

Dendrimer-Stabilized Nanoparticles for Next-Generation Catalysts

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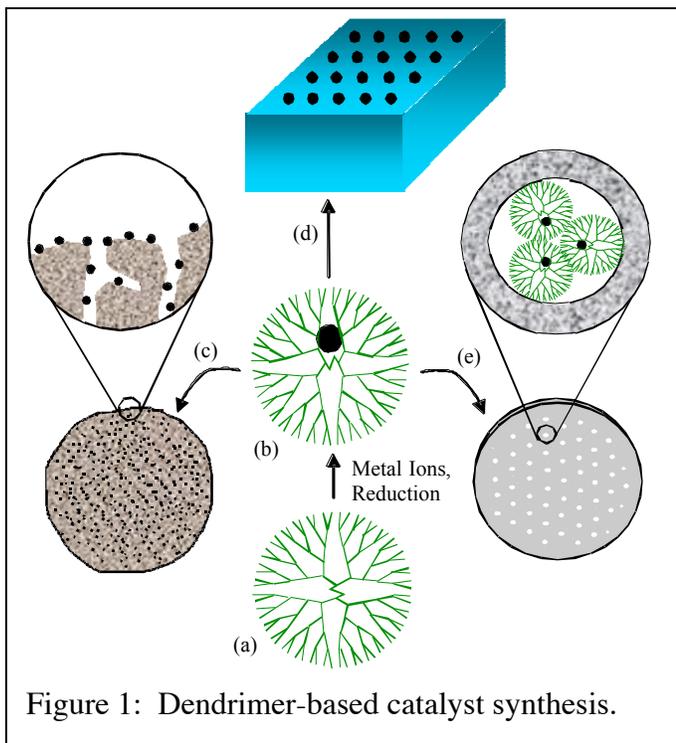
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Our research team is developing dendrimer-templated nanoparticles – zerovalent transition metals, bimetallic alloys, and transition metal oxides – for use as heterogeneous catalysts. The concept is straightforward: we are pursuing “atom-up” design and fabrication of dendrimer-stabilized nanoparticles and seeking ways to self-assemble and immobilize them on supports to create new, nanostructured, heterogeneous catalytic materials. Our efforts build on a substantial body of literature that demonstrate (1) the utility of poly(amido amine) dendrimers (PAMAM) for synthesis of 1-2 nm metal nanoparticles, and (2) their activity as homogeneous catalysts. Building on this foundation, we are synthesizing bimetallic nanoparticles with compositions not possible via organometallic precursors, and are exploring new possibilities for making heterogeneous catalysts with unprecedented control of activity, selectivity, and nano- to meso-scale structure.

Our research activities span (1) theoretical design and molecular modeling, (2) nanoparticle synthesis and catalyst fabrication, (3) physical and chemical characterization, and (4) catalyst performance evaluation. Figure 1 gives the “big picture” of the project. Dendrimers in solution (a) take up metal ions, followed by chemical reduction to produce nanoparticles (b) with controlled size, shape and composition. Nanoparticles can be (c) deposited within porous, high surface area support materials, (d) randomly deposited or self-assembled into ordered nanoarrays on flat surfaces, and/or (e) attached to the walls of nanotubular reactors or other “designer” meso-structures. For gas-phase catalysts, the dendrimer can be thermally decomposed under moderate conditions with minimal particle sintering. For liquid-phase catalysis, the dendrimers (via their terminal functional groups) can be used to covalently tether the nanoparticles to the support surface and protect the particles against aggregation without passivation of the metal. The dendrimers’ hyperbranched architecture nonetheless permits (possibly tunable) access to the nanoparticle catalyst by desired reactants in solution.

The following figures provide selected results from the first eighteen months of this project. Our team welcomes any inquiries that may lead to mutually beneficial collaboration.



Reference: For further information about this project, email Ploehn@engr.sc.edu

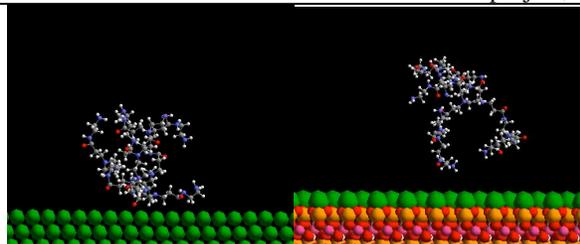


Figure 2: Snapshots from molecular dynamics simulations (Balbuena) of isolated, empty PAMAM dendrimers (G1OH = generation 1, OH functional) deposited on (left) Au(111) and (right) muscovite mica surfaces at 300K. MD results show that the surface dynamics are strongly dependent on the surface and the dendrimer generation. Preliminary results indicate that surface mobility actually increases with dendrimer generation, perhaps due to the more globular configuration of higher generation dendrimers. Surface mobility is higher on Au(111) than mica due to the strong ion-dipole interactions between PAMAM and the mica's surface potassium ions.

