Advanced Characterizations for the Identification of Catalyst Structures and Reaction Intermediates

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In recent decades, alternatives to traditional coal and fossil fuels were utilized to reduce carbon emissions. Among these alternatives, natural gas is a cleaner fuel and is abundant globally. Shale gas, a form of natural gas that also contains light alkanes (C2-C4), is presently being employed to produce olefins, which can be upgraded to higher molecular weight hydrocarbons. This thesis describes efforts to develop new catalytic materials and characterizations for the conversion of shale gas to fuels.

In the first half, silica supported Pt-Cr alloys containing varying compositions of Pt and Pt_3Cr were used for propane dehydrogenation at 550°C. Although a change in selective performance was observed on catalysts with varying promoter compositions, the average nano-particle structures determined by *in situ*, synchrotron x-ray absorption spectroscopy (XAS) and x-ray diffraction (XRD) were identical. Further, this work presents a method for the characterization of the catalytic surface by these methods to understand its relationship with olefin selectivity. From this, we can gain an atomically precise control of new alloys compositions with tunable surface structures.

Once formed by dehydrogenation, the intermediate olefins are converted to fuel-range hydrocarbons. In the second half, previously unknown single site, main group Zn^{2+} and Ga^{3+} catalysts are shown to be effective for oligomerization and the resulting products follow a Schutlz Flory distribution. Mechanistic studies suggest these catalysts form metal hydride and metal alkyl reaction intermediates and are active for olefin insertion and β-H elimination elementary steps, typical for the homogeneous, Cossee-Arlman oligomerization mechanism. Evidence of metal hydride and metal alkyl species were observed by XAS, Fourier transform infrared spectroscopy (FTIR), and H_2/D_2 isotope exchange. Understanding the reaction intermediates and elementary steps is critical for identifying novel oligomerization catalysts with tunable product selectivity for targeted applications.

Through controlled synthesis and atomic level *in situ* characterizations, new catalysts compositions can be developed with high control over the resulting performance. An atomically precise control of the catalyst structure and understanding how it evolves under reaction conditions can help shed light on the fundamental principles required for rational catalyst design.