Dendrimer Encapsulated Gold Nanoparticles for Room Temperature CO Oxidation in Aqueous Solutions

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Introduction

Traditional CO oxidation catalysts are typically noble metal nanoparticles dispersed on metal oxide supports. Previous work [1], has shown that the support itself may participate in the reaction; thus it is important to study the catalytic nature of the noble metal nanoparticles in the absence of a metal oxide support, to understand the contribution of the metal oxide. Dendrimers offer a new synthesis pathway for the formation of noble metal nanoparticles. Until the first work with Dendrimer Encapsulated Nanoparticles (DENs) by Crooks et al.[2], unsupported noble metal nanoparticles comparable to those formed on metal oxide supports have not been readily available.

Materials and Methods

Hydroxyl-terminated fifth-generation (G5.OH) polyamidoamine (PAMAM) dendrimers with ethylenediamine cores were obtained as 5% methanol solution (Sigma-Aldrich). $HAuCl_4$ (Alfa Aesar), HCl, and $NaBH_4$ (Sigma-Aldrich) were used without further purification. 18Ω-cm Milli-Q deionized water (Millipore, Bedford, MA) was used as solvent.

Aqueous Au DENs were prepared according to the literature [3,4]. In brief, stock solutions of aqueous hydroxyl-terminated, fifth generation PAMAM dendrimer (G5.OH) and $HAuCl_4$ were mixed at a 55:1 Au:G5.OH ratio with varying overall concentrations. After stirring for 2 min, reduction of Au was carried out by the addition of 10x excess of $NaBH_4$ in 0.2M NaOH to form G5.OH(Au_{55}) DENs. All aqueous DENs were dialyzed against 4L of water for >12 h with Spectra/Por Dialysis Membrane (MWCO: 3,500) to remove residual Cl^- ions.

Results and Discussion

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 DENs versus Ru supported on Al_2O_3 [5].

The AuDENs are active for room temperature CO oxidation when in a liquid thin film system at high partial pressures of CO. A comparison of the reaction rates achieved by a selection of different G5.OH(Au_{55}) catalysts can be seen (Fig. 2). The properties of these DEN materials as CO oxidation catalysts will be reported. UV-VIS and TEM characterizations of catalyst shelf life and post reaction will also be presented.

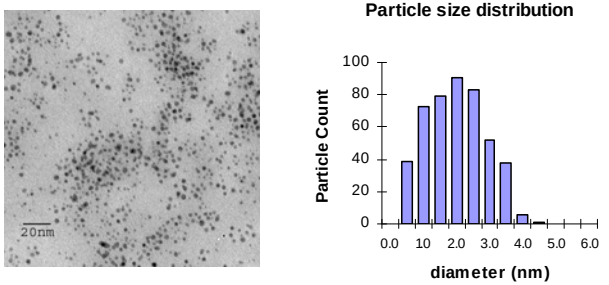

Figure 1. TEM image of G5.OH(Au_{55}) and particle size histogram (only Au nanoparticles show up in TEM image as dendrimers are not electron rich enough to be visible)[6].

catalyst	Au weight (mg)	batch time (h)	ν_0
4ml 15μM 15A-120 (aged)	0.65	4.5	3.57E-03
6ml 15μM 15B-30	0.98	4.0	5.47E-04
4ml 15μM 15B-64 (aged)	0.65	3.5	2.41E-03
3ml 40μM 40-7	1.3	4	1.38E-04

Figure 2. CO oxidation activity of select G5.OH(Au_{55}) catalysts, ν_0 = rate in terms of moles CO per sec normalized per mole Au in catalyst [6].

Significance

DENs can be used as metal nanoparticle shells to allow reactants through while keeping the metal dispersed. While much work has been done using DENs in catalyst preparation, the idea of using the free-standing dendrimer encapsulated gold nanoparticles as catalysts for the CO oxidation reaction is new.

References

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