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

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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-epoxydocadecane producing G5C12anch. Solution 1H NMR and ATR-FTIR spectroscopies were used to follow and confirm the anchoring and alkylation reactions. Spectrophotometric titration of G5C12anch 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 G5C12anch 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.

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.

Materials and Methods

Amine terminated generation 5 PAMAM dendrimers (G5NH2) were anchored to polystyrene resin beads (EMD Biosciences) and alkylated with 1,2-epoxydocadecane (Aldrich) to produce G5C12anch. 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-succinimide)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.

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