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Research Note

Preparation and application of highly dispersed gold nanoparticles supported on silica for catalytic hydrogenation of aromatic nitro compounds

Yangying Chen [a], Jieshan Qiu [a,*], Xinkui Wang [b], Jinghai Xiu [a]

[a] *State Key Lab of Fine Chemicals, Carbon Research Laboratory, Center for Nano Materials and Science, School of Chemical Engineering, Dalian University of Technology, 158 Zhongshan Road, Dalian 116012, China*

[b] *Department of Chemistry, School of Chemical Engineering, Dalian University of Technology, 2 Lingong Road, Dalian 116024, China*

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Abstract

Highly dispersed gold nanoparticles supported on silica were successfully prepared by a novel and simple in situ reduction technique that makes use of the 3-glycidoxypropyl group, $–CH_2CH_2CH_2OCH_2CHCH_2O$, on modified silica as reductants. In the new procedure, the organic groups are introduced onto silica via a sol–gel process of tetraethyl orthosilicate (TEOS) and 3-glycidoxypropyl-trimethoxysilane (GPTMS) assisted by ammonia water, with gold nanoparticles uniformly in the range 7.0–9.0 nm. The silica-supported gold nanoparticles were evaluated for the liquid-phase catalyze reduction of various aromatic nitro compounds by molecular hydrogen, and their corresponding amines with high chemoselectivity were obtained under the reaction conditions of 140 °C, 4.0 MPa, and 2.5–5 h, particularly for chloronitrobenzenes, the undesirable dechlorination reactions could be avoided completely.

Keywords: Silica-supported gold nanoparticles; In situ reduction; Aromatic nitro compounds; Hydrogenation

1. Introduction

Gold was less well studied in the catalysis field because it was considered chemically inert and uninteresting for many years. However, ever since Hutchings' discovery that gold is the catalyst of choice for acetylene hydrochlorination [1] and Haruta's discovery that gold nanoparticles supported on a certain kind of supports are very active for CO oxidation at low temperatures [2,3], the study of the catalytic properties of gold nanoparticles has been booming [4,5]. One major reason for neglecting or ignoring gold catalysis for many years is that in most cases, supported gold particles prepared by the traditional incipient-wetness impregnation method exceed a critical nanosize range outside of which the gold catalysts are not active. To overcome this problem, deposition-precipitation [6] and coprecipitation [7] methods have been widely adopted and have proven effective for many oxide supports; however, the preparation of silica-supported gold nanoparticles with high activity remains a challenge because of the limitation of the isoelectric point of silica. To make highly active gold catalysts, sol–gel [8,9] and microemulsion [10] methods have been developed; however, the dispersion and size distribution of gold nanoparticles on silica are far from satisfactory. Recently, a chemical grafting and reduction process was reported in which $(CH_3O)_3Si(CH_2)_2NHCH_2CH_2NH_2$ (TPED), $(CH_3O)_3Si(CH_2)_3NH_2$ (APS), or $(CH_3O)_3Si(CH_2)_3N(CH_3)_3Cl$ (TPTAC) with basic NH_2 and R_4N^+ moieties were used to react with Si–OH groups on the internal pore surfaces of mesoporous silica, after which $HAuCl_4$ was introduced via a neutralization reaction, followed by an H_2 reduction step to get the active gold nanocatalysts [11,12]. This process has proven effective to some degree, but has one disadvantage in that two separate steps are involved for the introduction and reduction of $HAuCl_4$, which is tedious and usually results in poor reproducibility. Here we present a novel and simple process in which the introduction and reduction of $HAuCl_4$ is completed in a single step after reductive organic groups are introduced to silica via a sol–gel process. With this new approach,

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[*] Corresponding author. Fax: +86 411 88993991.
E-mail address: jqiu@dlut.edu.cn (J. Qiu).

