



Reduction of 4-nitrophenol to 4-aminophenol over Au nanoparticles deposited on PMMA

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ABSTRACT

Gold nanoparticles (Au NPs) were directly deposited on commercially available poly(methyl methacrylate) (PMMA) beads by the deposition reduction method by adding dropwise of NaBH₄ into the aqueous solution of Au(en)₂Cl₃. The average diameter of Au NPs was 6.9 nm and, in contrast to the case of rapid addition, there were no aggregated particles larger than 20 nm. Catalytic activity of Au/PMMA was tested for the reduction of 4-nitrophenol to 4-aminophenol with an excess amount of NaBH₄. Gold NPs on PMMA showed the highest catalytic activity among polymer supported Au NPs previously reported. The reaction rate is the pseudo-first-order with respect to 4-nitrophenol. The pseudo-first-order rate constant and the activation energy were estimated to be 7.2–7.9 × 10⁻³ s⁻¹ at 295 K and 38 kJ mol⁻¹, respectively.

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1. Introduction

Gold catalysts have been a rapidly growing research area owing to the intriguing catalytic properties of Au nanoparticles (NPs) deposited on base metal oxides in CO oxidation at a temperature as low as 200 K and propylene epoxidation with H₂–O₂ mixture [1–3]. In recent years, Au NPs supported on activated carbons [4] and polymers [5] have also been investigated for applications to liquid phase reactions such as the aerobic oxidation of alcohols.

Concerning polymer supported Au catalysts, the structures and surface functional groups of polymers are expected to play important roles to deposit small Au NPs preventing them from aggregation and to exhibit significant catalytic activity. Because of the weak interaction between polymer supports and Au NPs, direct deposition of Au NPs onto polymers such as polystyrene from Au(III) complex compounds was considered to be difficult to achieve. Accordingly, it has been thought that well-designed polymer structures are necessary to obtain small Au NPs and several kinds of polymer structures have already been prepared [6–20]. Scheme 1 classifies polymer supports into six kinds of structures; micelles [6,7], gels [8–10], brushes [11,12] or star polymers in which Au NPs are inside the cores [13], hollow capsules [14,15], macro-

porous particles such as ion-exchange resins [16–18] and beads [19,20].

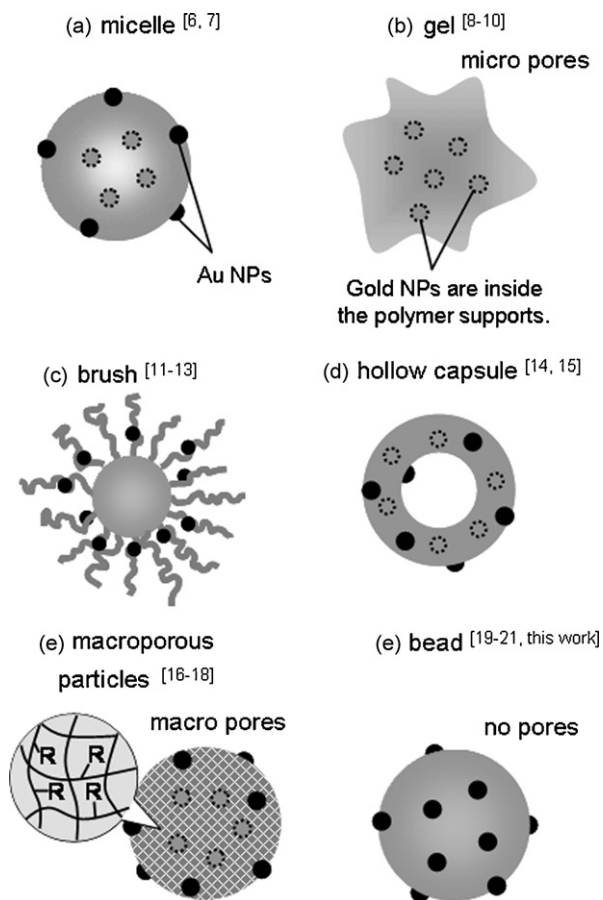
The reduction of 4-NP to 4-aminophenol (4-AP) with an excess amount of NaBH₄ has often been used as a model reaction to examine the catalytic performance of metal NPs. For example, the size-dependence of the catalytic activity of Au NPs (8–55 nm) supported on ion-exchange resins has been studied by Pal and co-workers and the rate constant for Au NPs of 20 nm was estimated to be 1.6 × 10⁻⁴ s⁻¹ at 298 K [18]. The rate constant increased with a decrease in the size of Au and was proportional to the total surface area of Au NPs. Polymer brush stabilized Au clusters with a mean diameter of about 1 nm successively improved the catalytic activity and the pseudo-first-order rate constant was estimated to be 5.1 × 10⁻¹ s⁻¹ m⁻² L per total external surface area of Au NPs normalized to the unit volume which was slightly lower than that of Pt NPs (5.6 × 10⁻¹ s⁻¹ m² L) and Pd NPs (1.1 s⁻¹ m² L) [12].

