V.N.10 Structure/Composition/Function Relationships in Supported Nanoscale Catalysts for Hydrogen

Investigators: Larry A. Curtiss, Jeffrey W. Elam, Jeffrey P. Greeley, Julius L. Jellinek, Christopher L. Marshall, Jeffrey T. Miller, Stefan Vajda, Peter C. Stair*

Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
Phone: (630) 252-6499
Email: pstair@northwestern.edu

DOE Program Manager: Raul Miranda
Phone: (301) 903-8014
Email: Raul.Miranda@science.doe.gov

Objectives

The research is geared toward the development of new methods for the preparation of solid catalytic materials with atomic precision and the utilization of these materials for fundamental understanding of composition/structure/ function relationships in supported, heterogeneous catalysts for reactions that produce hydrogen from hydrogen-rich molecules. The ability to control metal nanoparticle composition, size, and structure, as well as the supports and promoters, is investigated; along with roles in determining adsorptive and catalytic properties. One particular goal is to evaluate performance of novel catalyst material structures for hydrogen production from methanol. The catalysts are supported metal and alloy nanoparticles and clusters with an emphasis on sizes in the range <1 nm, i.e. ~2-50 atoms that have been stabilized by coating with ultrathin oxide layers.

Technical Barriers

Catalysts based on noble metal nanoparticles for reforming of hydrogen rich organic molecules, such as methanol, to produce molecular hydrogen exhibit poor activity at low temperature due to poisoning by CO and poor stability at higher temperature due to particle growth and carbon deposition. We hypothesize that catalyst activity and stability can be improved greatly by using subnanometer size metal and alloy particles on suitable supports combined with oxide overlayers that stabilize the particles against particle growth and selectively block surface sites that produce undesirable products. Advanced techniques for synthesis, stabilization, characterization, theory and testing are employed to prepare novel catalyst structures and understand their chemical and catalytic properties.

Abstract

The focus of this project is the synthesis, stabilization, characterization, catalytic evaluation and computation of supported metal particle catalysts in the size range ≤1 nm, i.e. ~2-50 atoms. New synthetic and stabilization methodologies, based on atomic layer deposition and computational understanding have been achieved for ultra-small, supported metal particles. These materials exhibit exceptional performance for catalytic transformations involving methanol and other small hydrocarbons. The novel structures that involve oxide coatings of the noble metal nanoparticles provide a wholly new and effective methodology for improving the performance of catalytic materials. The research integrates efforts in: 1) synthesis and stabilization of uniform, supported clusters and oxide promoters; 2) characterization of cluster size, atomic structure, stability, and electronic structure during synthesis, pretreatment, and catalytic reaction; 3) investigation of catalytic and chemical events on the clusters that are relevant to hydrogen production; 4) computational quantum chemical modeling to understand and predict experimental results.

Progress Report

New Catalyst Structures

The synthesis of new catalyst compositions and structures is a key to advancing the performance of practical catalytic processes. Atomic Layer Deposition (ALD) has been developed as an exceptionally powerful, flexible and precise method for synthesis of single-component and alloy metal nanoparticle catalyst materials with outstanding activity, selectivity and stability. The initial focus was synthesis of Pd nanoparticles supported on alumina because they exhibit high activity for conversion of methanol to hydrogen but suffer from lack of stability at reaction temperature. Using palladium (II) hexafluoroacetylacetonate [Pd(hfac)$_2$] as the Pd-precursor and formaldehyde (HCHO) as the reducing agent produced well-dispersed, uniform ~2 nm Pd nanoparticles. Starting with high-surface-area silica the support composition can be changed, as desired, by depositing a thin layer of oxide before the Pd deposition (e.g., Al_2O_3 to make alumina supported Pd) and/or the Pd particles can be stabilized by overcoating with oxide after the Pd deposition. The thickness of these oxide layers is controlled with atomic precision by the ALD chemistry. Our research has shown that, using deposition temperature and ALD support composition, Pd particles with uniform, selectable sizes from <1 to several nanometers can be formed. We have also shown that the scope of nanoparticle catalytic materials

that can be prepared by ALD includes single-component systems (Pt, Ir, Ru) and alloys (Pt-Ir, Pt-Ru, Ir-Ru, Pt-Pd).