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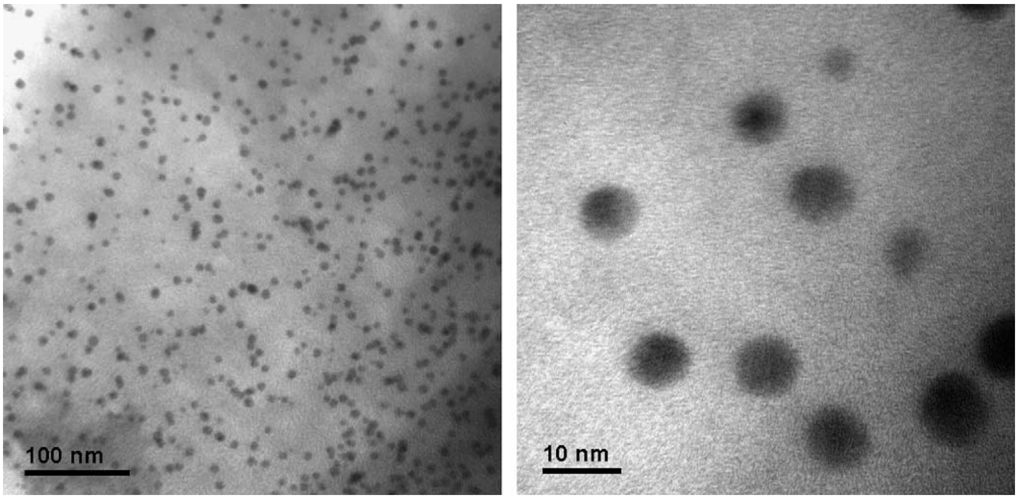


Fig. 1. TEM pictures of silica-supported gold nanoparticles.

the homogeneity and the amount of organic groups on silica can be easily tuned, resulting in high dispersion of gold nanoparticles. In the past decade, supported gold nanoparticles have been applied to catalyze many different types of reactions. However, the catalytic reduction of nitro groups over gold nanocatalysts has not been reported before. Herein we report the catalytic property of gold nanoparticles for the hydrogenation of aromatic nitro compounds over Au/SiO$_2$ catalysts.

2. Experimental

The silica-supported gold nanoparticles (Au/SiO$_2$) were prepared as follows. First, 3.0 mL of 3-glycidoxypropyltrimethoxysilane (GPTMS, 97%, Acros) and 3.0 mL of tetraethoxylsilicate (TEOS, AR, Xilong Chemical) were added into a mixture of 10 mL of aqueous solution of ammonia (27%) and 20 mL of deionized water. After stirring at room temperature for 24 h, the solution was evaporated at 80 °C. The solid thus obtained was further dried in air at 120 °C for 12 h, which yielded a solid white powder (denoted as CH$_2$O–SiO$_2$). Then 1.0 g of CH$_2$O–SiO$_2$ was suspended in 2 mL of HAuCl$_4$ solution (1 g of HAuCl$_4$ in 100 mL of water) and 30 mL of deionized water. After stirring for 2 h at 100 °C, the mixture was filtered and washed with an excess amount of deionized water until no chlorine ions were detected in the filtrate. The solid was dried in air at 120 °C for 12 h, and about 1.0 g of brown powder of the Au/SiO$_2$ catalyst was obtained. The loading of gold was found to be ca. 1.0 wt%.

The TEM images of the catalysts were obtained with a Philips Tecnai G^2 20 TEM equipped with a CCD camera operated at 180 kV. Powder XRD patterns were recorded on a Rigaku D/MAX 2400 diffractometer equipped with a Cu$K\alpha$ X-ray source operating at 40 kV and 50 mA. XPS analysis was performed using a Kratos HSi spectrometer; the spectra were acquired using a monochromatic Al $K\alpha$ radiation source operated at 300 W and at pressures below 7×10^{-7} Pa. The binding energy scale was referenced to C1 at 285 eV. The UV–vis spectra were recorded on an HP 8453 instrument. The FTIR spectra were measured on a Nicolet Impact 410 FTIR spectrometer.

The catalytic hydrogenation of various aromatic nitro compounds were carried out in a Parr autoclave under the following reaction conditions: 120–140 °C, 2.0–4.0 MPa, 0.1 g of catalyst, 0.5 g of substrates, and 50 mL of ethanol. The products were analyzed by gas chromatography (Agilent 6890N) equipped with an SE-54 capillary column and a flame ionization detector.

3. Results and discussion

3.1. Synthesis and characterization of Au/SiO$_2$

With a novel in situ reduction process developed in our lab, the organic group-functionalized silica was synthesized via a sol–gel process of TEOS and GPTMS, and the organic group subsequently reduced HAuCl$_4$ in water to metal gold on silica. The dispersion of gold nanoparticles could be tuned by changing the ratio of TEOS and GPTMS. Fig. 1 shows the typical TEM images of the Au/SiO$_2$ catalyst; clearly, the gold nanoparticles in spherical form had an average size of 7.0–9.0 nm and were highly dispersed on the silica support. The XRD pattern of the Au/SiO$_2$ catalyst showed mainly the peak of amorphous silica; the presence of a small and weak peak of Au(111) implies that gold particles were in the nanometer size domain. XPS for Au/SiO$_2$ showed binding energies of 83.7 eV for the Au 4f$_{7/2}$ electron and 87.3 eV for the Au 4f$_{5/2}$ electron; these binding energies indicate exclusively Au(0) particles with no trace of higher oxidized species, which should be detectable at concentrations in the percentage range with the equipment used. A high concentration of oxidized Au sites can thus be excluded, although a few sites below the detection limit of our XPS system may be present. Moreover, a strong interaction between gold nanoparticles and support can be proposed, because no gold nanoparticles can attach to the support without such interaction, and the interaction provides the Au/SiO$_2$ with high stability for catalysis.