Liu et al. reported that surface functional groups influenced catalytic behavior [19,20]. The strong interaction between Au and functional groups such as thiol and pyridyl groups prevented Au NPs from aggregation and provided smaller Au NPs, which was in contrast to the weak interactions between Au and carboxylic groups. However, such strong electronic interactions weakened the catalytic activity of Au NPs. These previously published reports indicate that the catalytic performance of Au NPs on polymers would be appreciably affected by both the size of Au NPs and the kinds of polymer structures.

Recently, we have developed a direct deposition method of Au NPs onto commercially available polymer beads such as polystyrene (PS) and poly(methyl methacrylate) (PMMA) by the

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Scheme 1.

dropwise addition of NaBH_4 and by the choice of an appropriate Au precursor based on the zeta potentials of the polymer beads [21]. These Au/polymer beads showed notable catalytic activity in the decomposition of hydrogen peroxide (H_2O_2) and the oxidation of glucose with H_2O_2 . In particular, Au NPs highly dispersed on PMMA showed higher catalytic activity despite of larger size of Au than those of Au NPs supported on nitrogen-containing polymers such as polyaniline and melamine-formaldehyde resin.

In this work, we have investigated the catalytic activity of Au/PMMA in the reduction of 4-NP with NaBH_4 to produce 4-AP. The catalytic performance in terms of the rate constant and the induction period was discussed through the comparison with the Au/polymer catalysts reported so far. Our catalysts appear to exhibit the best performance.

2. Experimental

2.1. Materials

Reagent grade ethylenediamine, $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, NaBH_4 , diethyl ether, EtOH, 4-nitrophenol, 4-aminophenol were purchased and used without further purification. Poly(methyl methacrylate) beads (mean diameter of 2.6 μm , EPOSTAR-MA-1002) were supplied by Nippon Shokubai Co., Ltd.

2.2. Bis(ethylenediamine)gold(III) trichloride [$\text{Au}(\text{en})_2\text{Cl}_3$]

To a solution of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (1.0 g, 2.4 mmol) dissolved in diethyl ether (10 mL), a solution of ethylenediamine (1.0 mL, 15 mmol) in diethyl ether (5.0 mL) was slowly added. The reaction

proceeded to form yellow precipitate, which was decanted. Water (1.0 mL) was added and then the precipitate was recrystallized from EtOH (10 mL). The resulting pale yellow solid was filtered, washed with EtOH, and dried under vacuum. The product was identified by ^1H NMR (D_2O) on a JEOL JNM-EX270 instrument at 270 MHz.

2.3. Preparation of Au/PMMA

To a suspension of polymer particles (1.0 g) dispersed in distilled water (200 mL), a solution of $\text{Au}(\text{en})_2\text{Cl}_3$ (11 mg, 26 μmol , Au loading 0.5 wt%) in H_2O (54 mL) was added. The mixture was stirred at 0°C for 30 min, and then 0.01 M NaBH_4 (3.8 mL, 38 μmol , 1.5 equiv.) was slowly added in 4 min. After additional stirring at 0°C for 1 min, the mixture was filtered, washed, and dried under vacuum to yield Au/PMMA.

