

Structure and Reactivity of Intermetallic Alloy Catalysts For Alkane Dehydrogenation

As the United States moves towards energy independence, shale gas has become an attractive domestic resource for use as a feedstock to produce liquid fuels. While the major component of shale gas is methane, it can contain up to 20% ethane and propane. One potential approach to utilize shale gas is to convert the C₂ and C₃ paraffins into olefins by catalytic dehydrogenation. While platinum catalyzes dehydrogenation, it is poorly selective. To achieve high selectivity a second metal is added to the Pt, forming alloys, which has been proposed to cause both geometric and electronic changes to the active metal. The purpose of this work is to study these alloying effects and the role each plays in increasing olefin selectivity during alkane dehydrogenation.

Alloys of Pd-In, Pt-In, Pt-Zn, and Pt-Fe were investigated for the dehydrogenation of alkanes. The alloys were significantly more selective and had slightly higher turnover rates (TOR) than monometallic catalysts. *In situ* characterization by X-ray absorption spectroscopy and X-ray diffraction revealed that the intermetallic compounds (IMC) which formed had similar structures to those of the initially formed monometallic active metal particles. In the IMC structures there are no large ensembles of catalytic atoms, which are thought to be responsible for methane formation, and thus are highly selective for olefins. *In situ* resonant inelastic X-ray scattering measurements and Density Functional Theory calculations were used to investigate the electronic structure of Pt in the Pt-Zn and Pt-Fe catalysts and show that the average energy of the filled Pt 5d-states decreases in the IMCs. While these electronic changes do not appear to have a major effect on selectivity, they are responsible for the slightly increased TORs. Although only applied to alkane dehydrogenation in the present study, using IMC structures to tune the geometric and electronic properties of metals could prove useful for other catalytic reactions.