



Supported nano-sized gold catalysts for selective reduction of 4,4'-dinitrostilbene-2,2'-disulfonic acid using different reductants

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ABSTRACT

Gold nanoparticles supported on three metal oxides, TiO₂, Al₂O₃ and Fe₂O₃, were prepared by a modified precipitation-deposition method using urea as an additive. These catalysts were tested in chemoselective reduction of 4,4'-dinitrostilbene-2,2'-disulfonic acid to 4,4'-diaminostilbene-2,2'-disulfonic acid. Three reagents, hydrogen, carbon monoxide, and sodium formate, were employed as reductants. It was found that >94% of the nitrostilbene was transformed into the aminostilbene without the reduction of olefinic group. In addition, these catalysts exhibited stable performance after regeneration by calcination at 400 °C for 5 h. This clean approach provides a promising application for synthesis of amino substituted stilbene sulfonic acid on an industrial scale.

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1. Introduction

4,4'-Diaminostilbene-2,2'-disulfonic acid (DSD), a typical amino substituted stilbene sulfonic acid, is an important industrial intermediate used widely in production of direct dyes, fluorescent brighteners and mothproofing agents [1]. Generally, it is produced from the reduction of 4,4'-dinitrostilbene-2,2'-disulfonic acid (DNS) with stoichiometric reducing agents, such as sodium hydrosulfite [2]. In addition, metals such as either iron, tin or zinc in ammonium hydroxide have been successfully applied in the reduction with high yields of ~98% [3]. However, these reducing agents are not environmentally sustainable, and generate significant amounts of solid wastes which are difficult to be disposed of [4]. Catalytic hydrogenation is a green and effective way, but commercial catalysts (Raney Ni) can also result in the reduction of olefinic and nitro groups [5]. A Pd supported on C (Pd/C) has shown high selectivity, but large quantities of additives are required for the reaction [6]. Separation of the additive from products increases the

cost of industrial production. Therefore, development of a facile and environmentally friendly chemoselective process has attracted substantial interest.

Gold nanoparticles supported on metal oxides have been used as catalysts for a number of reactions, including addition of multiple C–C bonds, cyclization reactions, rearrangements, C–C coupling reactions, oxidation reactions, and hydrogenations [7]. Selective reduction of nitro compounds in the presence of reducible functions is more challenging and has attracted tremendous interest. Corma et al. have shown that gold nanoparticles supported on TiO₂ and Fe₂O₃ can successfully catalyze selective reduction of nitro aromatic compounds containing olefinic bonds with H₂ [8]. Cao et al. used CO/H₂O as a hydrogen source and Au/TiO₂ for the selective reduction of nitro aromatic compounds containing olefinic bonds and achieved high chemoselectivity [9]. Formate is another hydrogen carrier, and ammonium formate has been used in the reduction of nitro compounds by copper nanoparticles. However, the selectivity for nitro aromatic compounds containing olefinic bonds was low at only ~57% [10].

In this study, we prepared a series of Au NPs-based catalysts using a deposition–precipitation method [11]. These catalysts were evaluated in the chemoselective reduction of DNS to DSD. H₂, CO and sodium formate were used as reductants for a comparative study. Excellent yields and high stability were achieved on these catalysts.

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2. Experimental

2.1. Materials and reagents

P25 titanium dioxide (ca. 80% anatase, 20% rutile; BET area ca. $50 \text{ m}^2 \text{ g}^{-1}$) was obtained from Degussa Co. (Germany). $\alpha\text{-Fe}_2\text{O}_3$ (30 nm, BET area $\geq 50 \text{ m}^2 \text{ g}^{-1}$), and $\gamma\text{-Al}_2\text{O}_3$ (10 nm, BET area $\leq 200 \text{ m}^2 \text{ g}^{-1}$) were obtained from Aladdin (China). 4,4'-Dinitrostilbene-2,2'-disulfonic acid (DNS), 4,4'-diaminostilbene-2,2'-disulfonic acid (DSD), 4,4'-diaminobenzyl-2,2'-disulfonic acid (DAD) and Raney Ni were provided by Huayu Chemical Company (Cangzhou, China). All chemicals and solvents (Merck) were either analytical or chromatography grade and were used without further purification.

