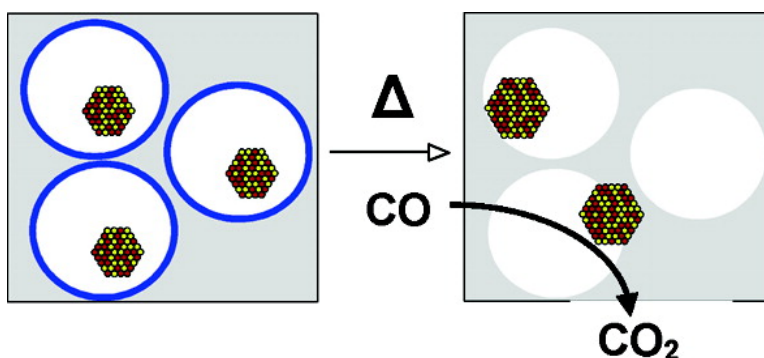


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Titania-Supported PdAu Bimetallic Catalysts Prepared from Dendrimer-Encapsulated Nanoparticle Precursors

Robert W. J. Scott, Chinta Sivadinarayana, Orla M. Wilson, Zhen Yan, D. Wayne Goodman, and Richard M. Crooks*

Department of Chemistry, Texas A&M University, P. O. Box 30012, College Station, Texas 77842-3012

Received September 13, 2004; E-mail: crooks@tamu.edu

In this communication, we report the synthesis and characterization of TiO₂-supported PdAu bimetallic nanoparticle catalysts prepared using dendrimer-encapsulated nanoparticles (DENs).¹ The key result is that the compositional fidelity of the original bimetallic DENs, and to some extent their size, is retained in the supported catalyst after removal of the dendrimer template by calcination at 500 °C. Additionally, the gas-phase catalytic activity for CO oxidation is higher for the bimetallic catalysts than that for the corresponding Pd-only and Au-only monometallics.^{2,3}

It has previously been shown that 1–3-nm diameter alloy and core–shell bimetallic PdPt,^{4,5} PdAu,⁶ PdRh,⁷ and AuAg⁸ nanoparticles can be synthesized within dendrimer templates.¹ The resulting materials are characterized by a high degree of uniformity in size, structure, and elemental composition, and in some cases they have enhanced solution-phase catalytic activities compared to the analogous monometallic materials.^{4–7} There are also a few examples of dendrimer/nanoparticle composites of various sorts being used to prepare supported Pt,⁹ Pd,¹⁰ Au,¹⁰ CuO,¹¹ and Fe₂O₃ nanoparticles.¹² In some cases, these were shown to be catalytically active.^{9,12} To the best of our knowledge, however, there is only one very recent example of a heterogeneous catalyst prepared from a bimetallic DEN precursor.¹³ The DEN approach to bimetallic nanoparticles is potentially simpler than many alternative methods. For example, organometallic cluster precursors containing two different metals have been used to prepare supported bimetallic catalysts, but continuous variation of the elemental composition of the resulting particles requires large precursor libraries.^{14–16} Most other methods for preparing supported bimetallic nanoparticles in the <5-nm size range lead to phase segregation of the two metals and thus poor control over the composition of individual particles,¹⁷ although limited success has been achieved using surfactant-stabilized nanoparticles.¹⁸

We prepared DENs consisting of PdAu alloys within fourth-generation, amine-terminated poly(amidoamine) (PAMAM) dendrimers (G4-NH₂(Pd_nAu_{55–n})) by co-complexation of the two corresponding metal salts followed by chemical reduction of the dendrimer/metal-ion composite.⁶ The synthesis was carried out in a 99% methanol solution using a procedure we previously reported for preparing DENs within amine-terminated dendrimers.¹⁰ For example, G4-NH₂(Pd_{27.5}Au_{27.5}) was synthesized as follows: 0.0924 g of a 14.2 wt % solution of G4-NH₂ in MeOH and 20 μL of 0.3 M HCl were added to 1 L of 99% MeOH, followed by 255 μL of a 0.10 M K₂PdCl₄ solution. The HCl was added to prevent cross-linking of the G4-NH₂ dendrimer by Pd²⁺ (Pd²⁺ is used to designate PdCl₄²⁻ and all its hydrolysis products).¹⁹ After being stirred for 10 min, 255 μL of a 0.10 M HAuCl₄ solution was added. After being stirred for an additional 2 min, 1 mL of a 1.0 M NaBH₄ solution was added (20× molar excess). The solution was stirred for 3 h under N₂ and used for the sol–gel synthesis described next. Transmission electron microscopy (TEM) indicated that the G4-

