478d Synthesis and Characterization of Dendrimer-Stabilized Bimetallic Pt-Cu Nanoparticles

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In this work, we have synthesized dendrimer-stabilized nanoparticles (platinum, copper, and bimetallic Pt-Cu) and characterized them using High Resolution Transmission Electron Microscopy (HRTEM), Atomic Force Microscopy (AFM), Energy Dispersive X-ray Spectroscopy (EDX), X-ray Photoelectron Spectroscopy (XPS), and Attenutated Total Reflection Infrared Spectroscopy (ATR-IR). Of several possible synthesis schemes, we have investigated the co-complexation, co-reduction route to bimetallics. We first mix metal precursors with generation 4, hydroxyl-terminated poly(amidoamine) dendrimers (PAMAM G4OH) in aqueous solutions, followed by reduction with hydrogen gas. The series of nanoparticle samples includes Pt40, Pt20Cu20, Pt30Cu10, and Cu20 (and possibly additional samples) where the numbers denote the nominal molar metal-to-dendrimer ratio. HRTEM and AFM images reveal the presence of approximately spherical particles with narrow size distributions and mean diameters less than 3 nm. EDX spectra show that Pt and Cu are intimately mixed on the 10 nm scale. XPS spectra indicate that the metals are reduced but not necessarily to zero valence. We use ATR-IR to investigate CO chemisorption at 300K on metal nanoparticles supported on alumina. We use the IR peaks associated with the amide groups to identify the presence of G4OH on the alumina surface and to show that G4OH-stabilized metal nanoparticles are strongly adsorbed. ATR-IR spectra of CO on bimetallic nanoparticles show a prominent vibrational band around 2171 cm-1, indicative of terminally adsorbed CO dicarbonyl species on Cu+ sites. The absence of an IR band for CO adsorption on Pt suggests a Pt core, Cu shell structure for these Pt-Cu nanoparticles. We will also present FTIR results for bimetallic Pt-Cu nanoparticles catalysts made with commercial metal oxide supports, appropriately activated, and used to catalyze CO oxidation. The combination of detailed structural characterization, spectroscopic analysis, and catalyst evaluation leads to new insights concerning the underlying synthesis mechanisms and catalytic properties of PAMAM-stabilized Pt, Cu, and Pt-Cu nanoparticles.