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

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)\textsubscript{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\textsubscript{2}O\textsubscript{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 Al₂O₃ ALD on the Pd nanoparticle surfaces. We discovered that the Al₂O₃ ALD on Pd nanoparticles proceeds by a self-poisoning, self-cleaning process. The Pd surface becomes poisoned by adsorbed CH₃* species during the trimethyl aluminum exposures, which prevents the formation of a complete monolayer of adsorbed Al species. During the subsequent H₂O exposures, the Pd surface is cleaned of CH₃* species, and the net result is a porous Al₂O₃ 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 Pd₈₋₁₂ clusters were found to promote decomposition to CO and hydrogen; however, with mediocre activity due to CO poisoning. The larger Pd₁₅₋₁₈ clusters preferentially produce dimethyl ether.

![FIGURE 1. Schematic illustration of porous Al₂O₃ ALD over-coat on Pd nanoparticle: (a) supported Pd catalyst; (b) dense Al₂O₃ film on oxide support with porous Al₂O₃ overcoat on Pd nanoparticle formed by ALD.](image)

![FIGURE 2. Pd particle size after methanol reaction (270°C, 6 hrs) with/without alumina overcoat](image)
and formaldehyde, without signs of poisoning. A thin ALD titania overcoat applied on the Pd\textsubscript{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\textsubscript{3} bond of the trimethylcyclopentadienyl-methyl Pt (IV) ALD precursor forming CH\textsubscript{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\textsubscript{4} and M\textsubscript{8} (M=Pd, Cu, and Co) clusters for methanol decomposition. For Pd (primarily Pd\textsubscript{4}) clusters, the decomposition of methanol begins through CH bond breaking to form hydroxymethyl (CH\textsubscript{2}OH), 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\textsubscript{3}O) and formaldehyde (CH\textsubscript{2}O), 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\textsubscript{3}OCH\textsubscript{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\textsubscript{4} and Pd\textsubscript{8} clusters indicated that larger Pd clusters and inclusion of the alumina support did not significantly affect the reaction pathways calculated for the Pd\textsubscript{4} cluster.

The reaction pathways on Cu\textsubscript{4} and Co\textsubscript{4} clusters provide a contrast to those of the Pd\textsubscript{4} clusters. The Co\textsubscript{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\textsubscript{4} cluster is less of a problem, but the dehydrogenation steps are not favorable. This finding
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**


