
Nanostructured Catalysts for Hydrogen Generation from Renewable Feedstocks

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for reforming, while maintaining CO₂ selectivity (and suppressing CO formation) remains a major challenge.

Abstract

The project involves collaboration between two university groups and one national lab. Our work over the past 18 months has been directed at understanding the role of various factors that influence activity and selectivity for H₂ formation, while minimizing the byproduct CO formation. Pd-Zn alloys have been shown to possess high selectivity towards CO₂ during methanol steam reforming, compared with monometallic Pd. It is commonly assumed that PdZn alloy formation is essential to achieve high selectivity towards CO₂. The simplest method to form a PdZn alloy is to treat a Pd/ZnO catalyst at elevated temperatures in H₂, which transforms Pd to PdZn, but also leads to particle growth. This makes it difficult to assess independently the role of particle size and composition on selectivity. We have used alternative activation treatments in order to vary independently the particle size and extent of alloy formation to understand the origins of selectivity. By using organic Pd precursors, we avoid the dissolution and etching of the ZnO substrate. The work on supported catalysts is complemented with studies of Pd deposited on ZnO(0001) surfaces. These model catalyst studies show clearly how Pd and Zn interactions modify the selectivity for steam reforming of methanol.

Objectives

This research program focuses on the development of highly active and selective catalysts for the production of hydrogen from alcohols. Alcohols, which can be produced from biomass or corn, have the potential to be an important renewable source of energy and may help to reduce our dependence on dwindling foreign and domestic oil supplies. Alcohols can be reformed to produce hydrogen, which can then be used in highly efficient energy conversion devices such as fuel cells. The specific objectives of this research program are to achieve advances in the design, synthesis, and characterization of catalysts at the nanoscale.

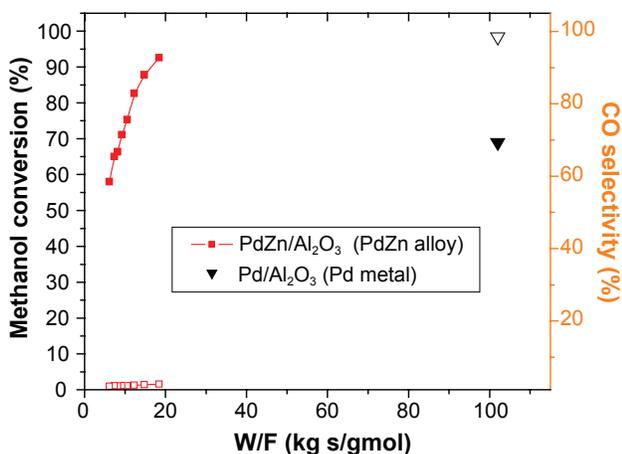
Technical Barriers

Metal particle size, composition and support structure play a major role in modifying the activity and selectivity of a catalyst. The underlying mechanisms are not well understood. We began our study with ZnO-supported catalysts. When Pd is supported on ZnO, it becomes an active catalyst for methanol steam reforming. But achieving the highest activity

