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Metal dependent catalytic hydrogenation of nitroarenes over water-soluble glutathione capped metal nanoparticles

Sachil Sharma *

Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India

ABSTRACT

The water soluble glutathione capped metal nanoparticles (M-GS, where M = Pd, Pt, Au and Ag; GS = glutathione) with size 2.4 ± 0.2 nm were synthesized by borohydride reduction of metal ions in the presence of glutathione as capping ligand and used as catalyst for the hydrogenation of nitroaniline in aqueous phase. The rate of catalytic hydrogenation was dependent on metal type and the trend of catalytic activity over these M-GS nanoparticles was found to be Pd-GS (k_{app} = 0.0227 ($\pm 3 \times 10^{-4}$)) s^{-1} $\gg$ Pt-GS (k_{app} = 0.0043 ($\pm 1 \times 10^{-4}$)) s^{-1} > Au-GS (k_{app} = 0.0015 ($\pm 0.2 \times 10^{-4}$)) s^{-1} > Ag-GS (k_{app} = 0.0008 ($\pm 0.2 \times 10^{-4}$)) s^{-1}. The similar trend of catalytic activity was found for the hydrogenation of nitrobenzene. Our experimental results, along taking into account the theoretical calculations done by other research groups, suggest that the observed catalytic activity trend is attributed to the "different rates of H$_2$ molecule adsorption and dissociation" on the M-GS nanoparticles. The "high rate of H$_2$ molecule adsorption" and "highly oxidized surface" make Pd-GS nanoparticles an ideal candidate for the rapid hydrogenation. On the basis of our experimental results, we proposed that small gaps between less densely packed branched thiol "glutathione molecules" provide the access to metal nanoparticle surface for the hydrogenation reaction.

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1. Introduction

Noble metal nanoparticles have drawn immense research interest owing to their importance in catalysis [1], sensing [2], surface-enhanced Raman scattering (SERS) [3] and biomedical applications [4]. The large surface area of ultrafine noble metal nanoparticles makes them an ideal candidate for catalyzing various reactions. The hydrogenation of nitroarenes to aniline derivatives catalyzed by noble metal nanoparticles is an important reaction from industrial, synthetic and environmental point of view. The functionalized aniline derivatives are important intermediates for pharmaceutical polymers, dyes, pigments and other fine agrochemicals [5–9]. The nitroarenes are also found as contaminants in industrial waste water and hence, hazardous to the environment. Therefore, it becomes necessary to reduce them to industrial chemicals and intermediates in order to clean the environment.

The hydrogenation of nitroarenes to corresponding amino benzenes catalyzed by nanoparticles immobilized on oxide supports such as Au—TiO$_2$/Fe$_2$O$_3$/MgO [10,11], Ag—TiO$_2$ [12] and Ag—rGO [13] has been studied vastly in the literature. However, the hydrogenation of nitroarenes over ligand capped fine metal

nanoclusters and nanoparticles are scantily reported. Recently, ligand capped novel metal clusters [14,15] have been explored as catalyst for a number of important reactions. Very recently, Fenger and co-workers [16] studied size dependent catalysis of Au nanoparticles, respectively for the hydrogenation of 4-nitrophenol. However, most of the literature on the catalytic hydrogenation of nitroarenes is still limited to Au nanoparticles and to the best of our knowledge, there is no report yet on the metal dependent catalysis by ligand capped metal nanoparticles. Thus, it becomes important to gain better understanding of metal dependence catalysis by ligand stabilized metal nanoparticles.

In present work, firstly, glutathione capped metal nanoparticles (M-GS, where M = Pd, Pt, Au and Ag; GS = glutathione) of same size were synthesized and then, their catalytic activity toward the hydrogenation of nitroarenes was compared. Herein, we report the metal dependent catalytic activity of water soluble glutathione (GSH) capped Pd, Pt, Au and Ag nanoparticles for the hydrogenation of nitroarenes. The trend of catalytic activity of the glutathione capped metal (M-GS) nanoparticles was found to be following: Pd-GS $\gg$ Pt-GS > Au-GS > Ag-GS. Our experimental results suggest that the observed catalytic activity trend is attributed to different rates of H$_2$ molecule adsorption and dissociation. However, high rate of H$_2$ adsorption along with high amount of surface oxidation on Pd-GS nanoparticles make them ideal catalyst for rapid hydrogenation of nitroarenes.

