

Technology Review

Catalysis Nanoscience and Nanotechnology at USC

Background

Catalysts improve the rate or selectivity of chemical reactions without being consumed in the chemical reaction. “Supported heterogeneous catalysts” consist of catalytic active sites carried on the surfaces of porous solids, known as “supports”. Such catalytic materials are especially important for chemical manufacturing because they minimize the loss of valuable catalytic materials and the need for catalyst separation and recovery. Homogeneous catalysts are distributed throughout the reaction medium on a molecular scale and may be eventually incorporated into the reaction products.

Catalysis has been the cornerstone of chemical manufacturing for decades. In 1998, over \$3 trillion in goods and services were created worldwide based on chemical processes employing catalysts valued at over \$12 billion in several sectors of the chemical industry, including polymers, pharmaceuticals, and petrochemicals. Improvements in catalyst activity and selectivity offer tremendous potential benefits for petrochemical and pharmaceutical manufacturing. Heterogeneous catalysis is also receiving new attention as a critical component of emerging technologies for environmental protection and alternative energy sources.

Nanometer-scale features control the activity, selectivity, and lifetime of catalysts. Recent advances in our ability to design, synthesize, characterize, and manipulate nanoscale catalyst features signify the emergence of “catalysis nanoscience” as a distinct research endeavor. Research in catalysis nanoscience seeks fundamental understanding of the relationships among catalyst synthesis procedures, active site structure on the atomic and nano-scales, chemical reaction mechanisms, and catalyst activity, selectivity, and lifetime. Advances in this area may ultimately lead to (1) first-principles design of catalysts for specific chemical reactions, as well as (2) conceptualization and design of novel catalytic reaction schemes that take advantage of self-assembly of “designer” catalytic sites in predetermined two- and three-dimensional configurations.

Recent attempts have been also made to bridge different catalysis areas from biocatalysis to homogeneous to heterogeneous processes. Bimetallic clusters represent one such bridging element between homogeneous and heterogeneous catalysis. The ultimate goal of this type of work is to combine the high selectivity of homogeneous cluster catalysts with the stability and versatility of supported heterogeneous catalysts.

Purpose

Current research in catalysis nanoscience at USC seeks a deeper understanding of the relationships among synthesis procedures, catalyst nanostructures, and catalyst performance (activity, selectivity, lifetime) for both homogeneous and heterogeneous synergistic bimetallic catalysts.

Specific Research Problems

Heterogeneous Catalysis: Despite the substantial advances in heterogeneous catalysis over the last four decades, bimetallic catalysts (featuring active sites with two or more metallic elements) remain poorly understood and underutilized in practice. Nonetheless, bimetallic systems have provided examples of some of the most active and selective catalysts yet discovered. Bimetallic catalysts offer performance advantages due to “synergy”: the two active metals somehow cooperate to enhance activity and/or selectivity in ways not seen in catalysts employing the individual metals. While many cases of synergy in bimetallic catalysts have been documented, we are just beginning

to understand how the atomic and nanoscale structure of the bimetallic active sites results in synergistic performance.

To achieve this understanding, we are investigating different synthetic techniques (described below) to create bimetallic nanoparticles with controlled particle size and composition. Deposition of nanoparticles onto porous inorganic supports with subsequent activation leads to model bimetallic catalysts. We evaluate the performance of these catalysts with an array of established techniques. Theoretical modeling tools help us to analyze and rationalize experimental observations at every stage.

This approach has several advantages. First, separation of the synthesis, deposition, and activation steps enables characterization of the nanostructure of the bimetallic active sites at every step of the catalyst preparation process. Second, this approach promises unprecedented control over synthetic variables with the possibility of making bimetallic alloys, such as Pt-Au, with atomic proportions not attainable via conventional means. Third, the approach will enable us to unambiguously relate nanostructural characteristics to catalyst performance, yielding mechanistic insights. This knowledge will eventually allow us to design catalysts from first principles – that is, knowing the desired reaction and the possible side reactions, we will be able to design a bimetallic nanoparticle and support with optimal activity and selectivity for the target reaction. We can use this capability to design – figuratively, and perhaps, literally – chemical manufacturing analogs of biological metabolic pathways.