Progress Report

Effect of Pd-Zn alloying

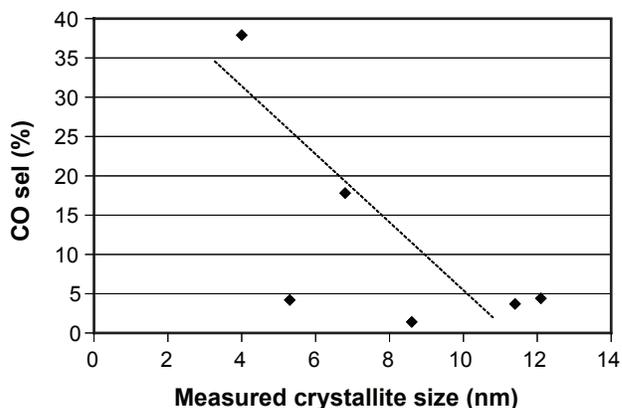
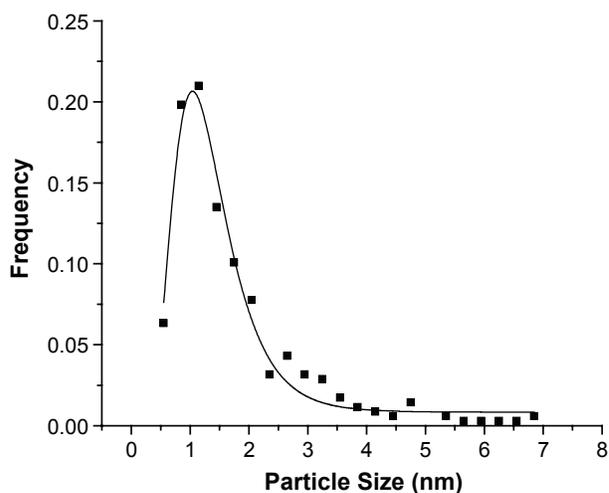
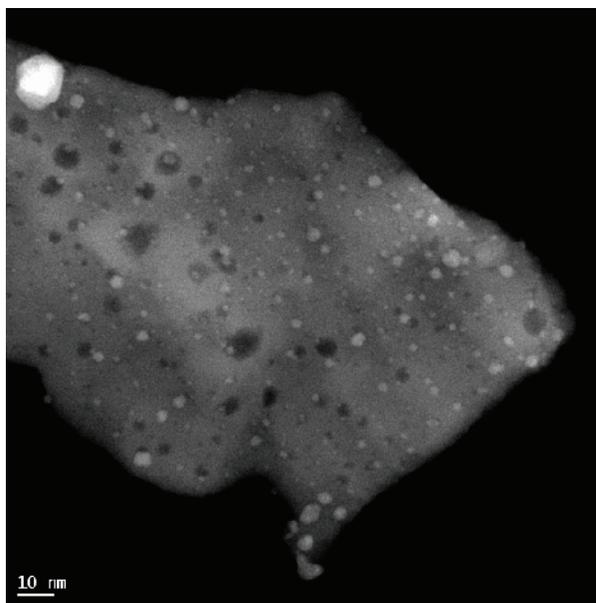
Monometallic Pd/Al₂O₃ leads to decomposition of methanol to form CO + H₂, while Pd-Zn on alumina completely shuts off the decomposition route, in favor of the reforming to produce CO₂ + H₂. The figure on the left shows this dramatic shift in selectivity (1). What is most surprising is that the Pd-Zn is far more reactive than the monometallic Pd catalyst (note the high conversion of methanol at low W/F ratios on the Pd-Zn catalyst). Previous work in the literature has been performed on ZnO supported Pd. The role of the ZnO support, the extent of alloy formation and the particle size, are not well understood. We therefore performed a detailed study of a co-precipitated Pd/ZnO catalyst. By choosing appropriate treatment conditions, it was possible to generate separate Pd and PdZn nanoparticles coexisting on the support, with the extent of alloy formation ranging from 25% PdZn to 100% PdZn. The



catalysts were characterized using HAADF imaging and the extent of alloying analyzed via EDS as well as XRD Reitveld refinement. While the lowest CO selectivity was generally achieved with increasing alloy content, the relationship was not monotonic. For any given extent of alloying, the lowest CO selectivity was achieved only when the smallest particles (<2nm), such as those seen in the figure below, had been eliminated.

Size effects

It appears that small particles are responsible for the formation of CO (which is undesirable since CO poisons the fuel cell electrocatalyst). The figure on the right shows a typical catalyst containing a large fraction of particles under 2 nm in diameter. We found that such catalysts always exhibited high CO selectivity. As the catalyst was treated at progressively higher temperatures, the Pd transformed into PdZn, but we also eliminated the smallest particles. Increasing extent of alloying to form PdZn was accompanied by an increase in mean particle size. It was therefore difficult to separate the two effects, the role of alloying and that of increasing particle size. By using carefully designed pretreatments, it was possible to retain small particle sizes. To our surprise, the smaller PdZn particles did not result in higher reactivity. Catalysts with a mean diameter of 9nm were just as reactive as those with mean diameter of 34nm. These results suggest that the support ZnO could be playing a significant role in the methanol steam reforming reaction and deserves more careful study. One problem with catalysts prepared with acidic Pd precursors is that the ZnO dissolves, leading to complete loss of ZnO morphology. Therefore, in order to understand the nature of particle size effects, free of these dissolution effects, it is essential to study the deposition of Pd from organic precursors using a non-aqueous route. Pd/ZnO catalysts were prepared (2) using an organic preparation method allow evaluation



of the effects of PdZn alloy crystallite size without the complication of ZnO morphology change typically occurring during conventional aqueous impregnation. Using this approach, we have been able to confirm that the size of PdZn alloy crystallites plays an important role in determining the CO selectivity (see figure on the previous page). Large sized PdZn crystallites dramatically suppress CO selectivity while providing high activity for methanol steam reforming.