2.4. Characterization of catalytic materials

Transmission electron microscopy (TEM) observation was performed by using a JEOL JEM-1025 operating at 100 kV with a SIS Mega View III CCD digital camera. Samples for TEM were prepared by the solvent casting method on a Cu grid with a carbon support membrane. In order to measure the rate of reaction, UV-vis absorption spectra were recorded on a Shimadzu UV-3100PC scanning spectrophotometer by using 1-cm quartz cell at room temperature.

2.5. Catalytic tests

To a suspension of 0.5 wt% Au/PMMA (3.5 mg, Au $8.8 \times 10^{-2} \mu\text{mol}$) dispersed in H_2O (8.0 mL), 4-NP ($9.0 \times 10^{-2} \text{mM}$, 15 mL) aqueous solution was added and the mixture was adjusted to a given temperature in the range of 276–300 K. Then, freshly prepared aqueous solution of NaBH_4 (0.65 M, 3.3 mL) was added. The initial molar ratio of $\text{Au}/4\text{-NP}/\text{NaBH}_4$ was 1/15/22,500. The reaction mixture (3.0 mL) was sampled at a fixed interval, and was filtered through a 0.45 μm membrane filter. The absorption spectra of the filtrate were measured in the range of 250–500 nm. The rate constants of the reduction process were determined through measuring the change in absorbance at 400 nm as a function of time. The product was identified by ^1H NMR (D_2O) by comparison with an authentic sample.

3. Results and discussion

3.1. Preparation of Au/PMMA

We have already reported that, Au NPs could be directly deposited onto commercially available polymer beads such as PMMA and polystyrene (PS) by choosing an appropriate Au precursor, either HAuCl_4 or $\text{Au}(\text{en})_2\text{Cl}_3$, based on zeta potentials of the polymer supports without stabilizers [21]. In the case of PMMA and PS, the polymer surfaces were negatively charged in a wide pH range, and accordingly $\text{Au}(\text{en})_2\text{Cl}_3$ was used as a precursor. Unexpectedly, the dropwise addition of a reducing agent into an Au(III) aqueous solution was effective to obtain small Au NPs and to prevent them from aggregation [21]. Gold NPs supported on PMMA was prepared by the dropwise reduction and Au NPs obtained had an average diameter of 6.9 nm with a standard derivation of 5.5 nm (Fig. 1). No aggregated Au particles larger than 20 nm were observed with a TEM.

3.2. Reduction of 4-nitrophenol to 4-aminophenol

The catalytic performance of Au/PMMA for the reduction of 4-NP to 4-AP was tested as a model reaction with an excess amount

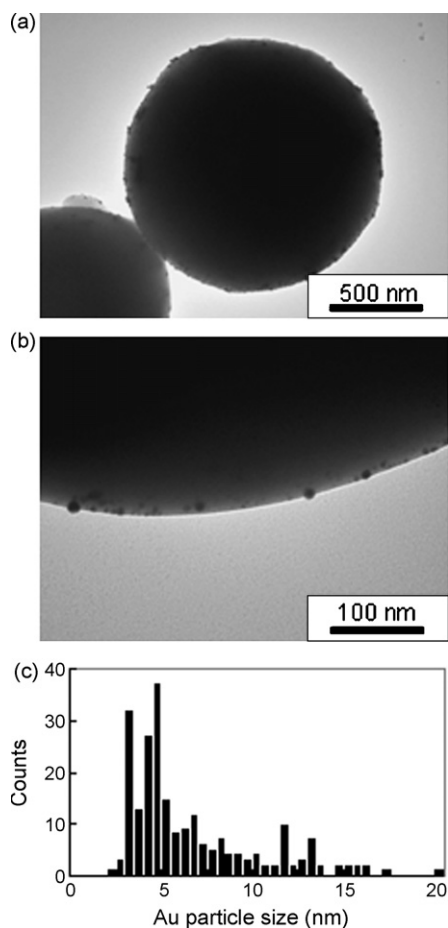


Fig. 1. TEM images of 0.5 wt% Au/PMMA (a), (b), and the size distribution of Au NPs (c).

