Sabnis, Kaiwalya D. Ph.D., Purdue University, December 2014. Structure-Activity Relationships for the Water-Gas Shift Reaction over Supported Metal Catalysts. Major Professors: Fabio H. Ribeiro and W. Nicholas Delgass.

The Water-Gas Shift (WGS) reaction ($CO + H_2O \rightarrow CO_2 + H_2$) is an important chemical process for industrial hydrogen production. The overall goal of this project is to use kinetic experiments and *in situ* characterization techniques in tandem, in order to derive structure-activity relationships for various catalytic systems. These relationships facilitate the rational catalyst design by identification of catalyst descriptors. In order to establish such relationships, various studies were undertaken, such as (i) effect of transition admetals on the WGS catalysis by molybdenum carbide (ii) effect of residual oxygen content on the performance of molybdenum carbide for WGS (iii) effect of cobalt as a secondary metal promoter over supported Pt catalysts.

In the first study, we were interested in the effects of various admetals on the WGS reaction rate and kinetic parameters measured over molybdenum carbide (Mo_2C). We focused on the determination of active sites over transition metals supported on Mo_2C. Molybdenum carbide is known to have WGS rate per gram of catalyst that is higher than the commercial $Cu/ZnO/Al_2O_3$ catalyst at 120°C. This rate is promoted further by using the Mo_2C as a support for admetals such as Pt, Pd, Au, Cu, Ni and Ag. The extent of promotion in the WGS rate normalized by the BET area of the catalyst is shown to correlate with the apparent reaction order with respect to CO. Based on a progressive decrease in the apparent CO order with increasing WGS rate per unit surface area, the CO adsorption strength over the sites created by the admetals is suggested as a potential descriptor for the rate promotion. *In situ* X-ray absorption experiments show that Au and Pt re-disperse on the Mo_2C support after a 600°C carburization pretreatment, making Mo_2C an ideal candidate for the synthesis of thermally robust supported metal catalysts. The difficulties in characterization of Pt/Mo_2C by electron microscopy were overcome by using Multi-Walled Carbon Nanotubes (MWCNT) as a 'TEM friendly' support. Pt-Mo alloy nanoparticles in intimate contact with the Mo_2C are identified as the dominant active sites.

In a follow-up study, the dependence of the WGS rates on the residual oxygen content over Mo_2C and the Pt-modified bulk Mo_2C was studied with temperature programmed reduction (TPR). Platinum was shown to enhance the oxygen removal from Mo_2C after various reduction pretreatments. For a passivated (oxygen covered) Mo_2C catalyst, the WGS rate per unit surface area at 120°C, measured after a 600°C carburization, is 9 times higher compared to the rate measured on the same catalyst after a relatively milder reduction at 300°C. However, for the Pt/Mo_2C catalyst, this factor of difference in the rates after the pretreatments at aforementioned temperatures was a factor of 1.5. Thus, a Pt/Mo_2C catalyst with ~6-7 times higher WGS rate per gram at 120°C compared to the commercial Cu/ZnO/

Al_2O_3 catalyst is reported with a reduction pretreatment that is viable for commercial practice.

In the final study, we have attempted to rationalize the promotion in the WGS rate over Pt supported on MWCNT with addition of secondary metal promoter such as cobalt. X-ray absorption and XRD characterization revealed that for a bimetallic catalyst prepared with sequential impregnation of Pt and Co, isolated cobalt phases (CoO_x) are formed along with Pt-Co alloy. The turnover rate for WGS at 300°C was promoted by an order of magnitude at the Co:Pt molar ratio of 3:1, in comparison to the monometallic Pt. A selective leaching treatment removed the CoO_x phase, without severely affecting the Pt-Co alloy (Pt-Co coordination number changed from 3 to 2.5). The WGS TOR at 300°C decreased 20 times after the CoOx was leached out. The formation of PtCo alloy was concluded to be inconsequential for promotion of the WGS TOR. The interface sites between CoO_x and the PtCo alloy particles are suggested to be the active sites for WGS.