2.2. Catalyst preparation

The catalysts were prepared using the deposition–precipitation method with urea (DP urea) [11,12]. Typically, the nano-sized metal oxides either TiO_2 , Al_2O_3 or Fe_2O_3 (1.0 g) was added to an aqueous solution of HAuCl_4 (100 mL, $0.9 \times 10^{-3} \text{ M}$) with urea (0.42 M). The suspension was heated to 85°C and kept for 6 h with vigorously stirring. Then the suspension was separated from the precursor solution by centrifugation (15000 rpm for 10 min). The obtained solids were washed three times with water to remove the residual Cl^- , and dried under vacuum at 100°C for 3 h. After that, they were calcined at 300°C for 4 h and reduced for 2 h at 250°C in a flow of 5% H_2/N_2 .

2.3. Catalyst characterization

Catalysts were examined by transmission electron microscopy (TEM) with a JEOL2010F microscope. The histograms of particle size of Au NPs were obtained from the measurement of ~ 300 particles. The size limit for the detection of the gold particle is 1 nm. The average particle diameter \bar{d} was calculated from the formula: $\bar{d} = \sum n_i d_i / \sum n_i$, where n_i is the number of particles of diameter d_i . The Au weight loading was determined by an inductively coupled plasma (ICP) technique, and the chemical state of the Au species on the catalysts was determined by X-ray Photoelectron Spectroscopy (XPS).

2.4. Catalytic activity tests

The hydrogenation of DNS was performed in a 50 mL autoclave. For each reaction, water (10 mL), DNS (0.05 g) were charged into the autoclave together with the catalyst (0.005 g). Before reaction, the reactor was flushed five times with hydrogen at 5 bar to remove air. Then the autoclave was heated to 120°C and pressurized at 5 bar. After 5 h, the products were analyzed by a HPLC. The reduction process was also performed by CO at 100°C . In addition,

HCOONa as a reductant was also used for the reduction of DNS at 130°C with HCOONa (0.3 g). In those tests, the reactor was purged with N_2 at 5 bar.

Sample analysis was carried out on a Finnigan Surveyor HPLC integrated with quaternary gradient pumps, photodiode array detector, auto injector, degasser and system controller (Thermo-Fisher Scientific, USA). A reversed-phase Hypersil ODS-2 C18 column ($250 \times 4.6 \text{ mm i.d.}$, $5 \mu\text{m}$ particle size, Thermo Scientific, US) was used for separation. HPLC conditions: 5:95 acetonitrile:water–0.01 M ammonium acetate, 254 nm (flow: 1 mL min^{-1}).

2.5. Catalyst stability

The catalyst stability of Au/TiO_2 was tested in the reduction of DNS with the three reductants. Firstly the catalyst (0.02 g) was used in a 40 mL reaction (fresh catalyst). After the first run reaction, the catalyst was recovered, filtered and washed three times with distilled water. Then, they were dried under vacuum at 100°C for 2 h and calcined at 400°C for 5 h. Secondly recycled catalyst (0.015 g) was tested in a 30 mL solution for second run reaction. After recovered, recycled catalyst (0.01 g) was tested in a 20 mL solution for the third run reaction.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the TEM images of the three catalysts. Al_2O_3 is non-reducible and it is different from other two supports. The diameters of the Au NPs on these supports had some differences. Size distributions of Au NPs on the catalysts are presented in Fig. 2. The \bar{d} of Au NPs on Al_2O_3 was 3.8 nm and most particles were in size of 2–4 nm. Other two catalysts had similar \bar{d} (Au/TiO_2 4.7 nm, $\text{Au/Fe}_2\text{O}_3$ 4.6 nm), and the Au particles ranged from 4 to 6 nm. Due to the reduction by H_2/Ar , the supported gold species are metallic states determined by XPS (Fig. 3). In addition, the gold loadings on these catalysts were found to be $\sim 1.5\%$ by Inductively Coupled Plasma (ICP).

3.2. Reduction of DNS to DSD

3.2.1. Hydrogen as a reductant

Hydrogen is an ideal and powerful reductant with water as a product. Hydrogen is always used to reduce nitro compounds with satisfactory yields on commercial catalysts. However, other functional groups can also be reduced, resulting in low selectivity to the reduction of nitro groups. For the reduction of DNS, the olefinic groups will be simultaneously reduced using commercial catalysts [13]. Corma et al. found that gold nanoparticles ($3.8 \pm 1.5 \text{ nm}$) supported on TiO_2 or Fe_2O_3 can produce high selectivities towards hydrogenation of 3-nitrostyrene [8]. Herein, three supported gold