of NaBH_4 . Accordingly, the reduction rates can be regarded as being independent of the concentration of NaBH_4 . After adding NaBH_4 into the aqueous solution of 4-NP, the color of the solution changed from light yellow to dark yellow due to the formation of 4-nitrophenolate ion. Then, the color of the 4-nitrophenolate ions faded with time after the addition of Au/PMMA. The progress of the reaction could be monitored by UV–vis spectroscopy. The characteristic peak of 4-NP at 400 nm decreased, while at 290 nm a new peak appeared which were assigned to 4-AP (Fig. 2a). The reaction was finished within 600 s at 295 K. The reaction did not proceed in this period in the absence of Au/PMMA catalyst or with PMMA beads alone. Fig. 2b shows a linear correlation between $\ln(A_t/A_0)$ (A_t : absorbance at the fixed intervals, A_0 : absorbance at the initial stage) and the reaction time at 295 K, indicating that the reaction is a pseudo-first-order. The pseudo-first-order rate constant (k) at 295 K was calculated from the slope to be $7.9 \times 10^{-3} \text{ s}^{-1}$ which was the highest value among the polymer supported Au catalysts. The reproducibility of the catalyst preparation and activity was investigated by using another batch of Au/PMMA prepared and the rate constant, k , was 7.2 s^{-1} . This value was even comparable to the highest one ($7.4 \times 10^{-3} \text{ s}^{-1}$) reported so far for poly(alginate-co-4-vinylpyridine) supported Au NPs [15].

Fig. 3 shows the Arrhenius plots of the reaction rate constants obtained in the range of 276–300 K. From the slope, the apparent activation energy (E_a) was calculated to be 38 kJ mol^{-1} . This value was relatively small but not unusual for reactions over gold catalysts. It was comparable to the values reported for CO oxi-

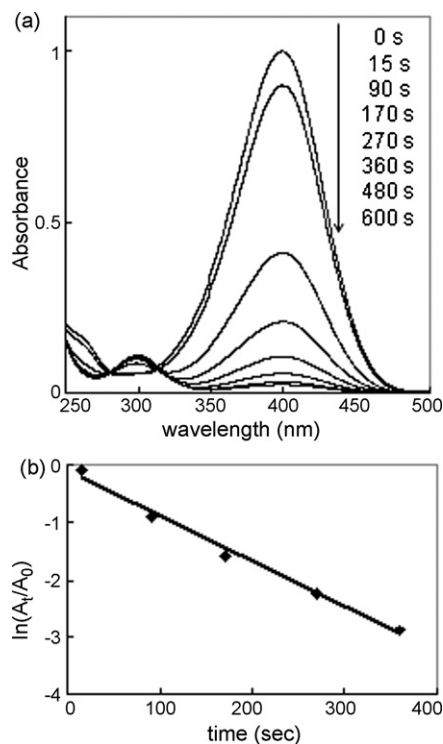


Fig. 2. UV–vis absorption spectra for the reduction of 4-NP over Au/PMMA with an excess amount of NaBH_4 in aqueous media at 295 K (a). Plot of $\ln(A_t/A_0)$ versus time for the reduction of 4-NP (b). Reaction conditions: 4-NP = $1.3 \mu\text{mol}$, NaBH_4 = 1.9 mmol , Au = $8.8 \times 10^{-2} \mu\text{mol}$, $T = 295 \text{ K}$.

dation [1,2], the reduction of 4-NP over Au/ion-exchange resin (31 kJ mol^{-1}) [18], and Au/polyelectrolyte brushes (43 kJ mol^{-1}) [12].

The previous studies on the reduction of 4-NP with Au/polymers are summarized together with our work in Table 1. Pal and his co-workers studied the dependency of the catalytic activity on the size of Au NPs dispersed on ion-exchange resin in the range of 8–55 nm and reported that the rate constant was $1.6 \times 10^{-4} \text{ s}^{-1}$ for Au NPs of 20 nm (entry 7) [18]. In the case of Au NPs with diameters of 8–20 nm, the catalytic activity increased with a decrease in the size of Au NPs, however, the reported rate constants were very low even though small Au NPs (8 nm) were used. In Table 1, the rate con-

