

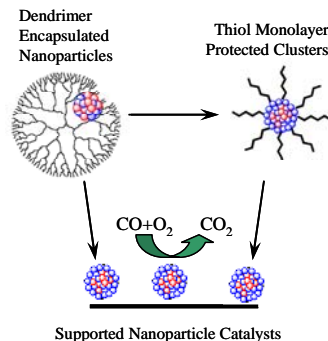
Tuning and Understanding Oxygen Activation by Gold: Synthesis and Characterization of New Au and Ni-Au Catalysts

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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).¹ 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, focusing on new Au and Ni-Au bimetallic nanoparticles. Structural and kinetic characterization show how Ni incorporation modifies the catalytic chemistry of Au.

Materials and Methods

Amine terminated generation 5 PAMAM dendrimers (G5OH) were anchored to a high surface area silica, alkylated, and used to template the new bimetallic particles. Briefly, $\text{Ni}(\text{NO}_3)_2$ was first deposited into the anchored, alkylated dendrimer. HAuCl_4 was added, followed by reduction NaBH_4 to yield dendrimer encapsulated NPs (DENS). The nanoparticles were then extracted with decane thiol, deposited onto P-25 titania, and the thiols removed under flowing H_2/N_2 .

CO oxidation catalysis was studied at 268-293 K with low conversions (<2%) and varying O_2 and CO pressures. Subsequent Michaelis-Menten treatment of the data allowed for the extraction of O_2 binding constants for the various catalysts. New catalysts were also characterized with AAS, FTIR, TEM, and XPS.

Results and Discussion

In developing new synthetic techniques for heterogeneous catalysts, we examined dendrimer templating for the controlled preparation of Ni-Au bimetallic catalysts, which cannot be prepared by traditional methods. The incorporation of Ni into Au nanoparticles causes dramatic changes in CO oxidation kinetics. The oxygen reaction order increases by a factor of 4 and the apparent activation energy drops to a value roughly one third of pure gold (top plot). Additionally, kinetic parameters extracted using the Michaelis-Menten model² show that the maximum rate increases with increasing Ni content while the stability of O_2 on the surface decreases by a factor of 40. These changes suggest that Ni incorporation greatly reduces the oxygen affinity of the catalyst, yet produces a greater number of active sites.

These results are evaluated in the context of fully characterized Au catalysts. This includes a new infrared spectroscopic measurement of the CO binding constant on industrial and newly prepared (dendrimer templated) Au catalysts. These measurements show that three different Au/ TiO_2 catalysts have identical CO binding properties within the measurement error. Additionally, the CO adsorption data indicates that only about 75% of the CO binding sites are occupied under catalytically relevant conditions, leaving a number of unoccupied sites for O_2 activation.

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. 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 heterometal incorporation.

References

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2. Long, C; Gilbertson, JD; Vijayaraghavan, G; Stevenson, KJ; Chandler, BD *J. Am. Chem.Soc.*, 130, 10103 (2008).