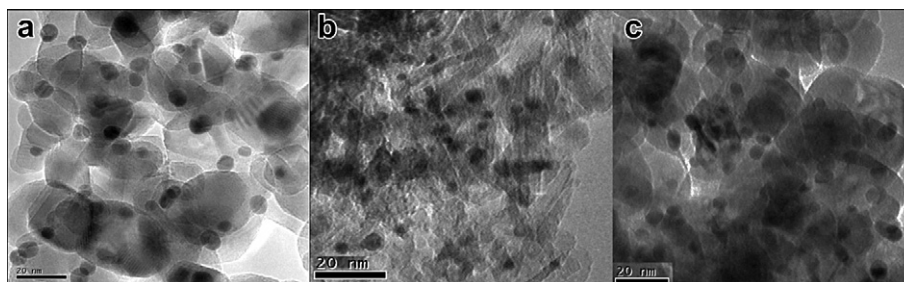


Fig. 1. TEM images of Au/TiO_2 (a), $\text{Au}/\gamma\text{-Al}_2\text{O}_3$ (b), and $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$ (c).

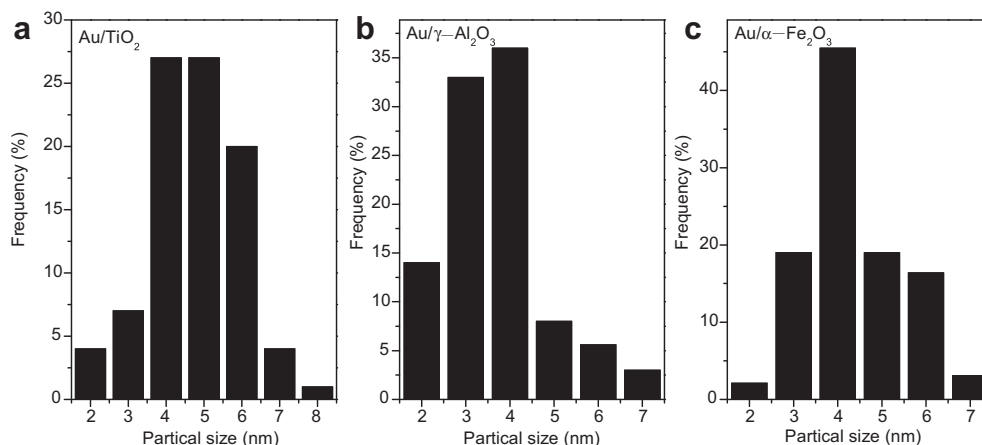


Fig. 2. Size distributions of Au NPs in (a) Au/TiO₂, (b) Au/γ-Al₂O₃, and (c) Au/α-Fe₂O₃.

nanoparticles were used in the reduction of DNS, and the results are shown in Table 1. A commercial catalyst-Raney Ni was also evaluated in the reduction of DNS for a comparison. It was found that the Raney Ni did not show any selectivity in the reduction of DNS to DSD and that the product was only 4,4'-diaminobenzyl-2,2'-disulfonic acid (DAD) (Fig. 4). For supported Au NPs, Au/Al₂O₃ was the most efficient catalyst with selectivity to DSD of 98.7%. Au/TiO₂ and Au/Fe₂O₃ were also efficient with selectivities to DSD at more than 90%. The determination of the reduction products was performed by HPLC-ESI-MS, and the identification was further confirmed by comparing their retention times with those of high purity standards (Fig. 5).

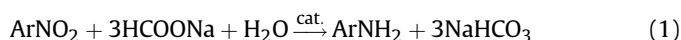
3.2.2. CO as a reductant

CO is a very attractive industrial reductant due to its low-cost, accessibility, and wide range of applications in the chemical industry [9]. The reduction of nitro groups using CO/H₂O has been known for many years. Herein, the reduction of DNS by CO/H₂O catalyzed by supported Au NPs was also investigated and the results are listed in Table 2. All three Au NPs containing catalysts could achieve selectivities of more than 99%, which are higher than those in H₂ reduction on the same catalysts. The results indicated that selective reduction of the nitro group over olefinic groups can be

realized more easily with CO/H₂O on gold nanoparticles [9,14]. It was proposed that the nitro groups could be reduced by the hydrogen gas generated from the low-temperature water–gas shift (WGS) reaction. However, it was found that supported gold for low-temperature water–gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$) was effective in the temperature range of 150–250 °C, which is higher than the reduction temperature of DNS (100 °C) [14–16]. In addition, a control experiment with DAD <1% also indicated the WGS reaction could not occur under the current experimental conditions. Commercial Raney Ni has no selectivity towards DSD with CO/H₂O, the same result as that for hydrogen as the reductant.