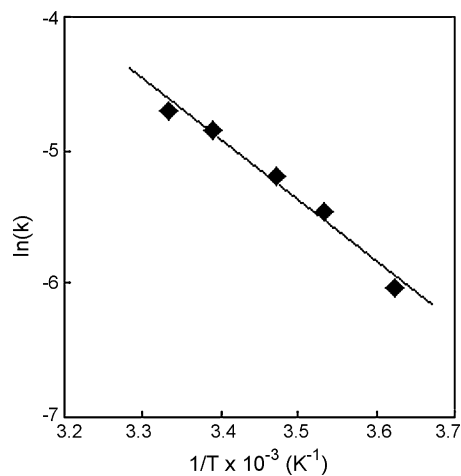


Fig. 3. Arrhenius plots of the rate constants of the reduction of 4-NP over Au/PMMA catalyst.

Table 1
Recent studies on the reduction of 4-NP over Au/polymer catalysts.

Entry	Polymer supports	Structure ^a	Size of Au ^b (nm)	T (K)	NaBH ₄ /4-NP/Au (mol/mol/mol)	Induction period	k (s ⁻¹)	Ref.
1	PNIPAM- <i>b</i> -P4VP ^c	a	3.3	298	167/5/1	No	1.5 × 10 ⁻³	7
2	Poly(VCL- <i>co</i> -AAEM) ^d	b	– ^e	293	190000/19000/1	Yes	4.0 × 10 ⁻³	10
3	PDMAEMA-PS ^f	c	4.2	298	28/0.14/1	No	3.2 × 10 ⁻³	11
4	PAEM-PS ^g	c	1.25	293	1000/1/– ^e	– ^e	5.1 × 10 ^{-1h}	12
5	PAMAM ⁱ	d	2.3	– ^e	1200/1/1	No	2.0 × 10 ⁻³	14
6	Poly(AG- <i>co</i> -VP) ^j	d	– ^e	288	51500/515/1	Yes	7.4 × 10 ⁻³	15
7	Anion-exchange resin	e	20	298	– ^e /0.27/1	No	1.6 × 10 ⁻⁴	18
8	Poly(DVB- <i>co</i> -AA) ^k	f	10	298	11000/296/1	No	6.0 × 10 ⁻³¹	19
9	PMMA ^m	f	6.9	295	22500/15/1	No	7.2–7.9 × 10 ⁻³	This work

^a Polymer structures were classified by Scheme 1.

^b Observed by TEM.

^c Poly(*N*-isopropylacrylamide)-*b*-poly(4-vinylpyridine).

^d Poly(*N*-vinylcaprolactam-*co*-acetoacetoxyethyl methacrylate).

^e No data.

^f Poly(2-(dimethylamino)ethyl methacrylate) grafted on to solid polystyrene core.

^g Poly(2-aminoethyl methacrylate) are densely grafted onto a solid polystyrene core.

^h The rate constant (s⁻¹ m⁻² L) normalized by the surface area of Au NPs and by the unit volume.

ⁱ Poly(amidoamine) based hollow capsules.

^j Poly(alginic acid-*co*-4-vinylpyridine).

^k Poly(divinylbenzene-*co*-acrylic acid).

^l The rate constant was calculated from the UV-vis absorption spectra given in Ref. [19].

^m Poly(methyl methacrylate).

stants of entry 1, 3 and 5 were lower than that of Au/PMMA in spite of the smaller size of Au NPs. Moreover, the rate constant for the polyelectrolyte-brush stabilized Au clusters (1.25 nm) was calculated to be 5.1 × 10⁻¹ s⁻¹ m² L per total external surface area of Au NPs normalized by the unit volume at 293 K (entry 4). Our rate constant per total Au, *k* (7.2–7.9 × 10⁻³ s⁻¹), was re-calculated to be 4.8–5.3 × 10⁻¹ s⁻¹ m² L per Au surface area and was comparable to that reported by Ballauff and co-workers (5.1 × 10⁻¹ s⁻¹ m² L) [12].

