

Controlled Catalyst Binding Strength Using Bimetallic Overlayer Structures for Improved Reactivity

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Introduction

Binding strength of the catalyst on the products or reactants defines the success of a catalyst. The catalyst needs to bind the reactant and product strong enough to facilitate the desired reaction but not so strongly as to result in an undesired reaction or to poison the surface. Catalyst/species binding is then controlled through the strain (distance) and ligand (electronic) properties of the metal. The periodic table provides a variety of elemental choices.

Often, the properties of certain metals for specific reactions are good, but improved performance is desired. A catalysts can facilitate a reaction of interest but a product or reactant might bind stronger than desired and block active sites. Overlayer bimetallic catalysts offer an opportunity to meet this binding strength challenge using a systematic approach. Overlayer (core@shell) can change the electronics of the overlayer[1] and increase or decrease the binding strength depending on the choice of core metal. We have synthesized a series of core@shell catalysts to investigate the ability of overlayer catalysts to improve reactivity when product and reactant binding issues are known to limit activity such as aqueous phase reforming (APR), hydrodeoxygenation (HDO) and hydrogenation[2-4].

Materials and Methods

A series of core@shell catalysts have been synthesized for specific reactions including: Ni@Pt, Co@Pt, Ir@Pt, Ni@Pd, and Cu@Pt. These catalysts were supported on alumina, silica, and silica-alumina as appropriate for the reaction of interest. All overlayer catalysts were synthesized using the directed deposition procedure. Monometallic and non-structured bimetallic catalysts were synthesized for comparison. Hydrogen chemisorption and the Clausius-Clapeyron was used to study the adsorption strength of the overlayer catalysts compared to the pure overlayer metal. Ethylene hydrogenation reactivity was also used as a descriptor for binding strength. X-ray absorption spectroscopy (XAS) and transmission electron microscopy (TEM) imaging was used to examine the formation and extent of the overlayer. APR of lactose to CO and H₂, aqueous phase HDO of glycerol, HDO of guaiacol, and hydrogenation of furfural were examined to investigate the overlayer effect.

Results and Discussion

Consistent with computational predictions, all overlayer catalysts showed a lower heat of adsorption compared to the pure overlayer metal. Ethylene hydrogenation results also demonstrated that reactivity could be reduced compared to the pure overlayer metal by using the core@shell structure. This implies that the desired reduced surface coverage and binding strength were observed. Comparison with the non-structured bimetallic catalysts demonstrated that overlayer catalysts behavior was not due to simple bimetallic behavior. Chemisorption and ethylene hydrogenation results demonstrate the ability for these techniques to be used as descriptors.

TEM and EDX showed that the overlayer metal was well dispersed (i.e., not agglomerated) and formed a consistent overlayer on the core metal particles. The overlayer metal was strongly associated with the core metal and not individually deposited on the support. Near edge XAS showed that the core@shell structure resulted in an electronic change. The near edge of the overlayer metal showed a reduction in edge height indicating a slight electronic donation to the core metal with a corresponding increase in edge height for the core metal. Structural analysis of the XAS data showed that the overlayer metal had both coordination numbers and interatomic distances consistent with an overlayer arrangement. Coordination numbers and interatomic distances for the overlayer catalysts were also distinct when compared to the random structure bimetallic catalysts.

Turnover frequencies for APR of lactose, HDO of glycerol and guaiacol, and hydrogenation of furfural increased compared to the pure metal or random structured alloys by the use of overlayer bimetallic catalysts. Ni@Pt and Co@Pt catalysts were able to increase the TOF for H₂ production via APR of lactose by a factor of approximately 5x compared to pure Pt.[2] Similar activity increases for HDO of glycerol to hydrocarbons was observed for Ni@Pt and Co@Pt catalysts.[3] Use of an Ir core allowed for the increased surface coverage of Pt (compared to Ni and Co cores) and also resulted in increased activity for HDO of glycerol. Ni@Pd and Ni@Pt showed approximately 2x increase for the HDO of guaiacol compared to pure Pd or Pt. In addition, the core@shell catalysts showed improved product selectivity to the desired complete deoxygenation products compared to the pure Pd or Pt. The Cu@Pt and Ni@Pt catalysts showed a significant activity increase compared to pure Pt for the hydrogenation of furfural.[4] Cu@Pt also demonstrated both high activity and high selectivity to furfuryl alcohol.

Significance

Multiple core@shell bimetallic overlayer catalysts were synthesized for applications where controlled changes in surface binding characteristics were desired for improved reactivity. Through the use of hydrogen chemisorption and ethylene hydrogenation, it was demonstrated that the overlayer structure results in a decrease in binding strength. Multiple reactions applicable to upgrading of biomass species has shown that these overlayer catalysts are capable of producing small, controllable changes in binding characteristics which result in improved reactivity and/or selectivity.

References

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