ABSTRACT

Cui, Yanran. Ph.D., Purdue University, December 2016. Influences of Interfaces and Promoters on the Water-Gas Shift Reaction Over Supported Noble Metal Catalysts. Major Professor: Fabio H. Ribeiro and W. Nicholas Delgass

The water-gas shift reaction (WGS) is an important reaction to produce high purity hydrogen for various industrial processes such as ammonia synthesis and hydrotreating of petrochemicals. Finding a catalyst with higher rates per unit of volume of catalyst is desired to allow operation at lower temperatures where the equilibrium conversion is higher. Supported noble metal catalysts have been identified as a class of active catalysts for this reaction. The interface sites between the metal and support play an important role in determining the overall reaction mechanism and can be modified by properly tuning the metal-support interactions. On the other hand, WGS reaction can be used as a probe reaction to study the fundamental catalytic processes over various heterogeneous catalysts. The overall goal of this work is to develop a model based approach to catalyst design that we call Discovery Informatics, which involves building a database with sufficient chemical and information diversity to allow identification of active sites, to model the kinetics, and to identify descriptors of the kinetic parameters that will accelerate the search for new and improved catalysts.

The first work focuses on Fe promotion effects on a rutile supported Au catalyst. By properly adding Fe to the Au/rutile catalysts, WGS rate per mole of Au at 120 °C could be promoted to a maximum of about 4 times. As Fe loading increased, significant changes in the WGS kinetics were observed; that is, a decrease in apparent reaction order with respect to CO (0.7 to -0.3) and an increase in apparent activation energy (53 kJ mol^{-1} to 98 kJ mol^{-1}). The changes in the WGS kinetics imply stronger binding of CO on the active sites. Operando FTIR experiments identified an increase in CO adsorbed on strongly backdonating Au sites as the Fe loading was increased. The results showed that Fe-doping can modify the CO adsorption properties of Au sites, which, in turn, change WGS rates.

Beside CO adsorption, H_2O dissociation is another important factor that influences the activity of WGS catalysts. The second part of this work focuses on studying the H_2O dissociation by using an Au/MgO catalyst as a model system. In this work, MgO and $Mg(OH)_2$ were adopted as supports and loaded with 2.5 wt% Au. WGS rates and kinetics were measured on these catalysts. Au/MgO showed higher WGS rates than $Au/Mg(OH)_2$ but a lower apparent order with respect to H_2O. This implies a higher H_2O/OH coverage over the Au/MgO compared with $Au/Mg(OH)_2$, which corresponds to a higher binding affinity for H_2O/OH on Au/MgO. A kinetic isotope effect (KIE), which is the ratio between the WGS rate with H_2/H_2O and WGS rate with D_2/D_2O, was measured for both catalysts and both showed the same KIE ratio of about 2.0±0.3. This

similar KIE implies a similar reaction mechanism on both catalysts and that breaking of a hydrogen bond is involved in the rate-determining step. Density Functional Theory (DFT) calculations also revealed a decrease of about 0.7 eV in the energy barrier for H_2O dissociation at the Au/MgO interface compared with pure MgO and pure Au. Further experimental studies on other supports such as TiO_2, ZrO_2, Al_2O_3, etc. also shows that a lower apparent order with respect to H_2O (about -0.3) results in a higher WGS rate. Thus the hydroxyl group participates in the rate-determining step and H_2O order can be used as a potential descriptor for the activity.

The last two studies focus on the active sites for WGS over supported Pt catalysts and the Na promotion effects on those catalysts. Multiple types of sites exist on supported Pt catalysts (single Pt atoms, Pt clusters and Pt nanoparticles) but it is still debated in the literature which kinds of sites are more important for the WGS reaction. A Pt/TiO_2 catalyst with only Pt nanoparticles on the support was prepared by organic solvothermal method. It showed similar activity and WGS kinetics to the normal Pt/TiO_2 catalyst, implying that single Pt atoms or small clusters of Pt atoms are not the dominant active sites. Variations of the rate with support reveal the importance of the Pt-support interface in controlling activity. Na has been reported to be able to promote supported Pt catalysts. In order to study the reason for promotion, a series of Pt-Na catalysts supported on multiwalled carbon nanotubes (MWCNT) was prepared with different Pt:Na ratios. Na was observed to be able to promote the turnover rate (TOR) of Pt/MWCNT catalysts by a factor of more than 20. The addition of Na changed the kinetic parameters of Pt/MWCNT (increase in apparent activation energy, decrease in CO and CO_2 orders) similarly to the modifications previously reported for Na-promoted Pt/Al_2O_3, Pt/TiO_2 and Pt/ZrO_2 catalysts. The finding that the response of the kinetic parameters for the catalysts to the presence of Na was independent of the underlying parent support for Pt suggests that Na leads to a support-type effect of its own. As confirmed by *in situ* ΔXANES experiments, Na enhanced the binding of CO with Pt. XAS data showed that Pt remained in a reduced or metallic state under the WGS conditions. It is suggested that Na forms islands over the Pt particles, creating a new type of Pt-NaOx interface as the active site. A washing procedure could remove the Na from the MWCNT and re-distribute it over the surface of Pt. The washed catalysts showed much lower Na loadings but similar WGS TOR at 250°C compared to their as-prepared counterparts, which further supports the conclusion that the Pt-NaOx interfaces are the active sites.