* Present address: Department of Applied Chemistry, Tokyo University of Science (TUS), Shinjuku, Tokyo 162-8601, Japan.
E-mail addresses: Sachilsharma79@gmail.com, a26909@rs.tus.ac.jp

2. Materials and methods

2.1. Materials

L-glutathione reduced (GSH, ⩾98%, Aldrich), Sodium borohydride (99%, Aldrich), Palladium(II) chloride (PdCl$_2$, 99.999%, Aldrich), Chloroplatinic acid hexahydrate (H$_2$PtCl$_6$·6H$_2$O, ACS reagent), Hydrogen tetrachloroaurate trihydrate (HAuCl$_4$·3H$_2$O, ACS reagent), Silver Nitrate (AgNO$_3$, ACS reagent ⩾99.0%, Aldrich), 2-nitro aniline (>99%, Tokyo Chemical Industry), Nitrobenzene (⩾99%, Aldrich), were used as received. Water was purified using a Millipore Milli-Q system (18.2 MΩ cm). Firstly, various M-GS nanoparticles with same size were synthesized and further used as catalyst for hydrogenation of nitroarenes. All synthesis and catalysis experiments were performed at room temperature and under air atmosphere. Transmission electron microscopy (TEM) images were obtained using JEOL JEM-2010 high contrast electron microscope operating at 200 kV. XPS measurements were carried out on an XPS system (VG ESCALAB 220i-XL) using monochromatic Al K$_\alpha$ X-ray source (1486.6 eV). Binding energies (BE) were referenced to the C 1s BE at 284.8 eV.

2.2. Synthesis of glutathione capped metal nanoparticles

The water soluble Pd, Pt, Au and Ag nanoparticles with same size 2.4 ± 0.2 nm were prepared by borohydride reduction of their respective metal salts in presence of glutathione as capping ligand. The glutathione capped Pd nanoparticles were synthesized using the procedure reported in our previous work [17]. However, glutathione capped Pt, Au and Ag nanoparticles were synthesized according to literature procedures [4,18,19] with the slight modification. The experimental details are described in the supplementary material.

2.3. Catalytic experiment procedure

In a typical catalytic reaction, 0.13 mL (130 μl) of aqueous solution of 5 mM nitroarene (2-nitro aniline and nitrobenzene) was first mixed with 2.5 mL aqueous solution of 0.3575 mg/L catalyst (2.4 nm M-GS nanoparticles) in a UV–Vis quartz cuvette while kept on stirring. Then, 0.87 mL (870 μl) of aqueous solution of 21 mM NaBH$_4$ was added into the above mixture while kept on stirring. Immediately following this, in situ absorption spectral changes were recorded till the completion of catalytic hydrogenation with a USB-4000 fiber optic spectrometer (Ocean Optics) equipped with magnetic stirrer. The base line correction was performed using water as solvent before taking absorbance measurements. The UV–Vis spectra of reaction products were found to be in agreement with UV–Vis spectra of the authentic compounds.

3. Results and discussion

Fig. 1 shows the characteristic UV–Vis spectrum of 2.4 nm glutathione capped Pd, Pt, Au and Ag nanoparticles. Their bright field TEM images show the narrow size distribution ∼2.4 ± 0.2 nm (Fig. S1 in supplementary material). Here it is important to note that the glutathione capped metal (M-GS, M = Pd, Pt, Au and Ag) nanoparticles with same size (∼2.4 ± 0.2 nm) were used as catalyst for the hydrogenation reaction to exclude the size effect.

To test the metal dependent catalytic activity of 2.4 nm M-GS (M = Pd, Pt, Au, and Ag) nanoparticles toward the aqueous phase hydrogenation of nitroarenes, we chose the 2-nitroaniline as a model substrate.

