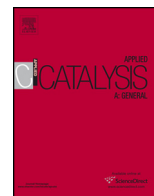




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Silica-supported gold/dendrimer nanocomposites with controlled sizes of gold particles

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ABSTRACT

Au/G4OH nanocomposites were synthesized in aqueous solutions under different conditions and used as precursors for the preparation of SiO₂-supported Au nanoparticles. Elemental analysis, UV–Vis, and STEM measurements were used to determine the nature and the extent of the Au–dendrimer interactions and to illustrate how the solution pH affects the Au–dendrimer complexation, as well as the final size of the gold particles formed. G4OH PAMAM dendrimers were found to reduce Au³⁺ ions and act as stabilizers for Au nanoparticles thus formed, yielding stable gold/dendrimer colloidal solutions. The solution pH and the Au/G4OH ratio were found to be two critical factors that control the size of gold particles. At pH 7, Au₅/G4OH nanocomposites with sizes of Au particles below 2 nm can be formed and used as precursors for the preparation of solid materials. Such nanocomposites can be deposited intact on the surface of SiO₂ and yield highly dispersed and nearly uniform Au nanoparticles with dimensions in the order of 1.3 nm.

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1. Introduction

In the early 1980s, it was shown that TiO₂-supported Au nanoparticles with sizes in the 2–5 nm range are active for CO oxidation at temperatures as low as –70 °C [1]. Since then, the list of chemical reactions catalyzed by Au nanoparticles has been extended to include epoxidation, amination, hydrogenation of different hydrocarbons, oxidation of alcohols, and C–C coupling reactions [2–4]. Some of these reactions require relatively large Au particles but some (i.e., oxidation and hydrogenation) proceed with much higher rates over supported Au nanoparticles with sizes below 2 nm, suggesting that the size of the supported Au particles must be controlled for each individual chemical process. The same is true in other research fields where Au nanoparticles are currently used, including electronics, optics, and medicine [5–8]. As a result, significant efforts have been focused on the synthesis of supported gold nanoparticles with desired dimensions and shapes. Conventional preparation techniques based on the impregnation of Au salts and subsequent high-temperature treatments provide limited control over the final Au particle size because Au easily aggregates at

elevated temperatures. The use of organometallic Au complexes as precursors has yielded better results [9–13], but the range for such preparations is limited because of the limited availability of organometallic gold complexes.

The synthesis of colloidal gold nanoparticles with desired sizes and shapes in solution and their subsequent delivery onto surfaces of solid supports could provide a relatively simple path for the controlled preparation of solid materials containing Au. In such preparation routes, the metal precursor is typically reduced in the aqueous solution in the presence of surfactants which preserve the colloidal state of the metal nanoparticles formed [14–17]. Among different available surfactants, poly(amidoamine) (PAMAM) dendrimers have attracted a lot of recent attention as nanoparticle stabilizers, because these macromolecules offer a variety of functional groups for complexation of metal cations and have interior voids which can trap and protect metal nanoparticles from aggregation. These dendrimer features offer an opportunity to control the architecture and the size of the metal nanoparticles in the solution and to maximize the uniformity of active metal sites in supported materials.

Several literature examples illustrate the successful application of this preparation route for the synthesis of Au–dendrimer nanocomposites. For example, Esumi et al. [18,19] examined the formation of Au nanoparticles in the presence of PAMAM dendrimers with amine, sugar, methyl ester, and alkyl groups at the periphery. In all these cases, however, nonuniform Au particles

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with dimensions in the 2.1–12.8 nm range were formed both in the interior and on the exterior of the dendrimer macromolecules. Amis et al. [20,21] reported the synthesis of Au nanoparticles in the 2.0–4.0 nm range from HAuCl_4 using amine-terminated PAMAM dendrimers. Furthermore, Crooks et al. [22] described the formation of nearly uniform Au nanoparticles with sizes in the 1.3–1.6 nm range using PAMAM dendrimers with both quaternary ammonium and primary amine groups on their periphery and concluded that the Au/dendrimer ratio effects stronger the size of the metal particles formed than the dendrimer generation. Finally, Luan et al. [23] prepared stable and uniform 2.7 nm Au nanoparticles by reduction of HAuCl_4 with NaBH_4 in the presence of hydroxyl-terminated PAMAM dendrimers.

In the majority of these examples, aqueous solutions of HAuCl_4 and a dendrimer were mixed for a short period of time (i.e., 2–5 min) before the mixture was further treated with a reducing agent, assuming that Au–dendrimer interactions are fast and take place in a short period of time. As a result, no detailed information related to the extent of Au complexation and the type of Au/dendrimer interactions is included in these reports. Nevertheless, some indications regarding the possible nature of Au/dendrimer interactions can be found. For example, since the AuCl_4^- aqueous solution loses its yellow color immediately upon mixing with the PAMAM- NH_2 solution, it has been suggested that protonated terminal groups of the PAMAM- NH_2 dendrimers ($\text{pK}_a \sim 9.7$) interact with the AuCl_4^- species electrostatically [24–26]. Furthermore, Imae et al. [27] have suggested that shifts in the position of the amide II and amide III FTIR bands indicate conformational changes in the G4 NH_2 dendrimer due to interactions with Au particles. Similarly, the observed increase in the UV–Vis absorbance in the 290 nm region in the case of Au/G5 NH_2 solutions may suggest the formation of ion pairs between G5 NH_2 and AuCl_4^- [24,26,28]. Finally, there are several reports indicating that hydroxyl-terminated PAMAM dendrimers can reduce Au cations in solution [19,29,30].

