

Synthesis of Mono- and Bimetallic Au-based Nanoparticle Catalysts Utilizing Solid Phase Dendrimer Templates

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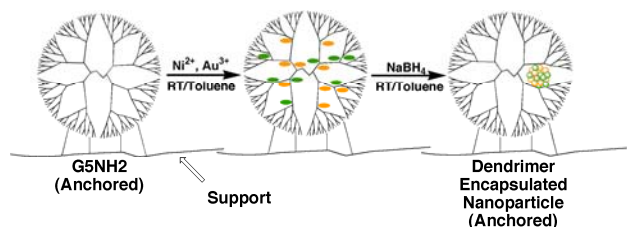
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Introduction

The desire to controllably tune catalyst properties 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. Starburst polyamidoamine (PAMAM) dendrimers are a specific class of nearly monodisperse, hyperbranched polymers that can be employed in nanoparticle syntheses.¹ PAMAM dendrimers can be used to both template and stabilize a wide variety of mono- and bimetallic metal nanoparticles (NPs). In this synthetic scheme, metal precursors are first bound to the interior amine groups of the PAMAM dendrimer; addition of a reducing agent prepares particles that are essentially trapped within the dendrimer interior. The dendrimer mediated synthesis allows for greatly increased control over particle size and composition. For bimetallic particles, well-mixed and core-shell particles on the order of 2 nm in diameter can be selectively prepared. It is also possible to anchor the dendrimer to a resin bead or other solid support to synthesize Au-based MPC catalysts.²



In this paper, we discuss advances in dendrimer mediated preparative methods for supported catalysts, focusing on new Au, Ni-Au, and Cu-Au bimetallic nanoparticles.

Materials and Methods

Amine terminated generation 5 PAMAM dendrimers (G5NH₂) were anchored to polystyrene resin beads (EMD Biosciences) and alkylated with 1,2-epoxydodecane (Aldrich) to produce G5C12_{anch}. Anchoring on templated silica was accomplished similarly, first treating the silica with anhydride terminated silanes purchased from GelEst. Dendrimer encapsulated nanoparticles (DENs) were prepared by adapting literature syntheses. Metal salt precursors (HAuCl₄, NiCl₂, CoCl₂, Cu(NO₃)₂), NaBH₄, and C₁₀SH were purchased from Aldrich and used without further purification. SiO₂ (Davisil) and TiO₂ (Degussa p-25) was calcined at 500 °C overnight. Trimethoxy(Propyl-succinic anhydride)silane (GelEst) was used as received. TiO₂ supported Au and Au-based MPCs were activated at 290 °C under flowing H₂/N₂ (5%) for 16 hours. SiO₂ supported DENs activations varied and will be discussed.

Results and Discussion

Amine terminated PAMAM dendrimers were anchored onto anhydride terminated polystyrene resins or functionalized silica through a direct reaction in DMF. The surfaces of the anchored dendrimers were then rendered hydrophobic by reacting the remaining (unreacted) primary amines with 1,2-epoxydodecane producing G5C12_{anch}. Solution ¹H NMR and ATR-FTIR spectroscopies were used to follow and confirm the anchoring and alkylation reactions. Spectrophotometric titration of G5C12_{anch} with toluene solutions of CoCl₂ showed that the anchored dendrimers bound 150 equivalents of Co²⁺, in good agreement with the value obtained for G5C12 in toluene solution (165 eq.). Control experiments showed no uptake of CoCl₂ or HAuCl₄ over several hours. Based on these results, it was determined that the dendrimers were successfully anchored on the corresponding support(s) and were functionally similar to solution G5C12 PAMAM dendrimers.

NiAu and CuAu DENs were prepared by adding HAuCl₄ and the corresponding Ni/Cu salt in EtOH to a toluene slurry of G5C12_{anch} followed by reduction with NaBH₄. Reflectance UV-Visible spectroscopy of the anchored DENs was comparable to solution spectra of the corresponding NiAu and CuAu DENs. The NPs were extracted from the dendrimer interior by vigorously stirring with decanethiol in toluene. The TEM micrograph and particle size distribution histogram in Figure 1 show that the extracted nanoparticles are small and relatively monodisperse.

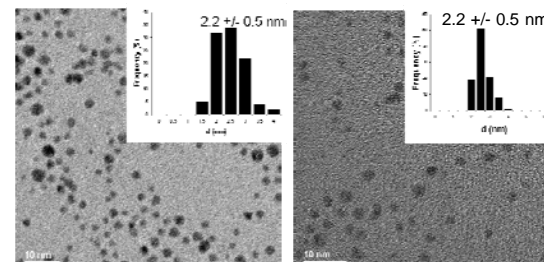


Figure 1. TEM micrographs and particle size distributions (inset, 100 particles) for NiAu Monolayer Protected Clusters (MPCs) left, and CuAu MPCs (right)

The synthesis of non MPC CuAu bimetallic catalysts on silica was also explored. These experiments involved the synthesis of the anchored CuAu DENs, which were then thermally treated to remove the dendrimer (instead of MPC extraction). The parameters for synthesis and thermal treatment of the DENs to produce bimetallic catalysts will be discussed.

Significance

This new preparative method allows for the facile synthesis and extraction of NPs (both mono and bimetallic) in nonaqueous solvents. This provides a new opportunity for the synthesis and study of bimetallic Au-based bimetallic NP catalysts.

References

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- Gilbertson, J. D.; Vijayaraghavan, G.; Stevenson, K. J.; Chandler, B. D. *Langmuir*, 23, 11239 (2007).