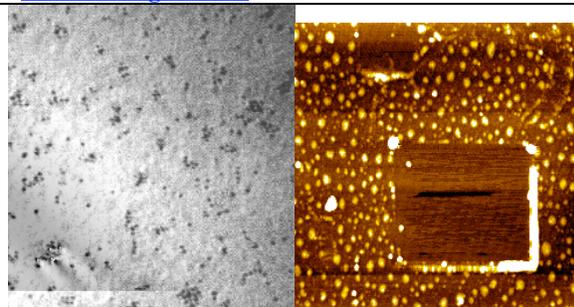


Figure 3: Size characterization of an "early batch" of Pt nanoparticles synthesized in G4-OH (Murphy). Left: TEM image of G4OH-Pt₄₀ indicates an average particle size of about 3 nm, much too large for 40 atom Pt clusters. Right: AFM topography image of the same sample deposited on mica (Ploehn). Contact AFM was used to scrape clean the two square areas, followed by noncontact-mode AFM for image acquisition. Although the metal cluster size was not in accord with results from identical published preps, the result shows our ability to use AFM for size characterization and surface manipulation of nanoparticles.

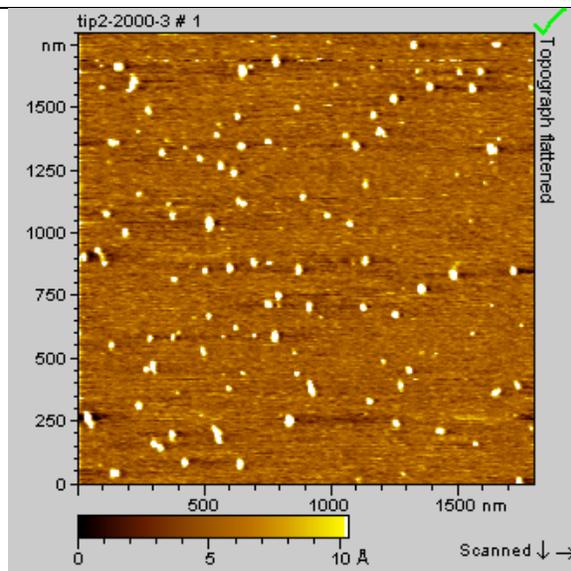


Figure 4: Size characterization of a "recent batch" of G4OH-Pt₄₀ nanoparticles deposited on mica (Ploehn). The distribution of feature heights in the AFM topography image yields an average particle size in the 1.1 to 1.3 nm range, consistent with the expected size of Pt₄₀ clusters.

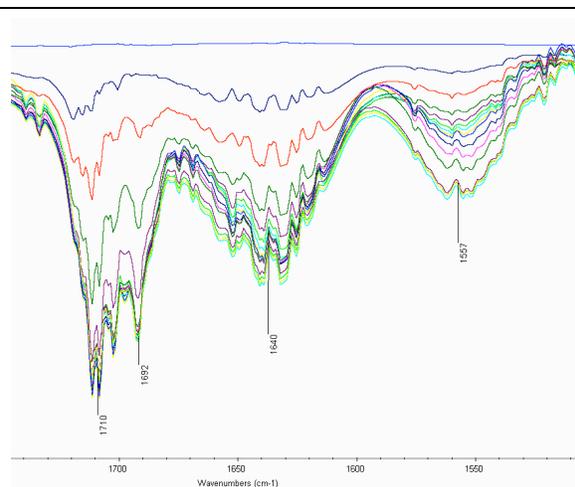


Figure 5: FT-IR spectra (Amiridis) characterizing dendrimer decomposition as a function of temperature in O₂. The sample is the "early batch" G4OH-Pt₄₀ supported on silica. Dendrimer decomposition begins as low as 50°C. Peaks associated with some functional groups stop evolving at temperatures greater than 200°C, while others continue to change up to 425°C.