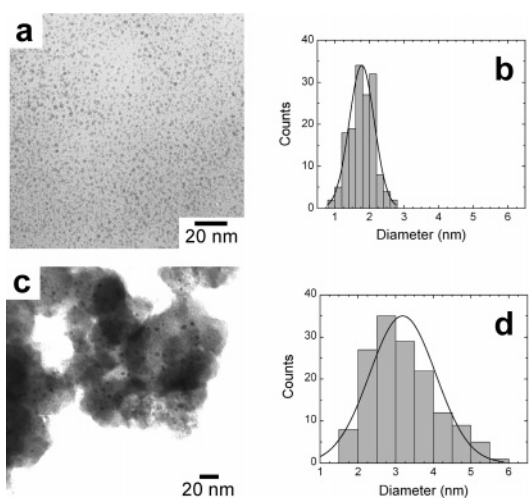


Figure 1. Bright-field TEM images and particle-size distributions for G4-NH₂(Pd_{27.5}Au_{27.5}) DENs prepared by co-complexation of the corresponding metal salts followed by reduction. (a), (b) As synthesized. (c), (d) After incorporation into the titania matrix and subsequent calcination at 500 °C under O₂ and H₂.

NH₂(Pd_{27.5}Au_{27.5}) DENs had an average particle size of 1.8 ± 0.4 nm (Figure 1), which is in accord with previous results for closely related materials.^{6,10} G4-NH₂(Pd₅₅) and G4-NH₂(Au₅₅) were prepared in a similar manner, and they also had properties similar to those reported previously.¹⁰

PdAu, Pd, and Au DEN solutions were used to prepare TiO₂ powders containing 1 wt % of the metals. The PdAu/TiO₂ composite was prepared as follows. To a solution of G4-NH₂(Pd_{27.5}Au_{27.5}), 0.3 M HCl was added to neutralize excess NaBH₄. After being stirred for 2 h, 3.52 g of Ti(OⁱPr)₄, dissolved in 5 mL of MeOH dried over molecular sieves, was added dropwise to the solution. The solution became turbid over a period of 30–60 s as the alkoxide precursor hydrolyzed. After 5 min, 100 mL of H₂O was added. The resulting solution was left for 24 h, and then the precipitate was filtered and dried at 100 °C for 24 h. The final product was recovered in yields of 40–60% (not all of the TiO₂ precursor was incorporated into the matrix). The powder was then sequentially calcined at 500 °C in flowing O₂ and then H₂ for 1 h each.²⁰

Thermogravimetric and elemental analysis of the G4-NH₂(Pd_{27.5}-Au_{27.5})/TiO₂ composite indicated that the dendrimer was removed during calcination (Supporting Information).¹⁰ The average particle size increased after calcination from 1.8 ± 0.4 nm to 3.2 ± 0.9 nm (Figure 1). This increase is consistent with the harsh pyrolysis conditions required to completely remove the dendrimer,²¹ and it is comparable to the increase in size observed for monometallic Pd and Au nanoparticles calcined under the same conditions (3.0 ± 0.6 nm and 2.7 ± 0.6 nm, respectively).¹⁰ Large-area energy-dispersive spectroscopy (EDS) of the calcined catalyst indicated an average composition of 48 ± 3% Pd and 52 ± 3% Au, which

