ABSTRACT

Cui, Yanran. Ph.D., Purdue University, December 2016. Influences of Interfaces 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 for hydrogen production and fuel cell applications, which are important for renewable energy. Higher conversions can be achieved at lower temperatures, but lower temperatures result in lower reaction rates, so high performance catalysts are desired to speed up the reaction. 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 identify descriptors of the kinetic parameters. High throughput kinetic experiments and in situ characterization techniques are used in tandem to derive structure activity relationships for various catalytic systems.

The first work focuses on Fe promotion effects on Au/rutile catalyst. In the present work, a series of Fe-doped rutile (TiO_2) were loaded with similar Au particle sizes and tested for WGS. WGS rate per mole of Au at 120 °C was promoted by a factor of 4 for 1 wt% Fe content. Significant changes in kinetic parameters were observed by varying Fe content.

Apparent orders with respect to CO decreased progressively and apparent activation energy increased progressively with Fe content increasing from 0 wt% to 5 wt%. A volcano correlation between WGS rates and apparent orders with respect to CO was observed. Operando Fourier Transform Infrared Spectroscopy (FTIR) was performed on the Fe-doped catalyst and the result was compared with Au supported on un-doped rutile. Stronger CO adsorption IR peaks at lower wave-numbers were observed and assigned to CO adsorbed on partially negatively charged Au atoms. This implies the active participation of both metallic and partially negatively charged Au towards WGS. The results showed that Fe-doping can modify the CO adsorption properties of Au/Rutile. WGS rates can be promoted with appropriate Fe content, accompanied by modification in the nature of the active sites.

H2O dissociation is another important factor that influences on the activity of WGS catalysts. However, the participation of hydroxyl groups in the WGS reaction mechanism is still not well understood. The second work focuses on studying the H_2O dissociation by using the Au/MgO catalyst as a model system. In the present work, Au supported on 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 and $Au/Mg(OH)_2$ showed similar kinetics except for the apparent order with respect to H_2O. Thus, these two systems provide one way to study the hydroxyl group influences on the WGS reaction. A lower apparent order with respect to H_2O was observed for Au/MgO (0.7 ± 0.1) than for $Au/Mg(OH)_2$ (1.0 ± 0.1). 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. Au/MgO is a more active catalyst than $Au/Mg(OH)_2$ for WGS at the same Au particle size.

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 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 could be used as a potential descriptor for the activity.

The last two studies focus on the active sites of supported Pt catalyst and the Na promotion effects. Multiple types of sites exist on supported Pt catalysts (single Pt atoms, Pt clusters and Pt nanoparticles). A special Pt/TiO2 catalyst was prepared with only Pt nanoparticles on the support. It showed similar activity with our normal Pt/TiO_2 catalyst, which implies that the interfaces between the Pt nanoparticle and support are the dominant active sites. Furthermore, a series of Pt-Na/MWCNT catalysts were prepared with different Pt:Na ratio. Na was observed to be able to promote the TOR of Pt/MWCNT catalyst 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) that are similar to the modifications previously reported for Na-promoted Pt/Al_2O_3, Pt/TiO_2 and Pt/ZrO_2 catalysts. Confirmed by *in situ* ΔXANES experiments, Na could enhance the binding of CO with Pt. XAS data showed that Pt remained in reduced or metallic state under the WGS conditions. The decrease in Pt dispersion indicates that Na covers Pt. The decrease in the

WGS rate per total mol Pt at 250°C with increase in the Na weight loading is attributed to the loss of surface Pt due to coverage by Na. The independence of apparent kinetic parameters on the underlying parent support for Pt suggests that Na leads to a support-type effect. Thus, we suggest that Na forms islands over the Pt particles and forms new type of Pt-NaOx interfaces as the active sites. Washing procedure could remove the Na on MWCNT and re-distributes the Na over the surface of Pt. The WGS TOR for the washed catalyst at 250°C is similar to the fully promoted as prepared catalysts at a significantly lower Na loading, which further proves that the Pt-NaOx interfaces are the active sites.