ABSTRACT

Author: Wu, Zhenwei. PhD
Institution: Purdue University
Degree Received: August 2018
Title: The Structure-Function Relationship of Intermetallic Compound Catalysts for Light Alkane Dehydrogenation
Committee Chair: Jeffrey Miller

Better utilization of fossil fuels with less emissions is crucial to meet the energy and environmental needs in the near future. The unprecedented revolution of shale gas production in the past decade motivates development of gas-to-liquid fuels technique starting with light alkane dehydrogenation. For better design of catalytic light alkane dehydrogenation, this dissertation synthesizes a wide range of new catalysts including intermetallic nanoparticles formed between Pd-In, Pt-In, Pt-Zn, Pt-Mn and solid solutions formed between Pt-Cu. Emerging techniques *in situ* Synchrotron X-ray Diffraction, *in situ* Difference X-ray Absorption Spectroscopy and Resonant Inelastic X-ray Scattering are developed and/or applied to characterize the long range, surface and electronic structures of the catalysts, respectively. The results shed light on the formation mechanism of intermetallic nanoparticles as well as the structure-functions relationship guiding rational catalyst design.

The structural evolution of Pd-In, Pt-In, Pt-Zn and Pt-Mn nanoparticles with different composition suggests that intermetallic formation is diffusion or kinetically limited. This solid state reaction starts from the surface of the noble metal NP, resulting in core-shell type nanostructures at relatively low loading of the second metal. Among the thermodynamically stable intermetallic phases in the bulk phase diagram for a certain binary system, only the phases with high crystal symmetry (PdIn, Pt_3In, $PtIn_2$, PtZn, and Pt_3Mn) are formed. This is a consequence of minimal structural transformation from the parent highly symmetric noble metal nanoparticles, which has the lowest activation barrier for solid state diffusion. This mechanism plays a key role for predicting the structure of new intermetallic catalysts.

Nanoparticle catalysts with different geometric structures (intermetallic compounds vs solid solution) are compared for their light alkane dehydrogenation selectivity. The two structure

types show very different light alkane dehydrogenation selectivity dependence on the promoter content, disclosing the surface site geometry requirement for an ensemble effect. For Pt-Cu solid solution catalysts which has a random surface atom arrangement of Pt and Cu, the selectivity gradually and almost linearly increases with Cu content. High dehydrogenation selectivity is only obtained at high Cu:Pt atomic ratio when Pt is guaranteed to be isolated by neighboring Cu. In comparison, for Pd-In, Pt-In and Pt-Mn catalysts which have intermetallic compounds structure, their selectivity jumps to very high level upon incorporation of only small amount of promoters. This is due to the preferential formation of ordered intermetallics on the nanoparticle surface at low promoter loading. An ordered intermetallic surface contains active sites uniformly separated by periodically distributed promoters. It is much more effective in geometrically isolate the active sites compared to solid solution.

For most bimetallic catalysts, electronic effect always occur simultaneously with geometric effect and separation of the contribution of electronic effect has been very challenging. By comparing two Pt-Mn catalysts containing the same Pt_3Mn surface with essentially the same geometric effect but different subsurface layers, an electronic effect was disentangled and confirmed to be present on such intermetallic catalysts. A Pt_3Mn subsurface instead of Pt significantly increases the selectivity and changes the turnover rate of propane dehydrogenation. This is found to relate with the much weaker adsorption strength of adsorbates on the former catalyst according to experimental measurements as well as Density Functional Theory. The change can be related with different 5*d* electron states upon intermetallic formation. Through Resonant Inelastic X-ray Scattering (RIXS), a downward shift of the occupied 5*d* states together with an upward shift of the unoccupied 5*d* states compared to Pt are observed. This is reflective of the strong heteroatomic interaction characteristic of intermetallic phases. Such electronic effect is correlated with the composition and structure of the catalysts, providing tremendous opportunities to tune the catalytic selectivity and rate via materials design.

Overall, through controlled synthesis and atomic level *in situ* characterization, new intermetallic nanoparticle catalysts have been identified with superior selectivity, stability and rate for dehydrogenation of light alkane. The rules behind the intermetallic formation as well as the structure-function relationship of the catalysts have been disclosed. An atomically precise understanding of the geometric effect and the electronic properties shed light on new principles for rational design of supported nanoparticle catalysts under realistic reaction conditions.