The following sections describe current and planned research in bimetallic nanoparticle synthesis and catalyst evaluation, followed by discussion of critical research needs, especially in the areas of nanoscale materials characterization and higher throughput catalyst evaluation.

Homogeneous Catalysis:

Research Activities

Two well-established groups are working to synthesize new nanoparticle catalyst materials with enhanced activity and selectivity for target reactions. Specifically, we are developing the means to control the size, shape, composition, and atom-level arrangement of bimetallic nanoparticles that will serve as catalytic active sites. In addition, we are learning how to deliver the particles to supports and activate them – essentially nanoscale fabrication.

Our synthesis efforts are focused in two main areas: dendrimer-templated synthesis, and bimetallic cluster complexes. Research on dendrimer-based routes to bimetallic catalysts is funded by the National Science Foundation via a \$2M NIRT grant awarded in 2001. Figure 1 depicts our catalyst synthesis scheme based on the use of poly(amidoamine) (PAMAM) dendrimers. Certain metal ions (Cu^{+2} , Pt^{+2} , Pd^{+2}) form complexes with the dendrimers' interior chemical groups due to favorable physical interactions or ligand exchange reactions (Figure 1a-b). Subsequent chemical reduction leads to precipitation of metallic nanoparticles. The dendrimers stabilize the nanoparticles and serve as the delivery agent for self-assembly and immobilization of nanoparticles on porous

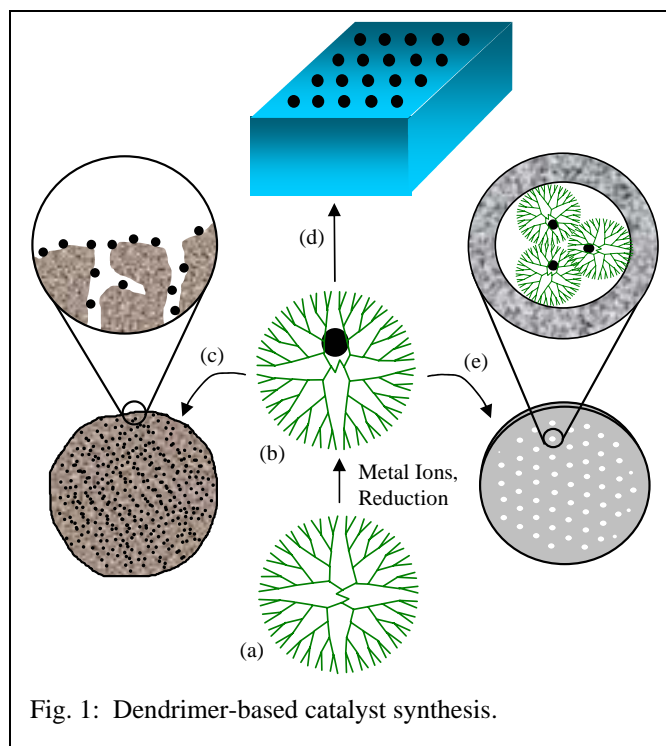
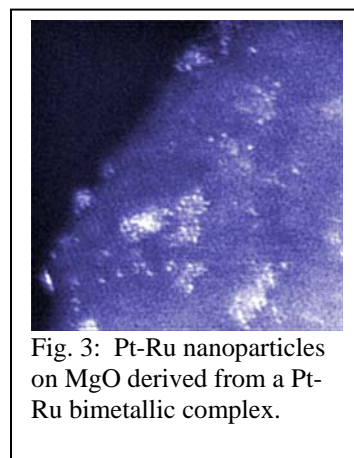
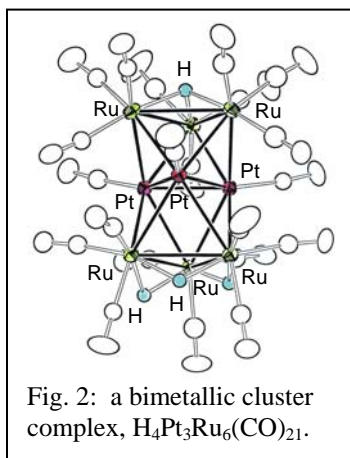


