

Supported gold catalytic nanoparticles with molecular control over the chemical and geometric environment

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Highlights

- One pot synthesis of 11-atom gold clusters
- Effect of bound ligands on different precursors of Au (I)
- Catalytic properties of supported clusters for oxidation of benzyl alcohol are presented

1. Introduction

Gold nanoparticles are important catalytic materials, due to their numerous fascinating catalytic properties [1]. Smaller gold nanoparticles (< 10nm) increase both the available surface area and the fraction of gold atoms of low coordination number, resulting in enhanced catalytic activity. These nanoparticles are usually stabilized via the addition of various agents, such as surfactants, ionic liquids or organic ligands, which control the final size and stability of gold nanoparticles. Hence, choosing an appropriate stabilizing agent is a crucial step while designing the synthesis procedure. Here, inspiration can be derived from nature, specifically from enzymes: their local environment, which generally involves complex moieties, largely influences the active site. Using a nature-inspired approach, organic bound ligands are employed in the synthesis procedure, to enhance the electronic properties and impart extra stability to the gold nanoclusters, and they are supported on nanoporous materials with controlled pore size [2, 3]. These supported gold clusters are used as catalysts in the selective oxidation of alcohols, which is of industrial significance. The aerobic oxidation of benzyl alcohol is known to undergo two main reaction pathways: either the desired oxidation to benzaldehyde, or the undesired disproportionation reaction to produce benzaldehyde and toluene in stoichiometric amounts [4]. In addition, the over-oxidation of benzaldehyde to benzoic acid is also to be avoided. We discuss how the proposed chemical and geometrical control over the gold cluster structure and its nano-environment impact catalytic activity, selectivity and stability for aerobic oxidation of benzyl alcohol to benzaldehyde.

2. Method

A very simple, one-pot synthesis of 11-atom gold clusters (Au₁₁) is introduced. Chloroauric acid trihydrate (HAuCl₄·3H₂O), triphenylphosphine ((C₆H₅)₃P) and sodium borohydride (NaBH₄) were mixed in a round bottom flask for ~ 2h, with ethanol as a solvent [5]. The HAuCl₄/NABH₄ ratio was optimized by selecting different equivalents (1, 4, 10 and 20) of NaBH₄ with respect to Au atoms. Using this synthesis method, Au₁₁ clusters can be immobilized (1 wt % gold loading) on various supports, such as TiO₂ or SBA-15, without any aggregation or alteration in their particle size. Further, in order to understand the role of organic bound ligands, different precursors of gold with varied steric hindrance have been used. The final particle size was characterized by UV/Vis spectroscopy and HAADF-STEM. A correlation was found between the steric hindrance imparted by the ligands and the final particle size of the nanoparticles. Catalytic activity of these supported gold clusters for the conversion of benzyl alcohol to benzaldehyde is tested in a microreactor setup, which has increased heat and mass transfer benefits over conventional reactors [4].

3. Results and discussion

The synthesized gold nanoclusters were analyzed using UV/Vis measurements. The peak at 420 nm confirms that the size of the particle is less than 2 nm (Figure 1A). To validate this result, transmission electron

microscopy (TEM) was used, demonstrating that the average core diameter of the gold clusters is ~ 1.2 nm. Gold (I) precursors chloro(triphenylphosphine)gold(I) (1), chloro(dimethylphenylphosphine)gold(I) (2), and chloro(trimethylphosphine)gold(I) (3) were selected to alter the steric hindrance around the phosphorus atom. The UV-Vis spectrum (Figure 1A) of (1) consists of a broad band at ~ 450 nm, revealing that the core diameters of synthesized gold clusters are slightly larger than the size of bare Au_{11} clusters. The UV-Vis spectrum of (2) and (3) showed a SPR band at ~ 515 nm and ~ 560 nm, respectively. Extensive analysis based on TEM showed that the average particle size of (1), (2) and (3) was ~ 2 nm, ~ 3 nm and ~ 10 nm, respectively (Figure 1B). The synthesized clusters were immobilized onto supports such as TiO_2 and SBA-15. TEM and DR UV-Vis spectroscopy confirm no variation in particle size after immobilization. A serpentine silicon microreactor set-up was used to calculate the catalytic activity of these supported clusters. Benzyl alcohol and oxygen were premixed and introduced as feed in the microreactor and the product was collected in a GC vial. The reaction was initially carried out at 120°C and slowly raised to 160°C . Final conversion and selectivity were quantitatively assessed by gas chromatography. Initial results of these catalysts show high selectivity towards benzaldehyde. Deactivation studies of these catalysts need to be tested over longer times and are in progress. The effects of various post-treatments (calcination and treatment with ozone) to remove the extra ligands on the support and impact activity, selectivity and stability are studied.

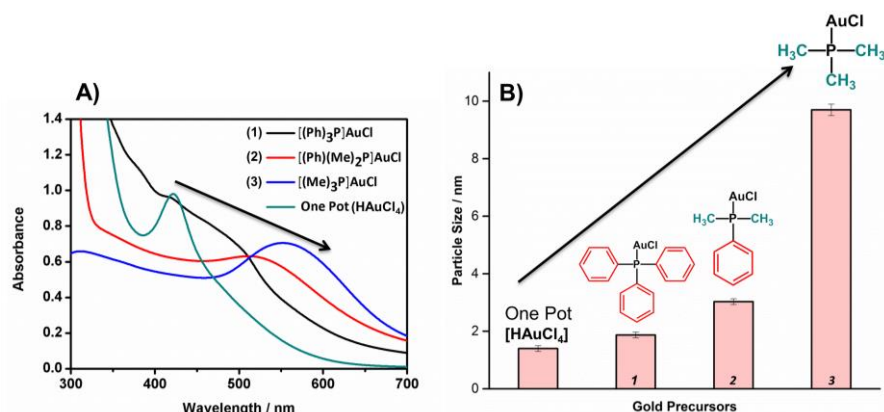


Figure 1. A) UV/vis spectrum of gold nanoparticles using different ligands; B) Bar graph showing different particle sizes calculated from TEM using different gold precursors.

4. Conclusions

We have successfully synthesized 11-atom gold clusters, Au_{11} , using a facile, one-pot methodology. Different gold (I) precursors led to different nanoparticle sizes, as a result of different steric hindrance around the Au core. These Au_{11} clusters were quite stable at least a month, as confirmed by UV/vis spectroscopy and TEM. Their shape and size were retained after immobilization onto various supports. Supported clusters were tested as selective catalysts for the conversion of benzyl alcohol oxidation to benzaldehyde in a continuous flow microreactor.

References

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Keywords

Au nanoclusters; ligand effects; steric hindrance; benzylalcohol oxidation