H_2 Production by Aqueous Phase Reforming of Bio-liquids: Correlating Catalytic Activity and Selectivity to the Local Coordination and Electronic Structure of Pt and PtNi

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Introduction and Objectives

Aqueous phase processing of biomass derived products (e.g. sugars, bio-oil) is an important step in the conversion of biomass to fuels [1, 2]. Understanding how to control the catalysts activity for C-C and C-O cleavage is crucial in order to tune the catalyst selectivity to the desired reaction pathway. The effect of the aqueous phase conditions on the electronic structure of the active metal and the physical structure of the alloy is not well understood. In addition, it is not clear whether the metal electronic structure is affected by the solution pH (bio-oil is acidic, pH ~ 2).

In this talk, we will present our recent *operando* XANES/EXAFS work on understanding the correlation between the local coordination and electronic structure of Pt and PtNi supported catalysts and their catalytic activity/selectivity during aqueous phase reforming (APR) of bio-liquids. In addition, we will discuss density functional theory (DFT) calculations to rationalize the experimental findings.

Results and Discussion

Testing of the catalyst for APR of glycerol was carried out in a microchannel reactor and the catalysts were characterized using an in-house built *operando* extended x-ray absorption spectroscopy cell (XANES and EXAFS) operating at 225 °C and 30 atm pressure. The catalyst was pre-treated by reduction in H_2, followed by exposure to the feed comprising 10% (wt.) glycerol (or ethylene glycol) in water at 225 °C and 30 atm pressure. Gas samples and liquid products were monitored by MicroGC and HPLC. The *operando* XANES/EXAFS results revealed a strong dependence of the Pt electron density on the solution pH and this had a strong effect on the Pt activity and selectivity. Addition of Ni resulted in more than twofold increase in reforming turnover frequency when Ni was located in the specific configuration in the bimetallic structure.

The structure of the bimetallic was found to change under aqueous phase reaction conditions compared with vapor phase reforming and reducing conditions. The correlation between the local coordination, electronic structure and the catalytic activity and selectivity will be presented. The effect of the electronic structure on the reaction pathways and strategies for optimizing the catalyst activity and selectivity will be discussed as guided by DFT calculations and microkinetic model predictions.

Conclusions

The solution pH and PtNi alloy formation affect the electron density on Pt and this has a pronounced effect on the activity and selectivity for bio-liquids reforming. The structure of the PtNi bimetallic is dependent on the reactant atmosphere and the structure/activity relationship is proposed using *operando* XANES/EXAFS and DFT calculations. .

References

[1] J.C. Serrano-Ruiz, J.A. Dumesic, Energy & Environmental Science 4 (2011) 83-99.

[2] C. Zhao, Y. Kou, A.A. Lemonidou, X.B. Li, J.A. Lercher, Angewandte Chemie-International Edition 48 (2009) 3987-3990.