Compared with that of the CH$_2$O–SiO$_2$ (Fig. 2b), the UV–vis spectrum of the Au/SiO$_2$ catalyst (Fig. 2c) had one more peak at

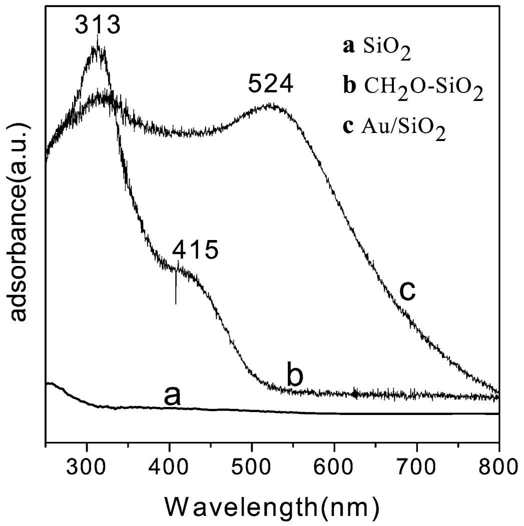


Fig. 2. UV–vis spectra of SiO_2, $CH_2O–SiO_2$ and Au/SiO_2.

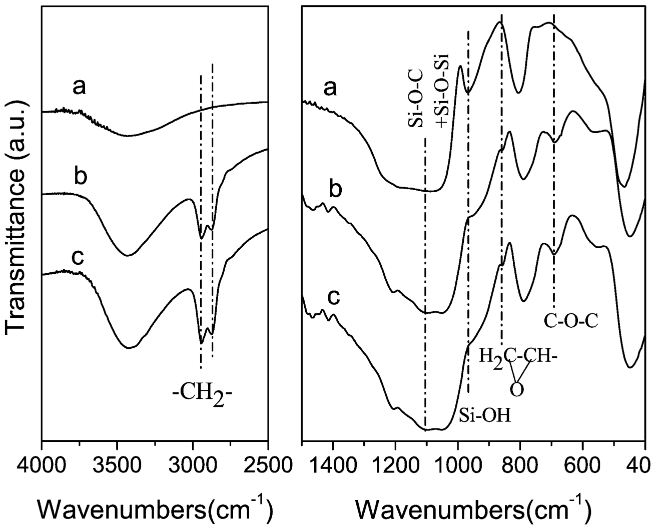


Fig. 3. FT-IR spectra of SiO_2 (a), $CH_2O–SiO_2$ (b), and Au/SiO_2 (c).

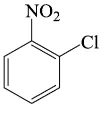
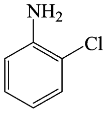
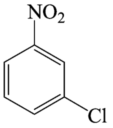
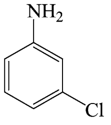
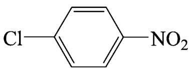
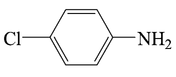
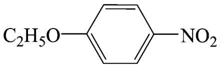
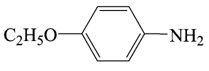
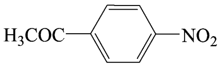
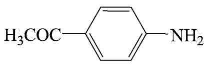
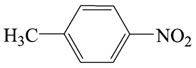
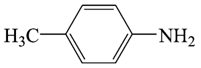
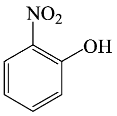
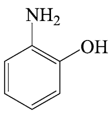
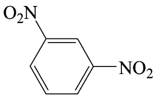
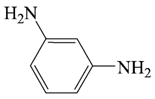
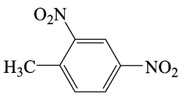
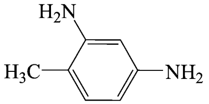
around 524 nm attributed to metallic gold [32], confirming that the gold ions were reduced in the preparation step. The peaks at 313 and 415 nm were due to the presence of organic groups, because no such peaks were present for pure silica (Fig. 2a). The peaks at 2946, 2870, 860, and 692 cm^{-1} appeared in the FTIR spectrum of $CH_2O–SiO_2$ (Fig. 3b), in contrast to that of pure SiO_2 (Fig. 3a); these peaks can be assigned to $–CH_2–$, $CH_2CHO–$, and C–O–C groups [13], indicating the presence of a glycidoxypropyl group, $–CH_2CH_2CH_2OCH_2CHCH_2O$, in $CH_2O–SiO_2$. So it is the glycidoxypropyl group on the silica that reduced gold ions to metallic gold, because no gold nanoparticles could be found on naked silica following the same procedure. This conclusion is also confirmed by the fact that 3-glycidoxypropyl-trimethoxysilane can directly reduce $HAuCl_4$ at low temperatures, whereas methanol cannot. As for the spectrum of Au/SiO_2 (Fig. 3c), no difference from that of $CH_2O–SiO_2$ was present. There are two possible reasons for these findings: (1) Only part of the glycidoxypropyl group reacted with $HAuCl_4$ or (2) FTIR was not sensitive enough to distinguish the glycidoxypropyl group and its product from reaction with $HAuCl_4$. As for the detailed reaction mechanism between $CH_2O–SiO_2$ and $HAuCl_4$, no suitable characterization techniques currently exist, and further study is under consideration. One further feature of Au/SiO_2 is that the presence of organic groups can enhance its hydrophobicity for subsequent catalytic reaction in organic solvents.