3.2.3. Sodium formate as a reductant

Sodium formate is an important hydrogen source. Sodium formate is mild in nature and conveniently available, and it has been proved effective in hydrogenation of nitro compounds in following reaction equation:



It was found that the reduction proceeded in the form of direct hydrogen transfer between the sodium formate and the nitro acceptor rather than a dehydrogenation-hydrogenation sequence [17]. Therefore, the selectivities during the catalytic reduction of DNS with sodium formate should be different from hydrogen reduction. The results of DNS reduction with HCOONa on supported Au NPs are listed in Table 3. All three metal oxide supported Au catalysts can provide selectivities of >99%, similar to CO/H₂O. The results indicated that reduction by HCOONa on gold catalysts is relatively mild.

It should be noted that formic acid and ammonium formate might also be effective, however, formic acid has high corrosive effect and ammonium formate can be decomposed to hydrogen cyanide (HCN) at a relative high temperature [17]. Commercial Raney Ni was also investigated with HCOONa as a reductant, and no DSD production could be observed during the reduction of DNS.

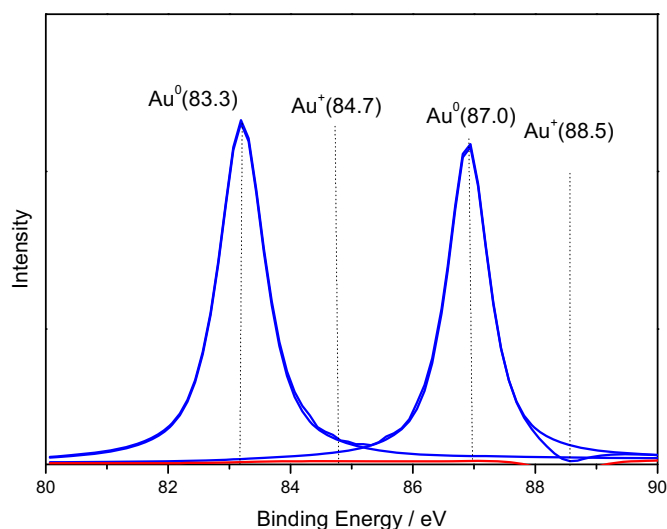


Fig. 3. XPS spectra (Au 4f) of Au/TiO₂ catalyst after reduction with H₂/Ar (the three catalysts have very similar results, so we take the spectra of Au/TiO₂ as an example).

Table 1
Reduction of DNS with H₂ by varies catalysts.

Catalysts – x ^a	T/°C	Au loading (wt.%)	Conv./%	Sel.(DSD)/%	Sel.(DAD)/%
Au/TiO ₂ – 4.7	120	1.7	100	97.8	<2.0
Au/Fe ₂ O ₃ – 4.6	120	1.6	100	94.6	3.6
Au/Al ₂ O ₃ – 3.8	120	1.5	100	98.7	1.2
Raney Ni	120	1.6	100	0	>99.0

^a The \bar{d} of Au NPs supported on each metal oxides.