Fig. 2a shows the time dependent UV–Vis spectral changes during the catalytic reduction of 2-nitroaniline over M-GS
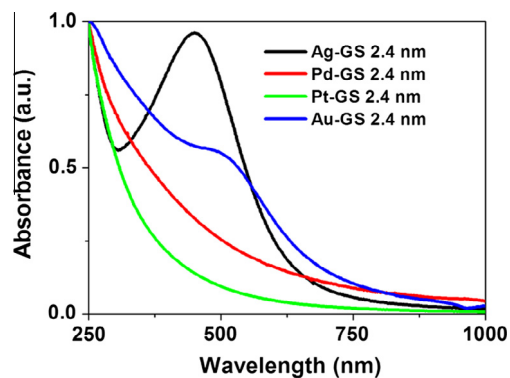

Fig. 1. Characteristic UV–Vis spectrum of 2.4 nm M-GS (M = Pd, Pt, Au and Ag) nanoparticles.

nanoparticles. After certain time, the peak at 412 nm was found to disappear completely, indicating the complete reduction of 2-nitroaniline. The completion of hydrogenation of 2-nitroaniline over M-GS nanoparticles was also noted manually by observing the complete fading of yellow color of 2-nitroaniline after certain time. The completion of catalytic hydrogenation reaction was confirmed by recording positive ion ESI-MS spectra of starting nitroarenes and crude final product. As shown in Fig. S2 (supplementary material), the intense peak at m/z = 139.04 for 2-nitroaniline was found to completely absent in the positive ion ESI-MS spectrum of crude final product. Whereas, the presence of most intense peak at m/z = 109.06 in the positive ion ESI-MS spectrum of crude final product indicates the formation of 2-phenyldiamine. The similar ESI-MS spectra were obtained after the complete hydrogenation of 2-nitroaniline over all M-GS (M = Pd, Pt, Au and Ag) nanoparticles. The plot of C_t/C_0 versus t (s) shows the exponential decrease of C_t/C_0 of 2-nitroaniline with time over various M-GS nanoparticles, which was plotted by taking into account the spectral changes at 412 nm (Fig. S3 in supplementary material). The time for 95% completion of the hydrogenation of 2-nitroaniline over 2.4 nm Pd-GS, Pt-GS, Au-GS and Ag-GS nanoparticles was observed to be 1.7, 10, 23 and 47 min, respectively. Fig. 2(b) shows the kinetic pseudo-first order rate plots of the reduction of 2-nitroaniline over 2.4 nm M-GS (M = Pd, Pt, Au and Ag) nanoparticles at 298 K. The values of slope (defined as apparent rate constants, k_{app}) were calculated to be 0.0227 ($\pm 3 \times 10^{-4}$), 0.0043 ($\pm 1 \times 10^{-4}$), 0.0015 ($\pm 0.2 \times 10^{-4}$), and 0.0008 ($\pm 0.2 \times 10^{-4}$) (s^{-1}), respectively for the hydrogenation of 2-nitroaniline over 2.4 nm Pd-GS, Pt-GS, Au-GS and Ag-GS nanoparticles. Thus, the order of catalytic activity of 2.4 nm M-GS nanoparticles was as follows: Pd-GS ≫ Pt-GS > Au-GS > Ag-GS for the hydrogenation of 2-nitroaniline. Similar trend in catalytic activity was also found for the hydrogenation of nitrobenzene over 2.4 nm M-GS (M = Pd, Pt, Au and Ag) nanoparticles (*vide infra*; Fig. 3).

Although, induction time was not observed for the catalytic hydrogenation of 2-nitroaniline over 2.4 nm Pd-GS nanoparticles (Fig. S3 in supplementary material). However, the induction time of 1.5, 3, and 7 min was observed for the catalytic hydrogenation over 2.4 nm Pt-GS, Au-GS and Ag-GS nanoparticles, respectively. Similar trend in the induction period was also observed for the catalytic hydrogenation of nitrobenzene (Fig. S7 in supplementary information). The induction time may be attributed: to (1) diffusion controlled adsorption of reactants on the metal nanoparticle surface, (2) the presence of dissolved oxygen in the reaction medium, and (3) metal surface restructuring induced by adsorbed substrate [15]. To check the effect of dissolved oxygen, we performed the catalytic hydrogenation reaction of 4-nitroaniline over 2.4 nm Au-GS nanoparticles after purging the reaction solutions by