Dendrimer Templates for Supported Au and Bimetallic Au Catalysts

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Introduction
The desire to controllably tune catalyst properties, supported by predictions based on a variety of computational models, has generated increased interest in the controlled preparation of supported nanoparticle catalysts. Particle size, composition, and morphology may have substantial influences on catalytic activity and, more importantly, selectivity. However, few preparative routes exist to prepare supported catalysts of well-defined morphologies; consequently, it is difficult to test many computational predictions with appropriate model supported catalysts.

Starburst polyamidoamine (PAMAM) dendrimers are a specific class of nearly monodisperse, hyperbranched polymers that can be employed as templates for a wide variety of mono- and bimetallic metal nanoparticles (NPs). Dendrimer mediated synthesis allows for substantial control over particle size as well bimetallic particle composition and morphology (well-mixed vs. core-shell particles). The dendrimer templated NPs can then be deposited onto a variety of oxide or carbon supports, and thermally activated to yield supported NP catalysts with known, reproducible synthetic histories.

In this paper, we discuss advances in dendrimer mediated preparative methods for supported catalysts. In particular, we focus on preparing new Au and Au-based bimetallic NP catalysts (Au-Pt, Au-Ni, Au-Co). Kinetic characterization is used to evaluate differences between new and traditional catalysts using the CO oxidation and NO decomposition reactions.

Materials and Methods
Hydroxyl terminated generation 5 PAMAM dendrimers (G5OH) were used to prepare Au NPs. Briefly, HAuCl₄ was added to G5OH in solution and reduced with NaBH₄ to yield dendrimer encapsulated NPs (DENs). Amine terminated dendrimers were also anchored to appropriate supports and alkylated to provide additional solid-phase nanoparticle templates. The Au NPs were removed from the dendrimer interior as monolayer protected clusters (MPCs) with an appropriate water or organic soluble thiol, and deposited onto Pt-25 titania. Au-Pt, Au-Co, and Ni core-Au shell (Ni@Au) NPs and MPCs were prepared similarly, first complexing K₂PtCl₆ or Ni(NO₃)₂ to the dendrimer interior amines.

DENs and MPCs were deposited onto appropriate oxide supports and activation conditions were evaluated. For Au-Pt/SiO₂ catalysts, NO decomposition activity was evaluated in order to compare with computational predictions. CO oxidation catalysis over Au/TiO₂ catalysts was studied at 268-293 K with low conversions (<2%) and varying O₂ and CO pressures. New catalysts were also characterized with IR spectroscopy, chemisorption and TPD.

Results and Discussion
A number of synthetic techniques for preparing monometallic Au NP catalysts using PAMAM dendrimer templates were developed. Depending on their end group, PAMAM dendrimers can soluble in aqueous or organic solvents; consequently, organic and aqueous MPCs were explored as catalyst precursors. Additionally, amine terminate dendrimers were anchored onto silica or Merrifield resin beads to provide non-aqueous routes to air and water sensitive metal combinations (Au-Ni, Au-Co). Monometallic Au NPs on the order of 2 nm (2.5 nm for anchored dendrimers) were successfully prepared via all the synthetic schemes. Bimetallic Au-Ni and Au-Co NPs were similarly prepared, and bulk composition confirmed by elemental analysis. Additionally, a synthetic route to 3 nm Ni core – Au shell NPs was developed. SQUID measurements showed these particles (TEM histogram in figure) to be superparamagnetic at 10 K; Evans’ method NMR techniques confirmed that magnetic properties are maintained at ambient temperatures.

The new nanoparticles were deposited onto oxide supports, activated, and evaluated as CO oxidation or NO decomposition catalysts. For Au catalysts, comparisons to the World Gold Council test catalyst (WGC) provided a detailed kinetic characterization of the new materials. Saturation kinetics in the O₂ dependence plots (see right) indicated that oxygen activation and a subsequent step are both important kinetic steps in the reaction.

Significance
This new preparative method allows for the facile synthesis of a wide variety of mono- and bimetallic nanoparticles, especially with compositions not available by traditional routes. Particle morphologies can also be controlled, leading to preparative routes to potentially active structures predicted by theory. Detailed kinetic studies can also be developed and employed as a characterization tool that directly probes changes to the catalytic active site as a function of preparative technique, particle morphology, and binary metal addition.

References