On route to understanding ligand control of catalysis on supported cluster surfaces

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Abstract: Using a substituted tetrairidium cluster as a uniform supported molecular active site, we investigate the effects of environment surrounding a metal site on its reactivity involving hydrogen transfer. Our approach controls and characterizes a new type of single-site catalyst, in which the active site is located at the apical iridium atom of a tetrahedral cluster, and is supported on a basal plane of three iridium atoms below it, where other ligands bond. A combination of synthesis, in-situ spectroscopy, kinetics, and electronic structure calculations inform on structure and function in catalysis involving hydrogen transfer, in a high level of detail.

Keywords: hydrogen transfer, noble metal, single site catalyst

1. Introduction

The goal of design of catalysts for whole classes of reactions through understanding of relationships between molecular-level structure and reactivity of active sites is most readily realized when the catalysts are molecular.[1] In the work reported here, we investigated supported molecular catalysts with the goal of understanding the effects of ligands such as oxygen on catalysis involving hydrogen transfer on a metal – a question that has captivated scientists for more than one hundred years.[2] To shed light on this, our approach has been to reduce the complexity of the active site as much as possible, using a single atom active site that is located at the apical position of a silica-supported tetrairidium cluster (cluster **A**). Each cluster **A** consists of a tetrahedron of Ir atoms, the basal plane of which consists of three Ir atoms, each substituted with a sterically bulky calixarene phosphine ligand, as shown in Figure 1.[3,4]

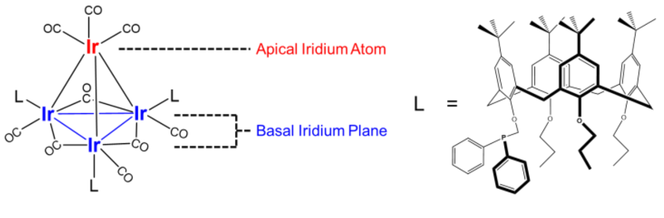
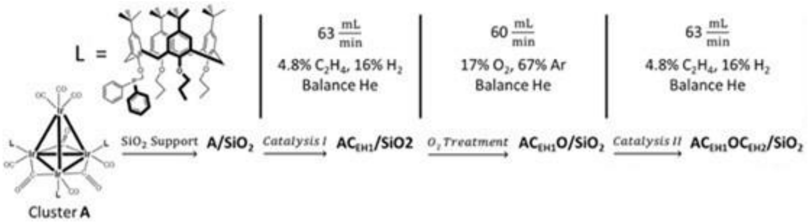


Figure 1. Schematic representation of a trisubstituted tetrairidium carbonyl cluster, closed cluster **A** ($Ir_4(CO)_9L_3$), with three bulky phosphine ligands on the basal plane of the tetrahedron (left); structure of calix[4]-arene phosphine ligand L shown at right.

2. Experimental

The schematic below represents reactions used to synthesize iridium cluster catalysts via oxygen activation of supported cluster **A** under mild conditions (323 K and 1 bar). Ethylene hydrogenation catalysis was investigated with a U-tube flow reactor and feed composition of 63 mL/min (16% H_2, 5% C_2H_4 balance He).



3. Results and discussion

The data of Figure 2 show the catalytic activity of the silica-supported tetrairidium clusters for ethylene hydrogenation, before and after incorporation of oxygen ligands. As previously reported,[3,4] the cluster prior to oxygen exposure, **ACEH1/SiO2**, has a low activity for ethylene hydrogenation, with a steady-state TOF of 0.16 ± 0.07 molecules (Ir atom)$^{-1}$ h^{-1} (on an Ir atom basis). After reacting the catalyst in flowing oxygen at 323 K and 1 bar, the activity increased by 100-fold from its value prior to O_2 flow, with a steady-state TOF of 16.8 ± 0.2 molecules (Ir atom)$^{-1}$ h^{-1}. Using a combination of in-situ spectroscopy (Raman, infrared, X-ray absorption), high-resolution scanning transmission electron microscopy (STEM), and electronic structure calculations, we elucidate the role of oxygen reaction, and in particular of permanently bound dioxygen ligands on the basal plane of silica-supported cluster **A**, in enhancing hydrogen transfer associated with hydrogenation catalysis.

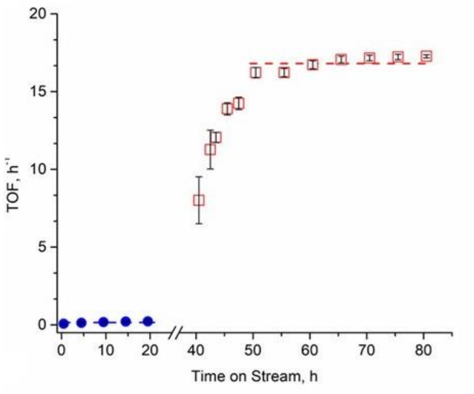


Figure 2. Ethylene hydrogenation for silica-supported $Ir_4L_3(CO)_9$ with and without reaction of catalyst in dioxygen in a flow reactor at 323 K and 1 bar (250 mg of catalyst, containing 1 wt.% Ir). After 20 h of first ethylene hydrogenation catalysis (blue), the feed was switched from C_2H_4, H_2, and helium to O_2 and helium flowing for 20 h (60 mL/min dry air and 10 mL/min helium). This switch was followed by another switch to the original conditions for a second period of ethylene hydrogenation catalysis, after exposure of catalyst to oxygen (red).

4. Conclusions

Reaction of supported tetrairidium cluster A with dioxygen under mild conditions leads to greatly enhanced rates of ethylene hydrogenation, with enhancements in TOF of over 100 fold. Because the active sites employed for this study are uniform, a great deal can be learned in terms of structure-function correlations, and these lessons in turn open wide vistas into designing and tuning catalysis on surfaces for reactions involving hydrogen transfer.

References

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