Fig. 1: Dendrimer-based catalyst synthesis.

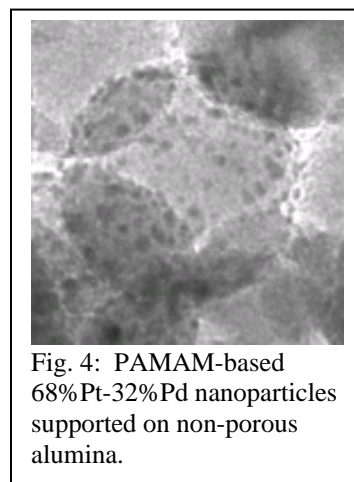
inorganic supports (Figure 1b) as well as in 2-D and 3-D structures on surfaces (Figure 1c, d). Oxidation and reduction treatments produce active catalysts without significant changes in nanoparticle size under optimized conditions.

Synthesis efforts based on bimetallic cluster complexes share many of the same objectives. In this approach, considerable effort goes into developing chemical synthesis routes to produce cluster complexes, such as one shown in Figure 2, with precisely defined structures and compositions. Preparation of catalysts from these complexes begins with deposition of the complexes within porous inorganic supports (silica, alumina, etc.), followed by reduction with H_2 at elevated temperatures. This produces nanoparticles in situ (Figure 3). Compared to the dendrimer route, bimetallic complexes offer better control of composition, but they do not enable direct control of the final nanoparticle size.

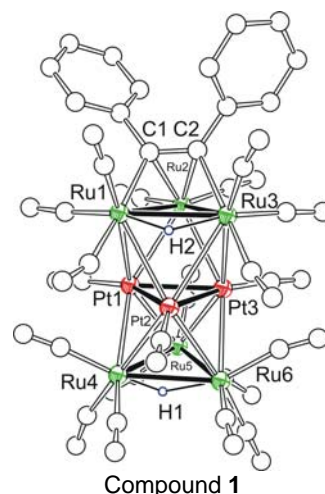


Recent Significant Achievements

Heterogeneous Catalysis: The Catalysis NIRT group has demonstrated proof-of-principle that active heterogeneous catalysts can be synthesized via PAMAM dendrimers. For the first time, PAMAM has been used to synthesize and deliver monometallic (Pt or Pd) and bimetallic (Pt-Pd) nanoparticles onto a high surface-area silica or alumina supports, creating active heterogeneous catalysts (Figure 4). Scanning probe and electron microscopy and an array of spectroscopic tools are being used to characterize nanoparticle size, shape, and atom-level morphology. Parallel FTIR studies of CO adsorption and kinetic studies of CO oxidation have been used to compare the activities of monometallic and bimetallic catalysts. We are currently engaged in an array of “campaigns” focused on synthesis, characterization, and catalyst evaluation of a wide variety of bimetallic systems, (Pt-Au, Au-Ag, Pt-Cu, and others).