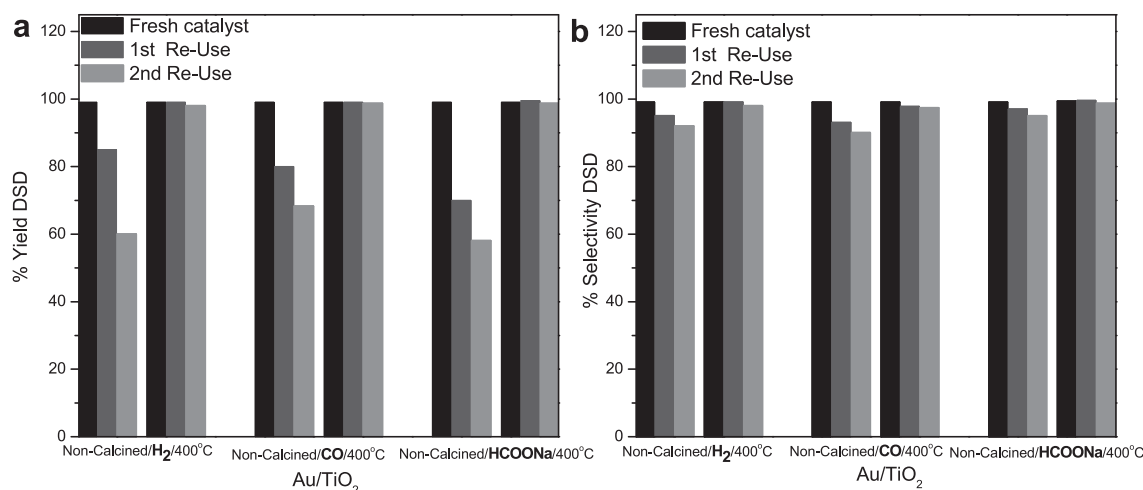


Fig. 6. Stability of the Au/TiO₂ catalyst for the DNS hydrogenation after recycling and regeneration of the catalyst. While activity needs an appropriate thermal treatment to recover the original level, no loss of conversion was observed for a third recycle (a), keeping high selectivity values (b).

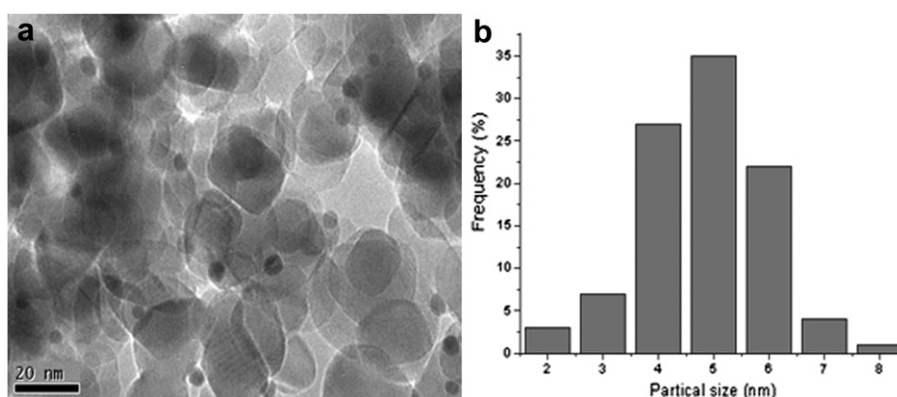


Fig. 7. The TEM image (a) and size distributions of Au NPs (b) of Au/TiO₂ (after the 2nd re-use bath); the average diameter (\bar{d}) of the Au NPs is ~ 4.8 nm.

olefinic group [18]. The lower selectivity to DSD by hydrogen suggested that is probably due to similar intrinsic rate for reduction of nitro and olefinic groups occurred in H₂ reduction.

3.3. Catalyst stability

TiO₂-P25 is a commercially available support, so TiO₂ supported gold NPs (Au/TiO₂) can be produced on an industrial scale. The catalyst stability was thus evaluated in Au/TiO₂ system for the hydrogenation of DNS. The results are shown in Fig. 6. A decrease in DSD yield was observed (Fig. 6a) in 5 h reaction for non-calcined Au/TiO₂. While for the catalyst treated at 400 °C for 5 h, little decrease in yield could be observed for all three reductants. This indicated that some active sites of the catalyst might be poisoned by the organic molecules, and the activity can be recovered by calcined at 400 °C [8]. On the other hand, Fig. 6b showed that no changes in selectivity to DSD were observed for the non-calcined and 400 °C-treated catalysts. For the Au/TiO₂ with 400 °C treatment, more than 98% selectivity could be obtained after three run regenerations.

The selectivity to the nitro and olefinic group reduction was related to the size of supported Au NPs. The change of Au NPs diameters was also investigated in the H₂ reduction. It was found that the average diameter of Au NPs slightly increased (from 4.7 to 4.8 nm) after two calcinations (Fig. 7). Therefore, the selectivity can

be maintained at a high level for a third recycle. However, some active sites of the used catalyst might be poisoned by the organic molecules, and this could lead to the decrease of the yield. The calcination process at 400 °C can help restore the activity of the catalysts and maintain high yield [8].

4. Conclusion

Gold nanoparticles supported on three metal oxides were prepared and evaluated in the chemoselective reduction of DNS to DSD using H₂, CO and HCOONa as reductants. Compared with the commercial Raney Ni catalyst under the same conditions, excellent selectivity (>94%) was obtained on the three Au NPs containing catalysts. In addition, the catalysts maintained stability in three-run tests after regeneration by calcination at 400 °C for 5 h.

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