ABSTRACT

Author: Cesar, Laryssa Gonçalves. PhD
Institution: Purdue University
Degree Received: August 2019
Title: Light Alkanes to Higher Molecular Weight Olefins: Catalysts for Propane Dehydrogenation and Ethylene Oligomerization.
Committee Chair: Jeffrey T. Miller

The increase in shale gas exploitation has motivated the studies towards new processes for converting light alkanes into higher valuable chemicals, including fuels. The works in this dissertation focuses on two processes: propane dehydrogenation and ethylene oligomerization. The former involves the conversion of propane into propylene and hydrogen, while the latter converts light alkenes into higher molecular weight products, such as butylene and hexene.

The thesis project focuses on understanding the effect of geometric effects of Pt alloy catalysts for propane dehydrogenation and the methodologies for their characterization. Pt-Co bimetallic catalysts were synthesized with increasing Co loadings, characterized and evaluated for its propane dehydrogenation performance. In-situ synchrotron X-Ray Powder Diffraction (XRD) and X-Ray Absorption (XAS) were used to identify and differentiate between the intermetallic compound phases in the nanoparticle surface and core. Difference spectra between oxidized and reduced catalysts suggested that, despite the increase in Co loading, the catalytic surface remained the same, Pt_3Co in a Au_3Cu structure, while the core became richer in Co, changing from a monometallic Pt fcc core at the lowest Co loading to a PtCo phase in a AuCu structure at the highest loading. Co^{II} single sites were also observed on the surface, due to non-reduced Co species. The catalytic performance towards propane dehydrogenation reinforced this structure, as propylene selectivity was around 96% for all catalysts, albeit the difference in composition. The Turnover Rate (TOR) of these catalysts was also similar to that of monometallic Pt catalysts, around 0.9 s^{-1}, suggesting Pt was the active site, while Co atoms behaved as non-active, despite both atoms being active in their monometallic counterparts.

In the second project, a single site Co^{II} catalyst supported on SiO_2 was evaluated for ethylene oligomerization activity. The catalyst was synthesized, evaluated for propane dehydrogenation, propylene hydrogenation and ethylene oligomerization activities and characterized *in-situ* by XAS and EXAFS and H_2/D_2 exchange experiments. The catalysts have shown negligible conversion at

250ºC for ethylene oligomerization, while a benchmark Ni/SiO_2 catalyst had about 20% conversion and TOR of $2.3x10^{-1}$ s^{-1}. However, as the temperature increased to above 300ºC, ethylene conversion increased significantly, reaching about 98% above 425ºC. *In-situ* XANES and EXAFS characterization suggested that H_2 uptake under pure H_2 increased in about two-fold from 200ºC to 500ºC, due to the loss of coordination of Co-O bonds and formation of Co-H bonds. This was further confirmed by H_2/D_2 experiments with a two-fold increase in HD formation per mole of Co. *In-situ* XAS characterization was also performed with pure C_2H_4 at 200ºC showed a similar trend in Co-O bond loss, suggesting the formation of Co-alkyl, similarly to that of Co-H. The *in-situ* XANES spectra showed that the oxidation state remained stable as a Co^{2+} despite the change in the coordination environment, suggesting that the reactions occurs through a non-redox mechanism. These combined results allowed the proposition of a reaction pathway for dehydrogenation and oligomerization reactions, which undergo a similar reaction intermediate, a Metal-alkyl or Metal-Hydride intermediates, activating C-H bonds at high temperatures.