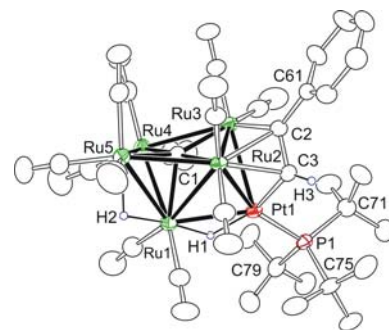


Homogeneous Catalysis: Polynuclear transition metal complexes, known as cluster compounds, have attracted attention as a new class of catalysts in the hope that they may exhibit a combination of the desirable features of the two traditional classes of homogeneous and heterogeneous catalysts. Our recent research has focused on aspects of the synthesis and reactivity of transition metal cluster compounds that may be important to the area of catalysis. The Adams group has recently prepared a new family of mixed metal cluster complexes that are distinguished by segregation of the metallic elements. For example, the complex $Pt_3Ru_6(CO)_{21}(\mu_3-PhC_2Ph)(\mu-H)_2$, 1 contains a layer of three platinum atoms sandwiched between two triangular layers of three ruthenium atoms. There is also a diphenylacetylene ligand coordinated to one of the groups of three ruthenium atoms. Compound 1 has been



found to be an effective catalyst for the hydrogenation of diphenylacetylene to cis-diphenylethylene. The great advantage of a true catalyst is that it will catalyze the reaction many times. Our work suggests that some mixed metal catalysts may have superior catalytic properties because the different metals promote different but reinforcing steps in the reaction. This effect is known as synergism.

We have also found evidence for participation of platinum in catalytic hydrogenation of phenylacetylene to styrene by a carbido platinum-ruthenium carbonyl cluster complex. An acetylene containing intermediate $\text{Ru}_5(\text{CO})_{13}(\mu_5\text{-C})(\text{PhC}_2\text{H})[\text{Pt}(\text{P}^t\text{Bu}_3)]$, that also contains activated hydrogen has been isolated and structurally characterized, see figure 2. Both the phenylacetylene ligand and one of the two hydride ligands are coordinated to the platinum atom.



Compound 2

Future Research Goals

At present, we are synthesizing new bimetallic complexes for use as precursors to heterogeneous catalysts on supports. The bimetallic complexes can be deposited on a selected support such as Al_2O_3 from solutions, see Figure 3. After the solvents are removed, the CO ligands can be removed by heating to $100^\circ - 200^\circ \text{C}$ under hydrogen or helium. The catalysts can then be used for a variety of organic transformations. Efforts are also underway to prepare metallic nanoparticles directly. These can then be added to supports without the need for subsequent ligand removal treatments.

Broad Implications and Applications

Heterogeneous Catalysis: Nanostructured catalytic materials can have a profound impact on chemical manufacturing in the future. Designing catalytic materials from the atom-scale up creates unprecedented opportunities for re-engineering the way chemical products (like polymers and pharmaceuticals) are manufactured. Nanostructured catalytic materials give us a tool for chemical process integration at the nanoscale. Chemical process integration entails the design of a chemical plant for better integration of its constituent units (like heat exchangers and chemical reactors) to conserve energy and raw materials. In the most general sense, *nanoscale* chemical process integration seeks to combine, in one process unit, multiple chemical reactions through rational, atom-up design of catalytic nanostructures. The architecture of these nanostructures will be optimized to direct the chemical transformation of raw materials towards the desired products, and away from unwanted byproducts. The result – in essence, chemical integrated circuits – will achieve the ultimate goal of “green” chemistry: chemical manufacturing optimized to minimize energy use and waste generation. Moreover, the concept of chemical integrated circuits will enable distributed, “point-of-use” chemical manufacturing that minimizes chemical inventory and mitigates process safety and environmental hazards. This would profoundly change the way that chemical products are manufactured, distributed, and used in our society.

Homogeneous Catalysis: Molecular complexes offer superior selectivity for catalytic processes. Today they are so selective that can be used to produce one enantiomer of a chiral pair of molecules virtually exclusively. This is especially important in the pharmaceutical industry for the synthesis of drugs when only one of the two enantiomers is bio-active. Homogeneous catalysis is important to the petrochemical industry for the large scale production of important hydrocarbons such as aldehydes and ketones.