

Novel Catalysts (Preparation of gold nanoparticles using dendrimers and their reactivity for CO oxidation)

Peter E. H. Kracke¹ Terry E. Haas, and Maria Flytzani-Stephanopoulos*
¹Tufts University, Medford, MA 02155 (USA)
*maria.flytzani-stephanopoulos@tufts.edu

Introduction

Traditional CO oxidation and water gas shift (WGS) catalysts are typically noble metal nanoparticles dispersed on metal oxide supports. It has been shown that not all the material loaded on the support is catalytically active, and the support itself may participate in the reaction [1]. One aspect that has been difficult to study has been the nature of interactions between the noble metal and the oxide support. Thus it is important to study the catalytic nature of the noble metal nanoparticles in the absence of a metal oxide support. One must create gold nanoparticles analogous to those found on the supports in traditional catalysts on non oxide supports. These nanoparticles should be in the 1-4 nm size range. Previous attempts to form nano sized Au clusters did not result in clusters in the desired size range [2]. Dendrimers offer a new synthesis pathway for the formation of noble metal nanoparticles. Until the first work with Dendrimer Nanocluster Composites (DNCs) by Crooks et al.[4], unsupported noble metal nanoparticles comparable to those formed on metal oxide supports have not been readily available.

Materials and Methods

Materials. Amine-terminated fifth-generation (G5.NH₂) PAMAM dendrimers with ethylenediamine cores were obtained as 5% methanol solution (Sigma-Aldrich). HAuCl₄ (Alfa Aesar), HCl, and NaBH₄ (Sigma-Aldrich) were used without further purification. 18Ω-cm Milli-Q deionized water (Millipore, Bedford, MA) was used as solvent.

Preparation. The following procedure was followed to synthesize varying concentrations of G5.NH₂ (Au₅₅) [4,5]. Gold precursor solution was added to a dilute G5.NH₂ dendrimer solution at a molar ratio of 55 Au equivalents per dendrimer. The resulting mixture was stirred at room temperature for 40 min, after which time the pH of the solution was adjusted to between 2 and 3 using HCl. Once the pH of the mixture became stable an amount of a 1.0 M solution of NaBH₄ in 0.3 M aqueous NaOH equivalent to 10x molar excess of NaBH₄ was added. Finally the pH of the mixture was adjusted to neutral if necessary.

Results and Discussion

Poly(amidoamine) (PAMAM) dendrimers are used to prepare gold nanoparticles. These gold nanoparticles are more monodisperse than those seen in conventional gold nanoparticles prepared on transition metal oxide supports (Fig. 1). Similar results have been reported for Ru DNCs versus Ru supported on Al₂O₃ [6]. The efficiency of these DNC materials as CO oxidation catalysts will be reported. These DNCs can now serve as part of a model catalytic system to better understand the mechanism and active species in CO oxidation on supported noble metal catalysts.

Figure 1. TEM image of G5.NH₂ (Au₅₅) (should be noted that only Au nanoparticles show up in TEM image as dendrimers are not electron rich enough to be visible with out staining)

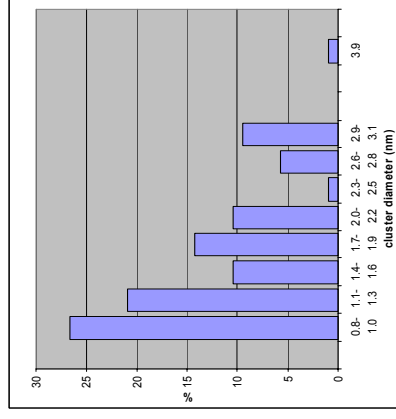
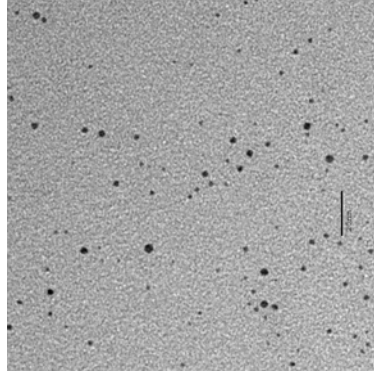


Figure 2. Histogram showing particle size distribution present in Fig. 1

Significance

DNCs can be used as catalysts to determine the effect of the missing oxide support to better understand the mechanism and active species in CO oxidation on supported noble metal catalysts. To properly investigate the role of the interaction between metal and oxide it is necessary to have a baseline activity of nanoparticles of the noble metal without the support study has been possible synergistic interactions between the noble metal and the support.

While much work has been done using DNCs in catalyst preparation, the idea of using the free-standing dendrimer encapsulated nanocluster colloids as catalysts for CO oxidation is new.

References

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