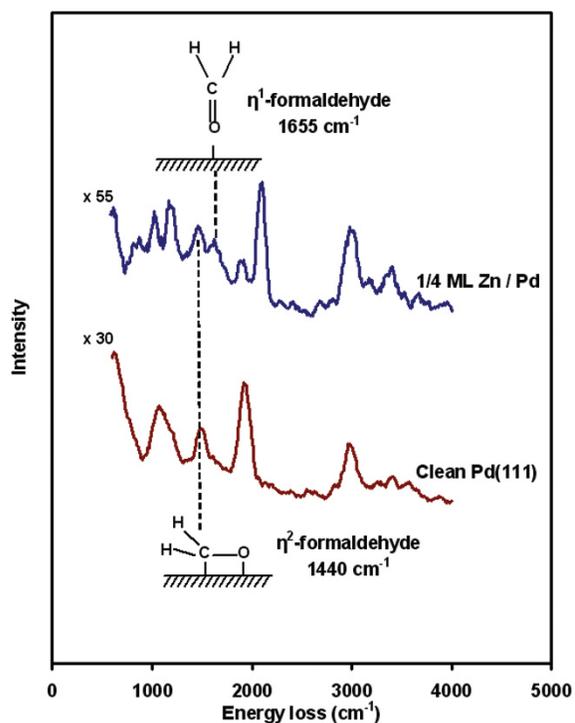
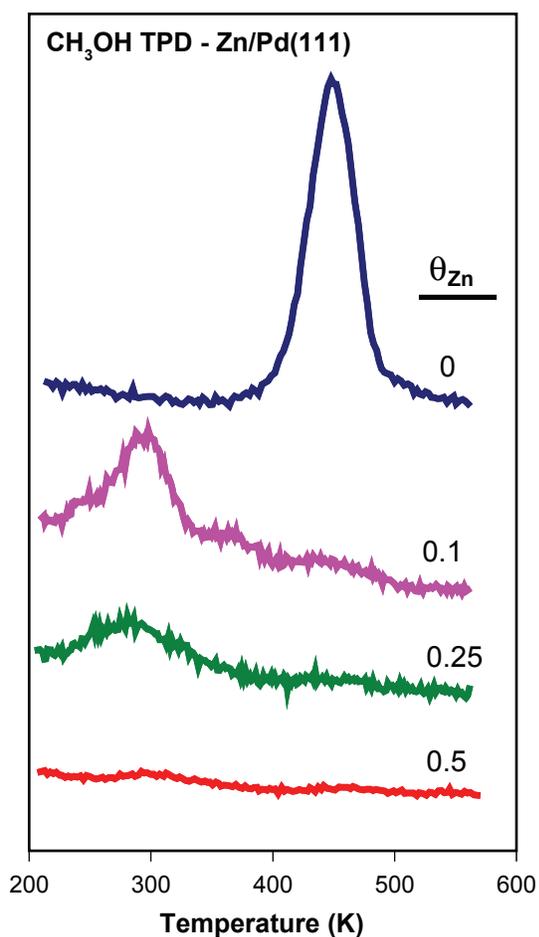
Model Catalysts

It is clear that model catalyst studies are needed to unravel some of the complexities in this system. Two separate model systems have been the focus of the work at UPenn: (1) Pd and PdZn films and particles supported on ZnO(0001) and (2) Pd(111) surfaces covered with submonolayer amounts of Zn.

