

## Bimetallic Pd-Zn and Pd-Fe Supported Catalysts for the Water-Gas Shift Reaction

W. Damion Williams<sup>1</sup>, Luis Bollmann<sup>1</sup>, Joshua L. Ratts<sup>1</sup>, Ajay M. Joshi<sup>1</sup>, Jorge Pazmino<sup>1</sup>, Yogesh V. Joshi<sup>1</sup>, Jeffrey T. Miller<sup>2</sup>, W. Nicholas Delgass<sup>1</sup>, Fabio H. Ribeiro<sup>1\*</sup>

<sup>1</sup> School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, Indiana 47907-2100 (USA)

<sup>2</sup> Chemical Technology Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, Illinois 60439 (USA)

\*fabio@purdue.edu

### Introduction

The water-gas shift (WGS) reaction ( $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ ) plays an important role in the areas of hydrogen generation and CO purification. Our goal has been to synthesize a catalyst with a turnover rate (TOR) as high as the commercial Cu catalyst and the robustness of noble metals. We report here on the enhanced rate per mole of noble metal of Pd-Zn and Pd-Fe catalysts for the forward WGS. At 240°C the addition of 19% Zn by weight to 2% Pd/ $\text{Al}_2\text{O}_3$  increases the rate per mole of Pd by a factor of 12, while the rate is 130 times faster after the addition of 14% Fe. At this temperature the rate per mole of Pd of Pd-Fe is 3 times higher than the rate per mole Cu on the commercial catalyst.

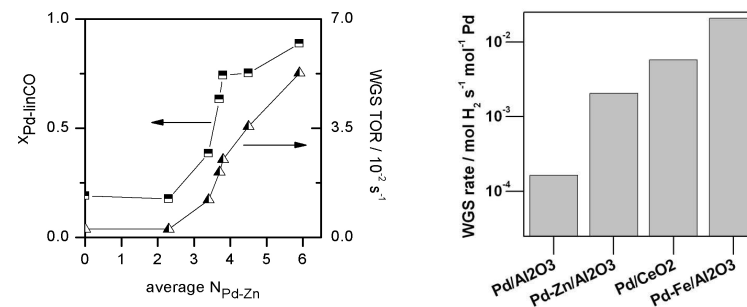
### Materials and Methods

The kinetic measurements were done in a plug-flow reactor configuration with CO conversions between 2 and 10% at 6.8% CO, 8.5%  $\text{CO}_2$ , 21.9%  $\text{H}_2\text{O}$ , 37.4%  $\text{H}_2$  at 1 atm total pressure. Extended X-ray absorption fine structure (EXAFS) measurements of the reduced samples were made in the insertion-device beam line of the Materials Research Collaborative Access Team at the Advanced Photon Source, Argonne National Laboratory. The adsorption of CO was studied using in-situ diffuse reflectance infrared spectroscopy under similar WGS conditions as in the kinetic studies.

### Results and Discussion

The effect of Zn addition on the Pd TOR for the WGS reaction was studied on 2 wt% Pd on alumina with Zn content from 0 to 19% Zn by weight [1]. The average Pd-Zn coordination number, as measured by EXAFS, increased monotonically from 0 to 4.5 as the Zn loading on alumina increased. At a loading of 2% Pd and 19% Zn on alumina the TOR increased by a factor of 12, as compared to the pure metallic Pd supported on alumina, to  $3.6 \times 10^{-2} \text{ mol H}_2 \text{ sec}^{-1} (\text{mol exposed Pd})^{-1}$  at 280°C, 6.8% CO, 8.5%  $\text{CO}_2$ , 21.9%  $\text{H}_2\text{O}$ , 37.4%  $\text{H}_2$  at 1 atm. The binding of adsorbed CO changed from 80% bridging on pure Pd to 90% linear on the 1:1 PdZn intermetallic compound as determined by diffuse reflectance infrared spectroscopy (DRIFTS) performed under WGS conditions. The fraction of CO binding linearly to Pd correlated linearly with the WGS rate per Pd on the surface. The correlation of the reaction rate with the types of sites on catalysts with six different Pd-Zn compositions shows that the data is consistent with an active site composed of surface Pd atoms with surface coordination of 2 Pd and 4 Zn atoms, which is the coordination expected for the (111) plane of the 1:1 PdZn intermetallic compound. The structure of the catalyst is destroyed upon oxidation at 280°C, however subsequent exposure to the WGS conditions is enough to regenerate the

reduced alloy. On  $\text{TiO}_2$ ,  $\text{ZrO}_2$  or  $\text{CeO}_2$  supports, PdZn catalysts had the same TOR as Pd/ $\text{CeO}_2$  and the relative enhancement in TOR compared to pure Pd on the same supports was less pronounced than on  $\text{Al}_2\text{O}_3$ . This trend suggests that role of the Zn in the PdZn intermetallic is similar to the role of  $\text{TiO}_2$ ,  $\text{ZrO}_2$  or  $\text{CeO}_2$  in that it provides a new pathway for the WGS reaction to proceed.



**Figure 1.** Left panel: (■) Fraction of surface Pd that binds CO linearly ( $X_{\text{Pd-linCO}}$ ) under WGS conditions and (▲) WGS TOR at 280°C as a function of the average Pd-Zn coordination number  $N_{\text{Pd-Zn}}$  measured by EXAFS. Right panel: Comparison of rates at 240°C per total mole of Pd for pure 2%Pd, 2%Pd-19%Zn and 2%Pd-14%Fe supported catalysts. All rates measured at 6.8% CO, 8.5%  $\text{CO}_2$ , 21.9%  $\text{H}_2\text{O}$ , 37.4%  $\text{H}_2$  at 1 atm total pressure.

For the 2 wt% Pd catalysts with Fe wt% loading between 2 and 14%, the rate per gram of catalyst correlates with the amount of  $\text{H}_2$  uptake measured by  $\text{O}_2$ - $\text{H}_2$  titration at 100°C. From X-ray photoelectron spectroscopy data, it is calculated that less than 15% of Fe is in the  $\text{Fe}^0$  state after reduction in  $\text{H}_2$  at 300°C. EXAFS data shows that on average only a third of the Pd atom neighbors are Fe. Since the particles are Pd-rich, the in-situ IR shows mainly CO adsorbed in the bridging conformation as in pure Pd. For all the Pd/Fe samples, the measured apparent reaction orders and activation energies are within 10 and 5% of each other, respectively. When the amount of Pd was decreased keeping the Fe loading constant, the rates per gram of catalyst decreased proportionally. These observations suggest that the activity of the catalysts is driven by reducible Fe species that are in close proximity to Pd centers.

### Significance

We have found two promoters that enhance the rate of Pd WGS catalysts. Addition of Zn induces the formation of a PdZn alloy which provides a new pathway for the WGS reaction to proceed. Following exposure to  $\text{O}_2$  at 280°C, this catalyst is able to recover its structure. The addition of Fe creates reduced Fe sites near the Pd centers. In both cases the presence of Pd is essential to facilitate the reduction of Zn and Fe.

### References

- [1] L. Bollmann, J.L. Ratts, A.M. Joshi, W.D. Williams, J. Pazmino, Y.V. Joshi, J.T. Miller, A.J. Kropf, W.N. Delgass, F.H. Ribeiro, J. Catal. 257 (2008) 43-54.