Polymer micelles (entry 1, structure a in Scheme 1), hydrogel (entry 2, structure b in Scheme 1), polyelectrolyte brushes (entries 3 and 4, structure c in Scheme 1), and polymer capsules (entries 5 and 6, structure d in Scheme 1) have been regarded as suitable supports to disperse small metal NPs, since the formation of metal NPs takes place mostly inside the cores, polymer networks, and brush layers but rarely on outside. They appear to have advantages over spherical polymer beads in forming small metal NPs to prevent them from aggregation. However, the above carrier systems might suffer from the diffusion limitation of substrates to the active sites of Au NPs. For instance, Au NPs (ca. 3 nm) deposited in the shell of polyalginate capsules showed similar catalytic activity to that of Au/PMMA (6.9 nm) (entry 6). However, the induction period was observed for Au/polyalginate capsules at the initial 300 s which was ascribed to polymer entanglements [15]. In addition, Au NPs deposited on microgel type poly(VCL-*co*-AAEM) also had induction periods (entry 2). The induction periods might be due to the coverage of the catalytic sites of Au NPs with polymer chains.

Esumi et al. demonstrated that polymer structures affected catalytic activity in the reduction of 4-NP by using Au NPs stabilized by poly(propyleneimine) (PPI) and poly(amidoamine) (PAMAM) dendrimers in quasi-homogeneous systems [22,23]. They proposed that there were two steps of 4-NP reduction; (i) diffusion and adsorption of 4-NP to the Au surfaces and (ii) electron transfer mediated by Au surfaces from BH₄⁻ to 4-NP. Poly(propyleneimine) had smaller hydrodynamic diameters than PAMAM, leading to the easier diffusion of 4-NP to Au surfaces and exhibited higher catalytic activity than that of PAMAM. As a consequence, they concluded that the first diffusion step determined the rate of reduction.

In heterogeneous systems, induction periods might be interpreted as a slow diffusion of substrates to the Au surfaces dispersed on polymers. On the other hand, Au NPs stabilized by PAMAM

hollow capsules does not show induction periods in spite of the coverage of Au NPs with polymers (entry 5). With a relatively higher molar ratio of Au to 4-NP, the diffusion of the substrate would not influence reaction rate. When the ratio of Au to the substrate decreased (entries 2 and 6), the diffusion rate of the substrate would be a ruling factor to determine the reaction rate. In contrast, induction period was not observed for Au/polymer beads with surface modification by –COOH groups (entry 8). This catalyst exhibited higher catalytic activity than those of other catalysts even though Au NPs were relatively larger (10 nm) [19]. Gold NPs dispersed on PMMA had no induction period and the reaction started immediately.

The above results indicate that the structures of polymer supports play an important role in determining the catalytic activities of metal NPs and that the polymer beads commercially available are one of the most suitable supports for metal NPs catalysts. Yang and co-workers reported that the catalytic activity of Au/polymers depended on not only the size of Au but also on the moderate interaction between Au NPs and polymer supports [19,20]. When the interaction between Au and polymer backbones including sulfur or nitrogen atoms was strong, the size of Au became smaller while the catalytic activity was depressed. In the case of Au/PMMA, the moderate interaction between Au and oxygen atoms in PMMA backbones might efficiently work in the catalytic reaction. These results suggest that the catalytic performance of Au NPs depends on both the structures and the surface functional groups of polymer supports.

The catalyst could be recycled, however, the catalytic activity decreased to almost half after the second cycle and to one third after the third cycle due to the aggregation of Au NPs. However, leaching of Au NPs into the reaction solution did not occur even after the third cycle.

4. Conclusions

Gold NPs could be directly deposited on PMMA beads without surface modification from the aqueous solution of Au(en)₂Cl₃. In opposite to presumption, the dropwise addition of NaBH₄ in aqueous media led to the formation of Au NPs exclusively on the surface of PMMA without producing Au NPs in the liquid phase. The mean

diameter of Au NPs was estimated at 6.9 nm with a standard deviation of 5.5 nm through TEM observation. Unlike to the case of rapid addition of NaBH₄, no aggregated particles larger than 20 nm were observed.

The catalytic activity was examined by the reduction of 4-NP with an excess amount of NaBH₄. The pseudo-first-order rate constant and the apparent activation energy were calculated to be 7.2–7.9 × 10⁻³ s⁻¹ at 295 K and 38 kJ mol⁻¹, respectively. This value of the rate constant was as large as the highest one reported for Au/polymers so far.

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