Objectives

The research is geared toward fundamental understanding of composition/structure/function relationships in supported, heterogeneous catalysts for reactions that produce hydrogen from hydrogen-rich molecules. The role of particle composition, size, and structure and the effect of supports and promoters on adsorptive and catalytic properties are investigated. A particular goal is to determine if the catalytic activity for hydrogen production from methanol can be significantly improved by preparing catalysts which only partially adsorb CO under reaction conditions. The catalysts are supported metal, alloy, carbide, and nitride nanoparticles and clusters with an emphasis on clusters in the size range <1 nm, i.e. ~2-50 atoms.

Technical Barriers

Catalysts for the reforming of hydrogen rich organic molecules, such as methanol, to produce molecular hydrogen exhibit poor activity at low temperature due in large part to poisoning by CO, an inevitable byproduct of the chemistry. We hypothesize that catalyst performance can be improved greatly by using subnanometer size metal and alloy clusters on suitable supports. Advanced techniques for synthesis, stabilization, characterization, theory and testing are employed to investigate and understand the chemical and catalytic properties of these materials.

Abstract

The objective of the research is a fundamental understanding of composition/structure/function relationships in supported, heterogeneous catalysts for reactions that produce hydrogen from hydrogen-rich molecules. The focus of the work over the last two years has been the synthesis, stabilization, characterization, catalytic evaluation and computation of supported metal cluster catalysts in the size range <1 nm, i.e. ~2-50 atoms. New synthetic and stabilization strategies and computational understanding have been achieved for ultra-small, supported metal particles. 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. Future work will emphasize experiments and computations of alloy, carbide, and nitride nanoparticles and clusters.

Progress Report and Future Plans

Experimental Catalyst Synthesis, Characterization and Reaction Studies

Pd nanoparticle catalysts were synthesized and stabilized by atomic layer deposition (ALD). Alternating exposures of palladium (II) hexafluoroacetylacetonate (Pd(hfac)₂) and formaldehyde (HCOH) produce well dispersed, discrete Pd nanoparticles on high surface area mesoporous silica gel supports. The average Pd particle size by TEM and EXAFS is ~2 nm. Smaller particle sizes have been achieved using lower reaction temperatures and by depositing support layers prior to metal particle reduction with HCOH. Additional layers of support serve to stabilize the particles against sintering and deactivation. Other ALD noble metal systems, including Pt, Ru, and Ir, were targeted for achieving sub-nanometer particles for hydrogen production. In-situ EXAFS revealed details of the Pt nanoparticle formation. Supported sub-nm Ir nanoparticles (<0.5 nm, Fig. 1a) were prepared, the smallest reported to date. A detailed study of ALD Pt-Ir alloys has also been performed, representing the first study of ALD metal mixtures. A variety of ALD noble metal alloy nanoparticles including Pt-Ir, Pt-Ru, Ir-Ru, and Pt-Pd (Fig. 1b) were prepared.
Size-selected cluster synthesis of various sized cluster catalysts using a mass-selected ion beam has been combined with the development of an in-situ reaction cell and surface-sensitive tools at 12-ID of the Advanced Light Source. Catalysts can be characterized by synchrotron-based X-ray absorption and scattering and simultaneously monitored for catalytic activity. [4,5]

The performance for methanol decomposition by the ALD catalysts is shown in Fig. 2. The methanol conversion increases monotonically with increasing temperature reaching ~100% at 280°C. At all temperatures the selectivity was nearly 100% to CO and H₂. Catalysts prepared using ALD ZnO as the underlying support showed much lower conversion and rapid deactivation at the higher temperatures due to Pd “dissolving” into the ZnO substrate. By applying one cycle of ALD Al₂O₃ on top of the Pd/ZnO catalyst, the activity was enhanced, and the catalyst deactivation was mitigated. This Al₂O₃ over-coating method stabilizes the Pd/ZnO and effectively prevents the dissolution of Pd into the ZnO substrate. [1]

Smaller Pd₈₋₁₂ clusters formed by ion beam deposition were found to promote decomposition to CO and hydrogen but suffered from poisoning. Larger Pd₁₅₋₁₈ clusters preferentially produce dimethyl ether and formaldehyde, without signs of poisoning. A thin ALD titania overcoat applied on Pd₁₅₋₁₈ improves the sintering-resistance via a mechanism involving partial encapsulation of the Pd. [6] It also changes the selectivity so that CH₂O prevails.