Pd/ZnO(0001)

Model catalysts consisting of vapor deposited Pd films supported on ZnO(0001) were investigated. XPS and LEED studies showed that the Pd film growth at

300 K proceeds via a two-dimensional island growth mechanism (2DI). Pd films grown in this manner are meta-stable, however, and agglomerate into particles upon heating but remained oriented with respect to the ZnO surface. Heating above 500 K was also found to induce reaction of the Pd with the ZnO surface to form a PdZn alloy. The reaction of CH₃OH on the Pd/ZnO(0001) model catalysts was characterized using temperature programmed desorption (TPD) as a function of Pd coverage and sample pretreatment conditions. A variety of trends were observed in this series of experiments, the most important of which these can be summarized as follows. The reactivity of (111) oriented Pd films on ZnO(0001) for dehydrogenation of CH₃OH to CO and H₂ is greatly diminished compared to that of Pd(111) suggesting that interactions between the Pd and ZnO affect the reactivity of the Pd even prior to formation of the PdZn alloy. Incorporation of Zn into the Pd film decreases in the interaction energy of CO with the metal as indicated by a decrease in the CO desorption temperature and causes a significant decrease in the methanol dehydrogenation activity of the metal film. There is exchange of oxygen between the supported metal particles and the ZnO lattice suggesting that in Pd/ZnO catalysts Zn may act as a redox site that provides oxygen for reaction with CO or other intermediates adsorbed on the metal to produce CO₂. These Zn sites could be located either at the Pd/ZnO interface or on the surface of the PdZn alloy.



Zn/Pd(111)

CH₃OH TPD studies as function Zn coverage for Zn/Pd(111) samples showed that complete dehydrogenation of methanol to CO and H occurs below 300 K on Pd(111). The addition of small amounts of Zn (<0.1 ML) causes a significant decrease in the dehydrogenation activity and, consistent with the Pd/ZnO(0001) studies, decreases the interaction energy of CO with the ZnO surface. Based on thermodynamic grounds a pathway that goes through CO as an intermediate can be ruled out as the operable pathway for MSR on Pd/ZnO since the observed high selectivities to CO₂ are not consistent with the equilibrium conversion of the water gas shift reaction (WGS). Thus, while the alteration of the methanol dehydrogenation activity by the Zn must play a role in MSR on Pd/ZnO, by itself, this does not explain the mechanism of MSR on these catalysts. If the reaction proceeds via aldehyde and carboxylate intermediates, as proposed in the literature, then the Zn is likely to play a role in the formation and/or stabilization of these intermediates. In order to understand the possible effects of Zn on these intermediates we have used HREELS to characterize the bonding and orientation of methanol- and formaldehyde-derived intermediates on Zn/Pd(111). The most important observation in this work to date is that on Pd(111) the CH₂O binds in an η^2 -configuration in which both the C and O atoms in the carbonyl group interact with the surface while on Zn/Pd(111) surfaces CH₂O binds in an η^1 in which only the oxygen end of the molecule is bound to the surface.

Future Work

The results of our studies of model catalysts already provide considerable insight into how Zn and the ZnO substrate affect the reactivity of Pd/ZnO catalysts towards methanol. Electronic interactions between Pd and Zn are clearly important and have the following effects (1) decrease the heat of adsorption of CO on the Pd surface, (2) significantly decrease the methanol dehydrogenation activity, and (3) alter the bonding configuration of aldehyde intermediates from an η^2 to an η^1 configuration which is likely to stabilize them from further dehydrogenation. Our data also indicates that reaction at sites at the PdZn-ZnO interface and exchange of oxygen across this interface

may be important. The former observation is consistent with the results obtained from the supported catalysts. Our results also leave many questions unanswered. For example, the TPD data for as grown Pd films on the Zn-terminated ZnO(0001) surface show that alloy formation is not required to suppress methanol dehydrogenation activity, suggesting that interactions between Pd and Zn cations on the surface of the support have a similar effect. To test this hypothesis it would be useful to study Pd films supported on the O-terminated ZnO(000 $\bar{1}$) surface where direct interaction between the Pd and Zn²⁺ cations in the support could be minimized. It would also be useful to know the evolution of the structure of the Pd and PdZn particles on the ZnO(0001) substrate as a function of annealing conditions in order to assess how interactions at the Pd-ZnO interface affect reactivity. It should also be noted that to date our studies have focused on only one aspect of the MSR reaction mechanism, namely the adsorption and dehydrogenation of methanol and formaldehyde on Pd/ZnO. Obviously, to elucidate the overall mechanism for this reaction we also need to understand the adsorption and reaction of water on Pd/ZnO and how water derived intermediates (i.e. O and OH) react with adsorbed methanol and methanol-derived intermediates such as formaldehyde. Future work will also include *in situ* IR studies under reaction conditions. *In situ* EXAFS will be used to improve our understanding of the small Pd and PdZn particles formed on these catalysts. All of these issues will be addressed in our proposed work over the next year.

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