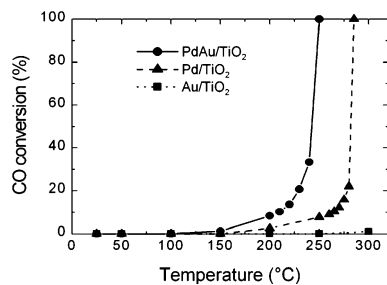


Figure 2. Percentage CO oxidation as a function of temperature for PdAu, Pd-only, and Au-only catalysts supported on TiO₂. The catalysts were prepared using G4-NH₂(Pd_{27.5}Au_{27.5}), G4-NH₂(Pd₅₅), and G4-NH₂(Au₅₅) DENs, respectively. Catalytic reactions were carried out using a 2:1 ratio of O₂/CO and a gas hourly space velocity of 20 000 cm³·g⁻¹·h⁻¹.

is in agreement with the molar percentages of PdCl₄²⁻ and AuCl₄⁻ used in the original synthesis mixture (50% each). Importantly, the composition of the individual nanoparticles in the catalyst can be controlled by varying the percentage of the two metal salts complexed within the dendrimer at the beginning of the synthesis. For example, quantitative, standardless EDS analysis of 13 particles prepared from a G4-NH₂(Pd₁₄Au₄₁)/TiO₂ precursor (Supporting Information) resulted in average Pd and Au compositions of 19 ± 2% and 81 ± 2%, respectively. These values are comparable to the molar percentages of PdCl₄²⁻ and AuCl₄⁻ originally complexed within the dendrimers (25 and 75%, respectively). The low standard deviations of the EDS measurements clearly indicate a high degree of compositional uniformity. This is a significant advantage of preparing the nanoparticles prior to immobilization on the support.¹⁷

As alluded to earlier, the dendrimer interior is a template for the encapsulated nanoparticles in that it controls their size and elemental composition. In addition, however, the exterior of the dendrimer templates the porosity of the titania support.^{10,11} This is important, because effective heterogeneous catalysts must have high surface areas and a significant degree of meso- and macroporosity.²² The surface area of the NH₂(Pd_{27.5}Au_{27.5})/TiO₂ composite was found to increase from 35.7 m²/g to 51.9 m²/g following calcination, and the BJH pore diameter of the calcined material reveals a well-defined peak centered at 3.5 nm (Supporting Information). This result indicates that the imprint of the G4-NH₂ dendrimer, which has a solution-phase diameter of ~4.5 nm,¹ remains in the titania following calcination.

Figure 2 compares the catalytic CO oxidation activity for TiO₂-supported catalysts prepared with G4-NH₂(Pd_{27.5}Au_{27.5}), G4-NH₂(Pd₅₅), and G4-NH₂(Au₅₅). The temperature for onset of catalytic activity (1% CO conversion) for the PdAu catalyst is 150 °C, while the Pd and Au catalysts are inactive at this temperature. Complete (100%) CO conversion occurs at 250 °C and 285 °C for PdAu and Pd DENs, respectively, which indicates a synergetic electronic ligand effect.^{2,3} Interestingly, the Au-only supported catalysts exhibited no activity toward CO oxidation at temperatures <300 °C.²³ Lifetime measurements of the PdAu catalysts indicated that 100% CO oxidation activity was retained for 24 h, but after this time there was a loss in activity of 60–80% over a period of about two days, possibly due to coking.

To summarize, we have described an approach for the synthesis of well-defined, bimetallic PdAu nanoparticles supported on TiO₂.

Single-particle EDS analysis of individual nanoparticles confirms that they are bimetallic and have approximately the same atomic composition as the ratio of the metal salts used in the original reaction mixture. The supported bimetallic PdAu nanoparticles prepared by this method showed a synergetic catalytic effect toward CO oxidation compared to supported Pd-only and Au-only catalysts. These results are important, because they provide a general and simple route for preparing supported bimetallic catalysts that are nearly monodisperse in both size and composition.

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Supporting Information Available: HAADF TEM image of G4-NH₂(Pd₁₄Au₄₁) DENs after calcination, thermogravimetric analysis, elemental analysis, gas adsorption isotherms, and BJH pore-size distributions for TiO₂-supported PdAu catalysts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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