Remarkable new catalyst structures with exceptional performance have been synthesized by overcoating the supported metal nanoparticles with alumina by ALD. Detailed studies of the alumina ALD overcoating chemistry show that the aluminum precursor reacts preferentially with edge and corner sites on the Pd nanoparticles. This blocks their participation in the reaction and results in a more structurally uniform catalytic metal surface consisting primarily of terrace site geometries. This picture has emerged based on combining *in-situ* experiments, *ex-situ* TEM, and DFT calculations of the initial stages of Al_2O_3 ALD on the Pd nanoparticle surfaces. We discovered that the Al_2O_3 ALD on Pd nanoparticles proceeds by a *self-poisoning, self-cleaning* process. The Pd surface becomes poisoned by adsorbed CH_3* species during the trimethyl aluminum exposures, which prevents the formation of a complete monolayer of adsorbed Al species. During the subsequent H_2O exposures, the Pd surface is cleaned of CH_3* species, and the net result is a porous Al_2O_3 film. This porous structure retains the catalytic activity of the Pd nanoparticles by providing reagent gases with access to the Pd surface sites. This is depicted schematically in Figure 1. Additional studies showed that even after complete encapsulation by thick alumina layers, new pores can also be opened in the overcoat by calcination/dehydration at 700 °C. This restores access to the Pd particle surface and provides a strategy for manipulating the pore structure of the catalyst.
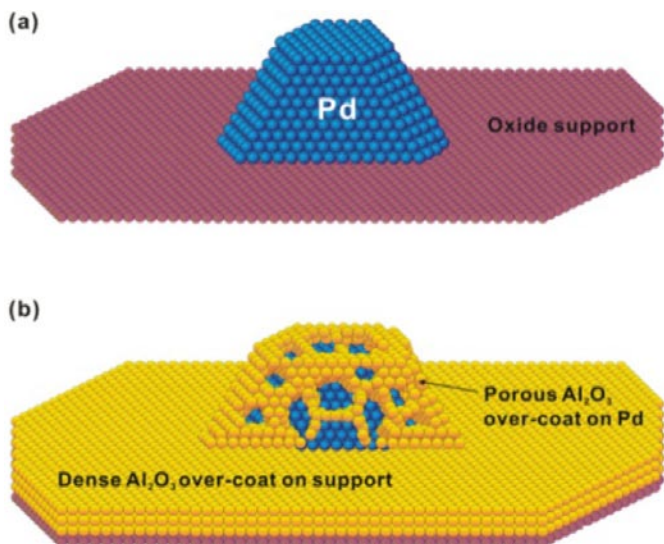
Catalyst Performance
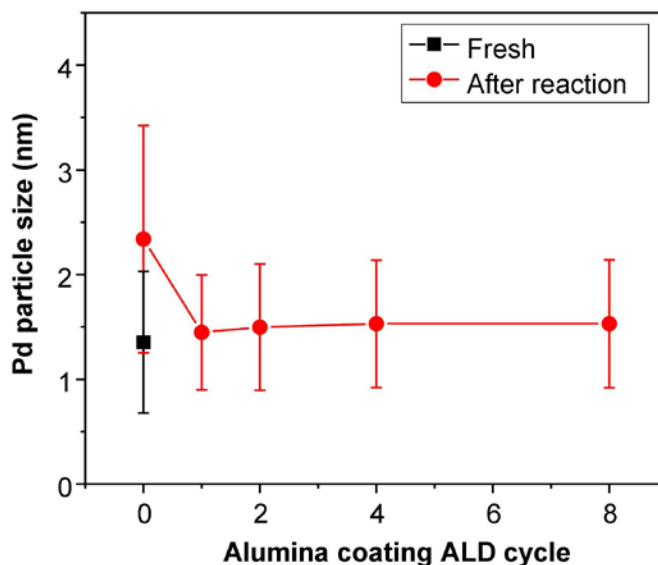
The performance of ALD-synthesized catalyst structures has been investigated for methanol decomposition and ethane dehydrogenation. The overcoated structure stabilizes nanoparticle size even under severe reaction conditions (e.g. 800 °C calcination, 270 °C methanol decomposition, or 675 °C ethane dehydrogenation). Figure 2 depicts the Pd particle size stability achieved for methanol reaction conditions. Without overcoating (0 ALD cycles) the particle size has doubled, resulting in lower catalytic activity. Particle size is stable for materials with 1-8 cycles of overcoating. Rather than causing an expected loss in catalytic activity Figure 3 shows that overcoating actually produces an increase in catalytic activity that is essentially constant up to the thickness produced by 16 ALD cycles. Beyond 16 cycles the Pd particles become increasingly encapsulated until by 32 cycles they are no longer accessible to the methanol reagent. Catalysts prepared by opening new pores in thick alumina overcoats (via calcination) were examined for ethane dehydrogenation activity, selectivity, and stability at 675 °C. Figure 4 shows that these materials exhibit high selectivity to ethylene, low selectivity to undesirable methane production and stable performance with no coking over time. This methodology may have far-reaching application to prolong catalyst lifetimes under severe reaction conditions.

