

Structure, Dynamics, and Dehydrogenation Properties of a Supported Single-site Organoiridium Catalyst

Neng Guo¹, Hongbo Li², R. Tom Baker², Alfred P. Sattelberger³, Jeffrey T. Miller¹ and Christopher L. Marshall^{1*}

¹Chemical Sciences & Engineering Division, Argonne National Laboratory, Argonne, IL 60439

²Chemistry Division, MS J582, Los Alamos National Laboratory, Los Alamos, NM 87545

³Energy Sciences and Engineering Directorate, Argonne National Laboratory, Argonne, IL 60439

marshall@anl.gov

Introduction

Direct transformation of abundant saturated hydrocarbons (alkanes) to other value-added chemicals such as alcohols, esters, and polymers has far-reaching implications; however, very few practical processes exist. Conversion of alkanes to olefins and subsequent functionalization of C=C is an attractive alternative. Although current industrial scale steam cracking and thermal dehydrogenation produce olefins, these processes are highly energy intensive and nonselective. Moreover, the catalysts have to be regenerated regularly due to coke formation.¹

Supported single-site “molecular” catalysts, which are synthesized by covalent immobilization of organometallic complexes onto metal oxide supports, represent a major advance in the field of catalysis and show promise for a variety of catalytic reactions such as olefin polymerization,² alkane metathesis,³ and even dinitrogen reduction.⁴ Such a strategy combines the advantages of both heterogeneous (activity, stability, and recyclability) and homogeneous (well-defined structure and tunability) catalysts.

In this contribution, we present the synthesis, characterization, structural dynamics, and cyclohexane dehydrogenation properties of a supported organoiridium catalyst. A thorough understanding of the catalytically active species is important in aiding future catalysts design.

Materials and Methods

Manipulations of air-sensitive materials were performed with rigorous exclusion of O₂ and moisture in Schlenk-type glassware on a dual-manifold Schlenk line or in a argon-filled Vacuum Atmospheres glove box (<1 ppm O₂ and H₂O). Hexane, cyclohexane, diethyl ether (Sigma-Aldrich) were dried over CaH₂ for at least a week and were freshly vacuum-transferred prior to experiments. BuLi and IrCl₃·3H₂O were purchased from Sigma-Aldrich and was used as received. Sn(allyl)₄ was purchased from Gelest and was vacuum-distilled prior to use. Tris(allyl)iridium was synthesized according to literature procedures.⁵ Solution ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Varian Innova 400 MHz spectrometer at room temperature. γ-alumina (125-250 μm) was treated under He flow at 1000 for 20 min to afford the fully dehydroxylated alumina.

X-ray absorption fine structure spectroscopy (XAFS) studies were performed at the Materials Research Collaborative Access Team (MRCAT) beamline at the Advanced Photon Source, Argonne National Laboratory. The set-up was similar to that outlined by Castagnola, et al.⁶ The backscattering amplitudes and phase shifts of the Ir–Ir and Ir–C contributions were based on Pt foil and Pt(NH₃)₄(NO₃)₂, respectively.

Results and Discussion

Reaction of Ir(allyl)₃ with fully dehydroxylated γ-alumina affords Ir(allyl)₂(O–)/Al₂O₃ and one equivalent of propylene. The supported organoiridium catalyst was characterized by a variety of analytical and spectroscopic techniques. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) revealed that the iridium loading is ~ 1.9 wt%. Solid state NMR suggests that upon immobilization onto the support, the two remaining allyl groups on the iridium center become equivalent. EXAFS data shows that there are 6 carbons around the iridium center with an average distance of 2.11 Å, corresponding to two allyl groups. In situ XAFS shows that under cyclohexane dehydrogenation conditions, the supported Ir³⁺ begins to lose the allyl ligand at temperature above 100 °C and metallic iridium (Ir⁰) begins to form at temperatures ~ 180 °C (Figure 1). The pure supported Ir³⁺ catalyst exhibits very low activity for the dehydrogenation of cyclohexane. The fully reduced Ir⁰ catalyst (3.2% H₂ in Ar, 370 °C, 1 hr) selectively dehydrogenates cyclohexane to benzene between 180 and 300 °C with an estimated activation energy of 41.0 KJ/mol.

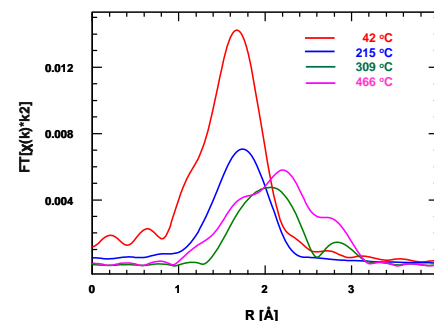


Figure 1. Magnitude of the Fourier transform for the k^2 -weighted EXAFS function for Ir(allyl)₂(O[–])/Al₂O₃ at different temperatures under cyclohexane flow.

Significance

This work demonstrated that in situ XAFS is a powerful tool to probe the structure of the catalytically active species under real reaction conditions.

References

1. Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507-514.
2. Nicholas, C. P.; Ahn, H.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 4325-4331.
3. Vidal, V.; Theolier, A.; Thivolle-Cazat, J.; Basset, J.-M. *Science* **1997**, *276*, 99-102.
4. Avenier, P.; Taoufik, M.; Lesage, A.; Solans-Monfort, X.; Baudouin, A.; de Mallmann, A.; Veyre, L.; Basset, J.-M.; Eisenstein, O.; Emsley, L.; Quadrelli, E. A. *Science* **2007**, *317*, 1056-1060.
5. John, K. D.; Salazar, K. V.; Scott, B. L.; Baker, R. T.; Sattelberger, A. P. *Organometallics* **2001**, *20*, 296-304.
6. Castagnola, N. B.; Kropf, A. J.; Marshall, C. L. *Appl. Catal. A: General* **2005**, *290*, 110–122.