Conversion of Shale Gas with Supported Metal Catalysts

Author: Johnny Zhuchen

Committee Chair: Jeffrey T. Miller

As shale gas exploitation has been developed, production of shale gas in the US has rapidly increased during the last decade. This has motivated the development of techniques to covert shale gas components (mainly C_1 to C_3) to liquid fuels by catalytic conversion. The main goal of the dissertation is to study the geometric and electronic structures of the metal catalysts, which are crucial for understanding the structure-property relationship.

The first project studies bimetallic Pt-Bi catalyst for non-oxidative coupling of methane. In a recent publication published in ACS catalysis, Pt-Bi/ZSM-5 catalyst has been shown to stably convert methane into C_2 for 8 hours under non-oxidative conditions. In this study, structure of the Pt-Bi/ZSM-5 was shown with HAADF imaging, synchrotron XAS and XRD. A new surface cubic Pt_3Bi phase on Pt nanoparticles with Pt-Bi bond distance of 2.80 Å was formed. Formation of noble metal intermetallic alloys such as Pt_3M may be the clue for non-oxidative conversion of methane.

The second and third project highlight strong metal-support interaction catalysts for propane dehydrogenation. Chemisorption showed partial coverage of the SMSI oxides on the surface of the nanoparticles. *In situ* X-ray absorption near edge (XANES), resonant inelastic X-ray scattering (RIXS), X-ray photoelectron spectroscopy (XPS) have shown that little electronic effect on the metal nanoparticles. The catalyst activity per mol of metal decreased due to the partial coverage of the SMSI oxides on the surface of the catalysts. The catalysts, however, had higher selectivity due to smaller ensembles inhibiting hydrogenolysis.

In the fourth project Pt-P catalyst was investigated to understand the promoting effect

of P. Pt-P catalysts had much higher selectivity for propane dehydrogenation (>95%). These give two types of catalysts, a PtP_2-rich surface on Pt core and full PtP_2 ordered structure, which were confirmed by scanning transmission electron microscopy (STEM), and *in situ* methods of EXAFS, synchrotron XRD, XPS, and Resonant Inelastic X-ray Spectroscopy (RIXS). The PtP_2 structure has isolated Pt atoms separated by P_2 atoms. In addition, XANES, XPS and RIXS indicate a strong electronic modification in the energy of the valence orbitals.