Size and support effects in the oxidative decomposition of methanol by means of <1 nm palladium clusters on an amorphous alumina support were studied under realistic reaction pressures and temperatures. Smaller Pd_{8-12} clusters were found to promote decomposition to CO and hydrogen; however, with mediocre activity due to CO poisoning. The larger Pd_{15-18} clusters preferentially produce dimethyl ether

FIGURE 1. Schematic illustration of porous Al_2O_3 ALD over-coat on Pd nanoparticle: (a) supported Pd catalyst; (b) dense Al_2O_3 film on oxide support with porous Al_2O_3 overcoat on Pd nanoparticle formed by ALD.

FIGURE 2. Pd particle size after methanol reaction (270°C, 6 hrs) with/without alumina overcoat
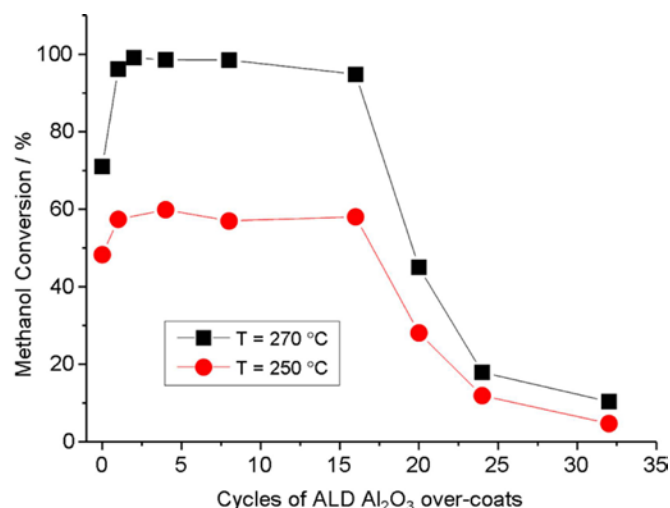
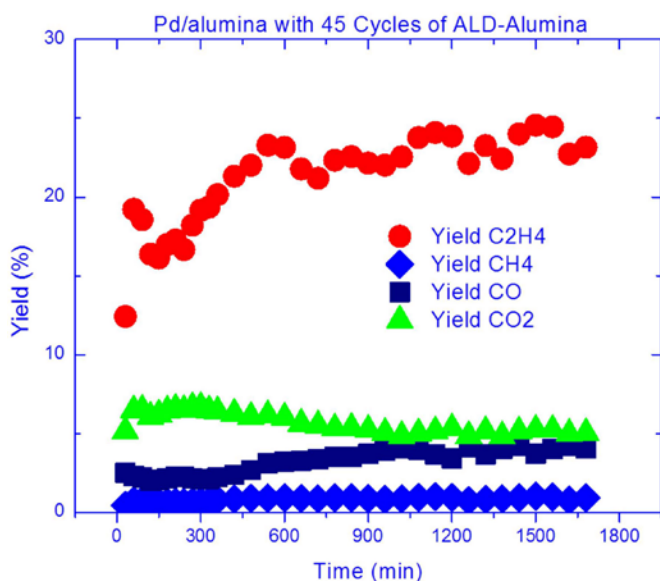**FIGURE 3.** Methanol conversion vs. overcoating thickness

FIGURE 4. Product yields during ethane dehydrogenation catalyzed by overcoated Pd nanoparticles

and formaldehyde, without signs of poisoning. A thin ALD titania overcoat applied on the Pd_{15-18} improves the sintering resistance in a manner similar to the alumina overcoats on larger particles.

Understanding and Predicting Catalysts

The need to characterize these small particles led to the development of new X-ray based techniques at the Advanced Photon Source (APS) at Argonne. *In-situ* XAS has been used in combination with TEM to confirm the size, structure, and composition of metallic and alloy nanoparticles prepared by ALD. In addition to the standard structural characterization of nanoparticle metal and alloy hydrogen production

catalysts, several new capabilities have been developed. An *in-operando* reactor, i.e., simultaneous measurement of reaction kinetics and XAS spectra has been developed. The plug-flow reactor can measure the reaction kinetics identically to that in the laboratory and has capabilities which allow for the XAS study of catalysts at temperatures up to about 400°C and 50 atm pressure. A recent improvement in the reactor materials from thick-walled quartz to vitreous carbon allows for *in-operando* XAS measurements of lower energy transition metals, e.g., 3d elements, at lower concentrations, or at faster acquisition times.