Future synthesis and catalytic experimentation efforts will target subnanometer alloy and nitride particles with weaker bonds to CO. Guidance in the selection of particle size and composition will be provided by computations as described below.

**Computational Catalysis Studies**

Periodic plane wave calculations were employed to determine the activity and reaction pathways of supported and unsupported M₄ and M₈ (M=Pd, Cu, and Co) clusters for methanol decomposition. [7,8] The structures of oxidized Cu clusters have also been studied. [9] For Pd (primarily Pd₄) clusters, the decomposition of methanol begins with C-H bond breaking to form hydroxymethyl (CH₂OH), followed by steps involving formation of hydroxymethylene (CHOH), formyl (CHO), and carbon monoxide (CO). This pathway is shown in Fig. 3. O-H bond breaking as the first step, followed by formation of methoxy (CH₂O) and formaldehyde (CH₂O), was slightly less favorable. C-O bond cleavage is much less energetically favorable, and
no feasible pathways involving C–O bond formation to yield dimethyl ether (CH$_3$OCH$_3$) were found. All reaction intermediates bind slightly more strongly to clusters than to extended surfaces. The effects of an alumina support were also calculated. [7] Overall, the results indicate that larger Pd clusters and inclusion of the alumina support did not significantly affect the reaction pathways. The combination of bare and supported cluster results clearly shows that CO adsorbs in a deep well (Fig. 3) that can poison the methanol decomposition reaction, supporting the proposal in the experimental studies of Vajda et al [6] where little product is observed until the temperature is high enough for CO desorption. The reaction pathways on Cu$_4$ and Co$_4$ clusters are distinctly different from the Pd$_4$ clusters. [8] Methanol decomposition to form CO and H$_2$ is shown in Fig. 3 for Cu$_4$ and Co$_4$ along with that of Pd$_4$. The overall trends are not affected by adding the support. The Co$_4$ cluster pathway is very favorable both thermodynamically and kinetically for dehydrogenation, but since CO adsorption is also very favorable, it is likely to poison methanol decomposition at low temperatures, similar to the result for Pd clusters. In contrast, CO poisoning of the Cu$_4$ cluster is less of a problem, but the dehydrogenation steps are not favorable. This 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. Pathways involving C–O bond cleavage are less energetically favorable for the Cu$_4$ and Co$_4$ clusters.

The data on adsorption energies and activation barriers can be analyzed in terms of Brønsted-Evans-Polanyi (BEP)-type curves. BEP relations are often implicitly assumed to hold for surface reactions, but to the best of our knowledge, this kind of relationship has not been considered for subnanometer clusters. Fig. 4 shows a BEP plot for all elementary reactions studied for Pd4 and Pd8 clusters. According to this BEP relationship, the thermodynamically most endothermic step should have the highest activation barrier and vice versa. C–O dissociation is the most endothermic step in Fig. 4. C–O, O–H and C–H scission have intermediate energetics, and C–H dissociation is the most exothermic. The equation relating transition and final state energies is provided in Fig. 4 and has a slope of 0.85; this value, close to unity, suggests that the transition states in the reaction networks are final state-like in character, where the final state is defined in the exothermic direction for each elementary step. This type of analysis has also been carried out for the reactions on Cu$_4$ and Co$_4$ clusters. The relationships derived will be utilized in screening studies in our future plans to identify promising systems.

**Publications**


