INSIGHT INTO PT-BI BIMETALLIC CATALYSTS FOR TUNING SELECTIVITY AND IMPROVING STABILITY

Yang Xiao and Arvind Varma*
School of Chemical Engineering, Purdue University
West Lafayette, IN 47907

Abstract

Biomass is an important renewable source for conversion to fuels and valuable chemicals, where heterogeneous catalysis plays a significant role. Low selectivity and unsatisfactory stability of catalysts, however, limit industrial applications. Bimetallic catalysts provide solutions to both above issues. In this work, both experimental and theoretical works are described to provide insight into the Pt-Bi catalyst, one such bimetallic system, which exhibits both high selectivity toward the target product and good stability against coking/carbon deposition.

Keywords

Pt-Bi bimetallic catalyst, Catalyst selectivity, Catalyst stability

Introduction

Owing to environmental concerns and scarcity of known reserves, more attention is being paid to developing new fossil or renewable resources, such as shale gas, tar sands and biomass. In particular, biomass has been shown to be an important renewable source, which can be converted into both sustainable fuels and chemicals (Savaliya *et al.*, 2015). Heterogeneous catalysis plays an important role in such processes, where noble metals are typically used since they show excellent properties to activate and convert biomass. Tuning the catalyst selectivity toward target products and improving its stability against coking/carbon deposit, however, remain challenging and limit industrial applications. Both issues can be addressed by use of bimetallic catalysts, containing a primary metal (e.g. Pt, Pd, Ru, Rh, etc.) and a promoter (e.g. Mo, Sn, Bi, etc.) (Alonso *et al.*, 2012).

In our prior works (Hu *et al.*, 2010; Hu *et al.*, 2011; Xiao and Varma, 2015), a series of Pt-Bi catalysts was prepared and optimized for selectively converting glycerol to 1,3-dihydroyacetone (DHA) and improving catalyst stability for reactions involving CH_4 (guaiacol deoxygenation using CH_4). In the present work, we report additional experimental and theoretical results to provide insight into Pt-Bi bimetallic catalysts for tuning selectivity and improving stability.

Experimental

Pt and Bi were loaded on supports using the sequential wet impregnation method with Pt loaded first, followed by Bi. The Pt and Bi precursors were dissolved separately in 1.2 mol/L HCl, and then added dropwise sequentially to the well-stirred support slurry, with stirring continued for at least 8 hrs at room temperature for each metal loading. The slurry was then rinsed, dried in air at 100 °C and reduced before use. The SEM, TEM, XRD, BET and chemisorption techniques were used to characterize the catalysts. Two reactions (glycerol to DHA and guaiacol deoxygenation using CH_4) were used to evaluate selectivity and stability of Pt-Bi catalysts, respectively.

* To whom all correspondence should be addressed

DFT calculations

The periodic plane-wave-based code Vienna Ab-initio Simulation Package (VASP) was used for the DFT calculations, employing the projector augmented wave (PAW) method for ionic cores and the PW91 form of exchange-correlation functional in the generalized-gradient approximation (GGA). The dimer (Henkelman and Jonsson, 1999) and/or climbing-image nudged elastic band (CI-NEB) (Henkelman and Jonsson, 2000) method was used to locate the structures of transition states (TS) in the reactions.

Results

Experimental results indicate that for glycerol oxidation, Pt-Bi increased the selectivity to DHA, relative to glyceraldehyde (GLA), and improved the stability of catalyst against coking/carbon deposit in reactions involving CH_4, as shown in Figure 1 and Figure 2 (Xiao and Varma, 2015).

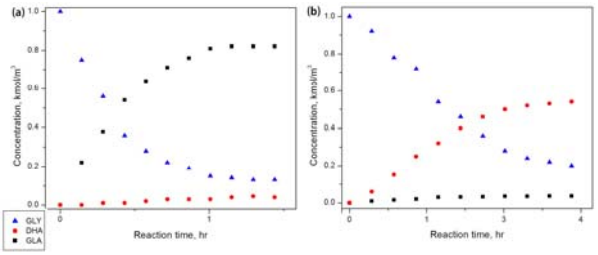

Figure 1. Product distribution of glycerol to DHA reaction: (a) Pt and (b) Pt-Bi catalysts

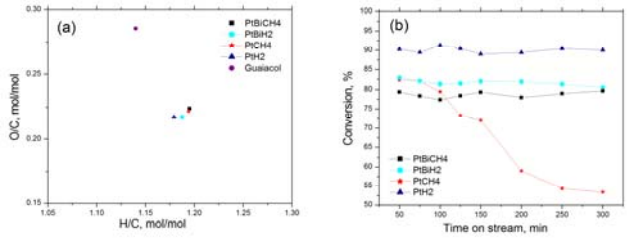

Figure 2. Catalyst performance for guaiacol deoxygenation using CH_4: (a) Van Krevelen diagram at 60 min time on stream (TOS), and (b) conversion vs. TOS

Both experimental and DFT optimization results show that Bi should be placed on top of Pt, rather than below Pt or in the support skeleton. DFT calculations also suggest that such catalysts exhibit a cooperative effect at the Pt-Bi interface, tuning catalyst selectivity to form DHA from glycerol, and unfavorable binding of carbon or CO species, improving the catalyst stability against coking/carbon deposit, as shown in Figure 3 and Table 1.

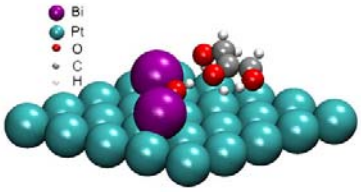

Figure 3. The cooperative effect at Pt-Bi interface

Table 1. Binding energies of C and CO over Pt and Pt-Bi catalysts, eV

Catalyst model	CO	C
Pt	-1.75	-1.10
Pt-Bi	-1.22	0.17

Conclusions

By both experimental and theoretical approaches, insight is obtained that Pt-Bi catalysts exhibit high selectivity for DHA formation in glycerol oxidation via a cooperative effect at the Pt-Bi interface. Additional insight into Pt-Bi catalysts is that good stability against coking and carbon deposit for reactions involving CH_4 is obtained via unfavorable binding of carbon or CO species.

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