3.2. Catalytic activity of Au/SiO_2 for hydrogenation of aromatic nitro compounds

The catalytic reduction of nitrobenzene was used to probe the activity of Au/SiO_2. For the Au/SiO_2 catalysts prepared by traditional impregnation methods, the conversion of nitrobenzene did not exceed 5% at 120 °C and 2.0 MPa. However, in the case of Au/SiO_2 catalysts prepared by the in situ reduction method, the conversion of nitrobenzene could reach 26% under the same reaction conditions. On further increasing the reaction temperature to 140 °C and the pressure to 4.0 MPa, the conversion of the substrate increased significantly to reach 100%; at the same time, no other byproducts due to the hydrogenation of aromatic ring were detected except aniline. The recycling experiments proved that the Au/SiO_2 catalyst was quite stable after three reuses. In addition, when $HAuCl_4$ and $CH_2O–SiO_2$ were used as catalysts, no reduction products were detected, yielding unambiguous evidence that it is the gold nanoparticles that function as real active sites.

The catalytic reduction of various aromatic nitro compounds over Au/SiO_2 was also examined (Table 1). For the hydrogenation of chlorine-containing nitro-aromatics, the reduction of nitro groups without dechlorination can be reached using some milder reducing agents [14–16]; however, the process of catalytic reduction by hydrogen has been pursued for environmental reasons [17,18]. In our case, the conversion of substrates and selectivity of products could reach 100%, and no dechlorination reactions occurred (entries 1–3), even though the reaction pressure of hydrogen is higher than that of other reported catalysts [17,18], with which, however, dechlorination side reactions cannot be avoided in most cases. For other aromatic nitro compounds with electron-donating groups, the efficient selective hydrogenation of nitro groups was also observed (entries 4–7). However, for compounds with two nitro groups, after a longer reaction time, the products with both reduced nitro groups were obtained with a selectivity of 65.4–70.5%, and the intermediate products with only one reduced nitro group were the main byproducts (entries 8 and 9). Although the reaction conditions adopted in the present study were relatively harsh for the reduction of the nitroarenes compared with those well-documented catalysts, such as Pd-based catalysts, that are effective under milder conditions, here for the first time the gold-based catalysts are reported to do the job; moreover, they show higher chemoselectivity than other catalysts, which helps shed new light on the catalytic applications of gold nanocatalysts.

Table 1
Catalytic hydrogenation of various aromatic nitro compounds over Au/SiO_2[a]

Entry	Substrate	Product	Time (h)	Conv. (%)	Sel. (%)
1			3	100	100
2			3	100	100
3			3	100	100
4			2.5	100	100
5			3	100	95.0
6			2.5	100	100
7			2.5	100	100
8			5	100	65.4
9			4.5	100	70.5

[a] Reaction conditions: 0.1 g catalyst, 0.5 g substrate, 50 mL ethanol, 140 °C, 4.0 MPa.

4. Conclusion

In this paper we have presented a novel and simple in situ reduction method for preparing highly dispersed and uniform gold nanoparticles on silica. The organic siliane that functions as a reductant in the novel approach can be introduced onto silica by a sol–gel process or by a modification of the silica surface, and the introduction and reduction of gold ions can be completed in a single step. The as-prepared Au/SiO_2 catalysts show good catalytic properties for reducing various aromatic nitro compounds to their corresponding amines by hydrogen, highlighting the great potential of silica-supported gold nanoparticles to act as effective catalysts for the selective hydrogenation of aromatic nitro compounds.

Acknowledgments

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