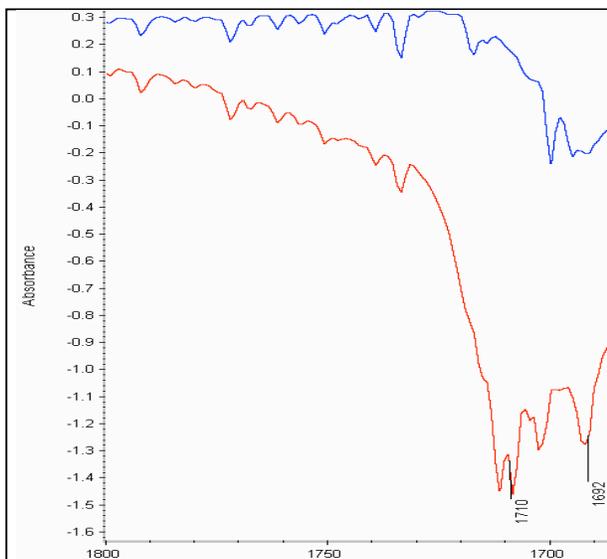


Figure 6: FT-IR spectra characterizing dendrimer decomposition at 400°C in O₂ (Amiridis). The blue curve is for “empty” G4OH (no Pt) on silica, while the red curve is for G4OH-Pt₄₀. This result shows that the encapsulated Pt cluster catalyzes the decomposition of its own dendrimer shell.

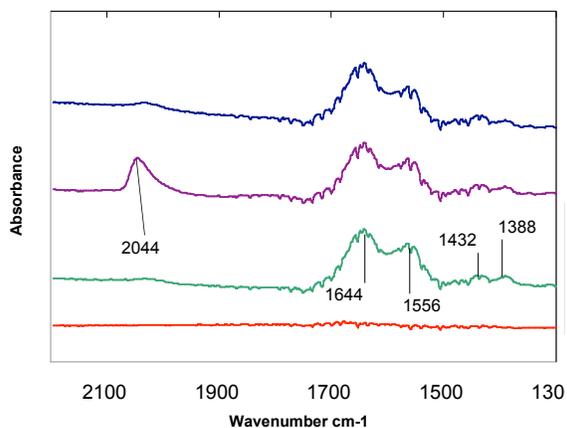


Figure 8: ATR-FTIR spectra for alumina-supported G4OH-Pt₄₀ catalysts (Williams). Bottom to top: baseline for alumina slurry on ATR stage; dendrimer peaks appear after flow-through deposition of G4OH-Pt₄₀ onto alumina; CO-on-Pt peak appears after exposure to CO-saturated water; CO peak disappears after flushing with O₂ solution. Thus CO can access the Pt particles through the dendrimer shell in solution.

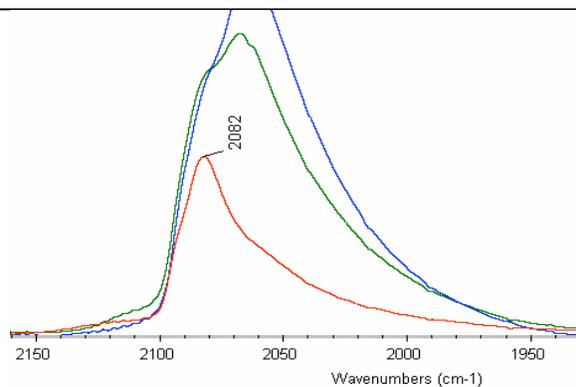


Figure 7: CO chemisorption studies of catalyst activation (G4OH-Pt₄₀ on silica) (Amiridis). Maximal CO chemisorption is achieved by (1) 2 hours of oxidation in 50% O₂ at 425°C, followed by (2) 4 hours of reduction in 100% H₂ at 300°C. This figure shows a maximum in CO chemisorption at 300°C (blue curve) compared to 200°C (red) and 400°C (green). TEM (not shown) suggests that H₂ reduction at higher temperatures leads to nanoparticle sintering and thus a decrease in Pt dispersion.

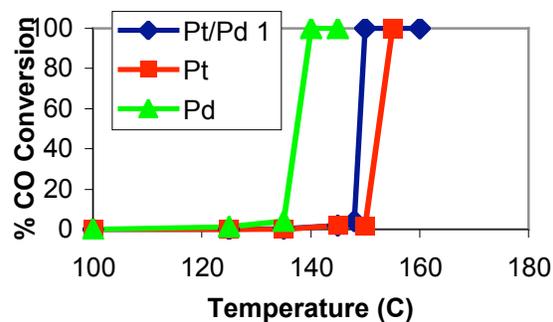


Figure 9: Kinetic study of CO oxidation. This result demonstrates proof-of-principle of our concept. For the first time, PAMAM dendrimers have been used to synthesize and deliver monometallic (Pt, Pd) and bimetallic (Pt/Pd) nanoparticles onto a high surface-area support material (alumina), creating an active heterogeneous catalyst. The activity of the bimetallic catalyst is between those of the monometallic catalysts. These results were obtained by undergraduates in our Chemical Engineering REU program (Williams).