While these examples provide some indications regarding the nature of the Au/dendrimer interactions, there is no strong consensus in the literature. It also remains unclear if the desirable complexation of gold with the dendrimer interior indeed takes place and leads to the formation of small and stable Au nanoparticles within the dendritic moieties. Moreover, only few attempts have been made to prepare solid catalytic materials through a gold–dendrimer nanocomposites route. For example, when $(\text{Au}_{55})/\text{G4NH}_2$ nanocomposites were deposited onto the surface of TiO_2 , the average size of the supported Au particles formed was in the order of 2.0 nm [22]. In the material thus formed, Au nanoparticles remain covered by the dendrimer and further treatments at elevated temperatures (approximately 400 °C) in oxygen/hydrogen atmospheres are required to remove the dendrimer component [31]. However, these treatments are known to lead to a significant sintering of Au [32].

To avoid such complications, Chandler et al. [33] have demonstrated a different approach which is based on the extraction of Au nanoparticles from Au/dendrimer nanocomposites with thiols into an organic phase. The thiols can be further removed from the surface of the supported Au particles under relatively mild conditions. This preparation route allows for a better control over the size of Au particles during thermal treatments, while maintaining relatively narrow particle size distributions. The average sizes of Au particles extracted from Au/G5OH nanocomposites and supported on TiO_2 were found to be in the order of 3 nm and remained nearly unchanged when thiols were removed under the flow of H_2/N_2 at 290 °C for 16 h. As a result, Au/ TiO_2 samples prepared through this route were found to be active for CO oxidation.

Alternatively, Somorjai et al. [34] have demonstrated that Au/G4OH nanocomposites with average sizes of Au particles in the order of 2 nm can be delivered intact onto the surface of a SiO_2

support, yielding a solid material with leaching-resistant properties that can be further used as a catalyst for liquid-phase reactions. In this particular case, it was even possible to transfer liquid-phase reactions from a batch to a flow mode without affecting the performance of the catalyst. While this example persuasively demonstrates the potential advantages of supported Au/dendrimer nanocomposites as heterogeneous catalysts for liquid-phase reactions, it also provides a strong motivation for developing a better understanding of the Au–dendrimer solution chemistry, since the Au–dendrimer interactions can provide a critical control parameter that affects the size and chemical properties of Au nanoparticles in the resulting nanocomposites.

In this paper, we examine the use of Au–G4OH nanocomposites for the preparation of Au–G4OH/ SiO_2 solid materials. We have shown previously the effect of preparation conditions (i.e., solution pH, dialysis, and metal/dendrimer ratio) on the extent of Rh–G4OH complexation and the subsequent sizes of Rh particles formed in supported materials. Therefore, our goal is to determine whether the knowledge gained from the Rh–G4OH case can be extended to the inherently more complex Au^{3+} –G4OH system. While the synthesis of supported Au nanoparticles via the dendrimer route has already been reported previously [33,35], there is no literature reports addressing the reduction of Au cations by dendrimers and, therefore, the growth of Au particles in dendrimer solutions. More specifically, the goal of this work is to explore the solution chemistry in the presence of both Au^{3+} and G4OH PAMAM dendrimers, determine how the extent of the Au^{3+} complexation and reduction by the dendrimer molecules depends on the solution conditions, and examine how these conditions affect the sizes of the Au particles formed in solution and subsequently, in supported materials. The results reported highlight the effect of the solution pH on the strength of the Au–dendrimer interactions and the size of the Au nanoparticles formed, explore in detail the kinetics of Au^{3+} reduction by the dendrimer in the absence of any additional reducing agents, and eventually help to optimize the preparation conditions for the synthesis of Au nanoparticles with specific dimensions on the SiO_2 support.

2. Experimental

2.1. Reagents and materials

Fourth-generation hydroxyl- and amine-terminated poly(amidoamine) (PAMAM) dendrimers (denoted as G4OH and G4 NH_2 , respectively) were purchased as 10 wt% solutions in methanol (Dendritech). Prior to further use, methanol was removed under N_2 flow at room temperature and 0.42 mM G4OH and 0.18 mM G4 NH_2 aqueous solutions of dendrimers were prepared and stocked. Water purified to 18.2 M Ω cm was used to prepare all aqueous solutions. Hydrogen tetrachloroaurate(III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) (99.99% purity, Alfa Aesar), *n*-methylacetamide ($\geq 99\%$ purity, Sigma-Aldrich), propanol (99.8% purity, Alfa Aesar), 2-propanol (99.7% purity, Alfa Aesar), and triethylamine (99% purity, Alfa Aesar) were used as-received. 0.1 N NaOH and 0.45 N HCl solutions were prepared by dilution of 5 N NaOH (Reagents, Inc.) and 37% HCl (BDH Aristar) solutions and further used for pH adjustments. A commercial SiO_2 powder support (Evonik) with a BET surface area of 148 m²/g was used as-supplied.

2.2. Preparation of Au–dendrimer nanocomposites

The method used for the preparation of Au–dendrimer nanocomposites with variable Au/dendrimer molar ratios was similar to that reported elsewhere [36]. In each case, G4OH (0.42 mM,

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