusters.

Significance

This work is new in exemplifying structural changes in a working catalyst, including metal–metal bond breaking and formation following step changes in the feed composition, determined in time-resolved EXAFS measurements at a third-generation synchrotron.

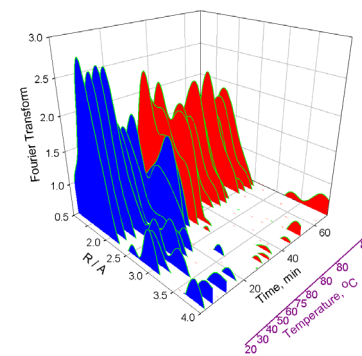


Figure 1. Radial distribution function determined from time-resolved EXAFS measurements recorded during heat treatment experiment in H_2 (blue) and C_2H_4 flow (red)

References

1. Zhao, A., Gates, B.C.J. *Am. Chem. Soc.* 118, 2458 (1996).
2. Argo, A. M., Gates, B. C. *J. Phys. Chem. B* 107, 5519 (2003).
3. Odzak, J. F., Argo, A. M., Lai, F. S., Gates, B. C. *Rev. Sci. Instrum.* 72, 3943 (2001).

Acknowledgments

The research at the University of California was supported by DOE, grant DE-FG02-04ER15600; that at the University of Southern California by DOE grant DE-FG02-04ER15598 and the Robert Ramsay Chair Foundation. We thank the staff at beamlines MR-CAT at APS and X-18B at NSLS.