Reforming of Oxygenates for H_2 Production on 3*d*-Pt(111) Bimetallic Surfaces

Orest Skoplyak, Mark A. Barteau and Jingguang G. Chen*
Department of Chemical Engineering, University of Delaware, Newark, DE 19716
*chenj@che.udel.edu

Introduction

Production of hydrogen for use in fuel cells can be achieved by selective reforming of biomass-derived oxygenates. Platinum has been identified as one of the most promising catalysts for reforming of oxygenates [1]. In this study the reactions of oxygenates, such as methanol, ethanol, and ethylene glycol, were investigated on Pt-based bimetallic surfaces using temperature-programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), and density functional theory (DFT) calculations. The formation of bimetallic surfaces alters the physical and chemical properties of the parent metals, which can lead to novel catalytic activity in certain reactions [2-5].

Materials and Methods

The ultrahigh vacuum chambers used in this study were equipped with HREELS, TPD and Auger electron spectroscopy (AES). The bimetallic surfaces were prepared through physical vapor deposition of the desired 3*d* metal onto Pt(111) single crystals at either 300 K or 600 K, using AES to monitor surface compositions.

Results and Discussion

Oxygenates reacted on 3*d*-Pt(111) to primarily form H_2 and CO. Surfaces prepared by deposition of a monolayer of Ni on Pt(111) at 300 K, designated as Ni-Pt-Pt(111), displayed increased reforming activity compared to Pt(111), subsurface monolayer Pt-Ni-Pt(111), and thick Ni/Pt(111), as shown by representative TPD spectra of ethylene glycol (Figure 1).

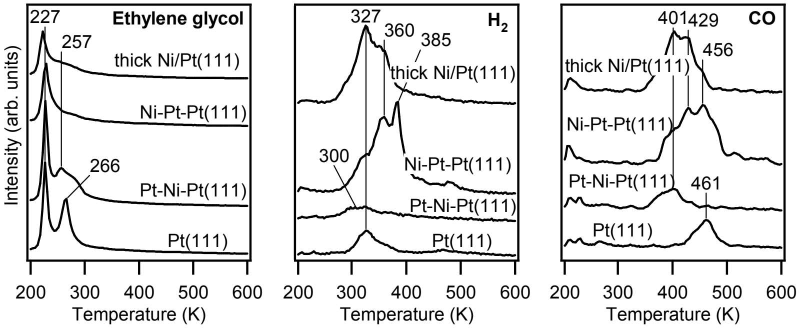

Figure 1. TPD spectra of ethylene glycol, H_2, and CO after ethylene glycol exposure on Ni/Pt(111) bimetallic surfaces.

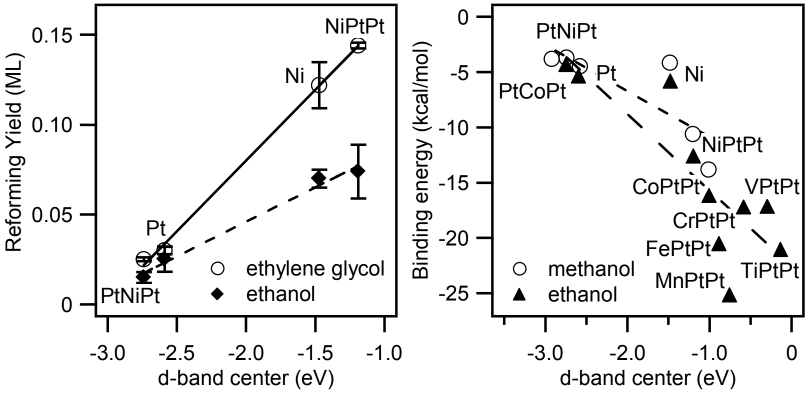

Figure 2. Correlations of reforming yield (left), and binding energy of methanol and ethanol (right) with the surface *d*-band center.

The experimentally measured reforming yield displayed a linear trend with the surface *d*-band center (Figure 2). The reforming activity increased as the surface *d*-band center moved closer to the Fermi level, opposite to the trend previously observed for hydrogenation reactions. DFT results indicated that the binding energy of methanol and ethanol increased as the surface *d*-band center shifted closer to the Fermi level, which could be achieved by choosing 3*d* metals from the left side of the periodic table as the surface monolayer. These results demonstrated that bimetallic combinations with varying compositions and structures may permit tuning of the product yields and kinetics for oxygenate reforming.

Significance

Selective reforming of oxygenates provides an alternative path for the production of hydrogen for use in fuel cells. The oxygenates may be derived from renewable biomass and offer advantages such as low toxicity, low reactivity and compatibility with the current infrastructure for transportation and storage.

References

1. Davda, R.R., Shabaker, J.W., Huber, G.W., Cortright, R.D., Dumesic, J.A., *App. Catal. B: Env.* 43, 13 (2003)
2. Hwu, J.J., Eng Jr., J., Chen, J.G., *J. Am. Chem. Soc.* 124, 702 (2002)
3. Kitchin, J.R., Khan, N.A., Barteau, M.A., Chen, J.G., Yakshinskiy, B., Madey, T.E., *Surf. Sci.* 544, 295 (2003)
4. Kitchin, J.R., Nørskov, Barteau, M.A., Chen, J.G., *J. Chem. Phys.* 120, 10240 (2004)
5. C.A. Menning, H.H. Hwu, J.G. Chen, J. Phys. Chem. B., 110, 15471 (2006)
6. O. Skoplyak, M.A. Barteau, J.G. Chen, J. Phys. Chem. B, 110, 1686 (2006)