In-situ XAS spectroscopy has also been applied for understanding the details in the steps of ALD nanoparticle synthesis. We determined that the support hydroxyl groups react with the $Pt-CH_3$ bond of the trimethylcyclopentadienyl-methyl Pt (IV) ALD precursor forming CH_4 and the supported dimethylcyclopentadienyl-methyl Pt (IV) complex. Subsequent ALD cycles showed that the precursor preferentially reacts with the support, rather than with metallic or oxidized Pt previously deposited on the support. These insights into the formation of Pt nanoparticles led to ALD strategies for formation of sub-nanometer Pd nanoparticles and bimetallic Pt-Ru nanoparticles mentioned above.

Periodic plane wave calculations were employed to elementary reaction pathways and energetics for methanol decomposition by supported and unsupported M_4 and M_8 (M=Pd, Cu, and Co) clusters for methanol decomposition. For Pd (primarily Pd_4) clusters, the decomposition of methanol begins through CH bond breaking to form hydroxymethyl (CH_2OH), followed by steps involving the formation of hydroxymethylene (CHOH), formyl (CHO), and carbon monoxide (CO). An alternative dehydrogenation pathway with O-H bond breaking as the first step, followed by formation of methoxy (CH_3O) and formaldehyde (CH_2O), was slightly less favorable. In contrast, pathways involving C-O bond cleavage are much less energetically favorable, and no feasible pathways involving C-O bond formation to yield dimethyl ether (CH_3OCH_3) were found. By comparison to extended Pd surfaces, all reaction intermediates were found to bind slightly more strongly to the clusters than to the surfaces. Modeling the effects of an alumina support on methanol decomposition over Pd_4 and Pd_8 clusters indicated that larger Pd clusters and inclusion of the alumina support did not significantly affect the reaction pathways calculated for the Pd_4 cluster.

The reaction pathways on Cu_4 and Co_4 clusters provide a contrast to those of the Pd_4 clusters. The Co_4 cluster pathway is favorable both thermodynamically and kinetically for dehydrogenation, but since CO adsorption is also favorable, it is likely to poison methanol decomposition at low temperatures, similar to Pd clusters. In contrast, CO poisoning of the Cu_4 cluster is less of a problem, but the dehydrogenation steps are not favorable. This finding
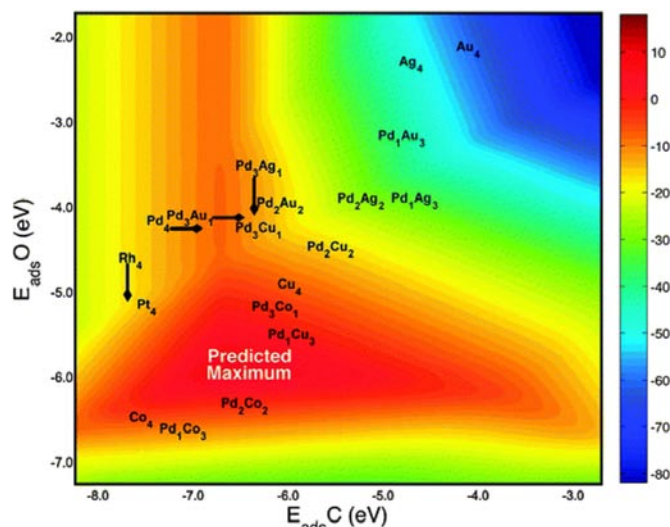
FIGURE 5. Volcano plot of methanol decomposition rate by two component clusters. Red is the highest rate. Blue is the lowest rate.

strongly indicates a need to find other clusters that combine the favorable aspects of the Co and Cu clusters for methanol decomposition while, at the same time, not suffering from the deficiencies of these elements. To this end Brønsted-Evans-Polanyi relationships have been calculated for two-component clusters using bond energies of atomic carbon and oxygen to the cluster as descriptors. The results shown in Figure 5 indicate that Pd-Cu and Pd-Co alloys should be active systems for methanol decomposition.

Future Directions

Formation of new catalyst structures and compositions by ALD appears to be a very promising direction for the future. The potential to create new pore structures with controlled length, diameter and wall composition could have a major impact on catalyst performance, regardless of the target reaction system. Given the extensive scope of materials possible with ALD, the exploration of its potential will benefit from high throughput experimentation. Associated characterization and theory will provide much needed guidance for identifying possible high performance combinations.

Publication list (including patents) acknowledging the DOE grant or contract

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