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Gold on thiol-functionalized magnetic mesoporous silica sphere catalyst for the aerobic oxidation of olefins

Yiyun Fang, Yuanzhe Chen, Xinzhe Li, Xingchun Zhou, Jing Li, Weijie Tang,

Jingwei Huang, Jun Jin* and Jiantai Ma*

The Key Laboratory of Catalytic engineering of Gansu Province, College of Chemistry and Chemical Engineering Lanzhou University, Lanzhou 730000, P. R.

China.

Abstract:

We have synthesized a new catalyst based on thiol-functionalized silica-coated magnetic mesoporous nanocrystals as support and Au nanoparticles as active sites through a facile and environment-friendly approach and characterized by transmission electron microscopy (TEM), N₂ adsorption-desorption, elemental analysis and inductive coupled plasma atomic emission spectrometer (ICP-AES), X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and vibrating sample magnetomety (VSM). The synthesized catalyst exhibited high catalytic activity in the oxidations of cyclohexene and styrene by molecular oxygen at atmospheric pressure. Furthermore, this catalyst had an excellent recyclability, evidenced by being extensively reused for five times without any substantial loss of activity, which was mainly attributed to the enough strong combination between the Au nanoparticles and thiol groups onto the surface of support. Meanwhile, the catalyst could be easily seperated from the reaction solution by applying an external magnetic field.

Key words: thiol-functionalized magnetite mesoporous silica; Au nanoparticles;

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recyclable catalyst; oxidation of cyclohexene and styrene.

*Corresponding author:

E-mail: jinjun@lzu.edu.cn (J.Jin); majiantai@lzu.edu.cn (J. Ma);

Tel.: +86-931-8912577;

Fax: +86-931-8912582

1. Introduction

It is well known that the oxidation of olefins is of significant importance in modern chemical transformations [1-4]. Traditionally, the organic or inorganic oxidants (TBHP or KMnO₄) are commonly used in the oxidation reaction. However, they often generate voluminous amounts of environmentally undesirable waste [5-8]. Hence, using a safer and cleaner oxidizing agent is of great practical importance. Molecular oxygen, which is universally accepted as a green, safe, clean and economic oxidant, is strongly desirable for a long time. However, it is still a challenge that efficient utilization of molecular oxygen in olefin oxidations at atmospheric pressure [9-11].

Recently, many metal (Cu, Co and V) compounds are active homogeneous catalysts for olefin oxidations [12-14]. Although the homogeneous catalysts are remarkably efficient, they share a universal handicap: separation, catalyst recycling and product contamination. Therefore, the design of efficient and recoverable catalysts has become an important issue. One approach to such an environmentally benign process is based on the development of heterogeneous catalysts because these heterogeneous systems are easy to handle, recover and are "green" processes [15, 16]. Generally, attempts included the use of biphasic systems or the immobilization of catalysts on solids, have been taken to improve catalyst recovery and recycling [17, 18]. In such circumstances, systems that use silica-coated magnetic mesoporous nanoparticles have drawn attention. These systems, which are comprised of magnetically recoverable solid supports, have unique physical properties including the

ordered pore arrangement, high surface area and superparamagnetism, can be easily and quickly removed from the reaction medium [19-21]. Nevertheless, a key challenge is to prevent their agglomeration and enhance the stability. To address these problems, metal affinity groups, such as -NH₂, -SiH, -SH groups have been post-grafted onto the surface of catalyst support to stabilize and disperse metal nanoparticles [22-25].

More recently, Au nanoparticles are widely used in a series of reactions due to their unique physical and chemical properties [26-30]. Particularly, olefin oxidations over supported Au nanoparticles using molecular oxygen have attracted much attention. Inspired by the work of Xiao and co-workers, who showed that Au/SBA-15-Py catalyst exhibit superior catalytic properties in the oxidation of cyclohexene and styrene [31], we began a study into the immobilization of Au on a thiol-modified silica-coated magnetic support with excellent catalytic and separation properties. It was found that the catalyst exhibited prominent catalytic properties in olefin oxidations with molecular oxygen at atmospheric pressure.

2. Experimental section

2.1 Synthesis of oleic acid coated magnetic nanoparticles (MNs)

Fe₃O₄ nanoparticles were prepared by co-precipitation method [32]. First, 4.8 g of FeCl₃·6H₂O (17.7 mmol), 2.0 g of FeCl₂·4H₂O (10.1 mmol) and 1 mL oleic acid were dissolved in 30 mL deionized water under nitrogen with vigorous stirring at 363 K. Then, 10 mL of ammonium hydroxide (26 wt%) was added rapidly to adjust the pH value about 9, and it immediately turned black. After 2.5 h, the black precipitate was

collected with a permanent magnet and resuspended in chloroform with an end concentration of 10 mg/mL oleic acid-capped Fe₃O₄.

2.2 Synthesis of magnetite nanocrystals embedded in mesoporous silica spheres (MSS)

The preparation route of magnetite nanocrystals embedded in mesoporous silica spheres (MSS) was according to reference [33]. Briefly, 100 mg of oleic acid stabilized MN dispersed in 10.0 mL of chloroform was added to 50 mL of aqueous solution containing 2.0 g of cetyltrimethylammoniun bromide (CTAB, 5.5 mmol). The resulting solution was stirred for several hours and a homogeneous oil-in-water microemulsion was obtained. After removing chloroform using a rotary evaporator, about 50 mL aqueous phase dispersed nanoparticles was generated. Then the resulting aqueous solution was diluted with 500 mL of deionized water. And then 20 mL of ethyl acetate (204.7 mmol), 12 mL of ammonia solution (80.6 mmol), and 2.0 mL of tetraethoxysilane (TEOS, 9.0 mmol) were successively added to the diluted aqueous solution containing the magnetite nanoparticles. The mixture was continuously stirred for 5 h at room temperature, then the resulting products were collected by centrifugation and then washed with water and ethanol for 5 times and dried under vacuum at 50 °C overnight. Finally, the Fe₃O₄ nanocrystals embedded in mesoporous silica spheres (MSS) were obtained by the calcination at 550 °C for 6 hours.

2.3 Synthesis of thiol-modified silica-coated magnetic mesoporous nanocrystals (MSS-SH)

The functionalization of the MSS with thiol was performed by adding 1 mL of

3-mercaptopropyltrimethoxysilane (MPS) to 100 mL dry toluene that contained 1 g MSS nanoparticles. The resulting solution was heated at reflux for 24 h and then washed with acetone and ethanol. The obtained solid material was dried under vacuum at 50 \square for 24 h.

2.4 Loading of Au on thiol-modified silica-coated magnetic mesoporous nanocrystals (MSS-SH-Au⁰)

In a typical synthesis, 1 g of above-synthesized MSS-SH were dispersed in 100 mL of deionized water by sonication for 30 min and then 6.0 mL of chloroauric acid (24mM) was added dropwise with vigorous stirring at room temperature. After stirring for 12 h, the resulting precipitate was collected by an external magnet and washed 3 times with deionized water and 3 times with ethanol. And then, the product was dried under vacuum at 50 \Box overnight. Finally, the catalyst was reduced directly by hydrogen in autoclave for 6 h at 80 \Box . Thereafter, the material was washed twice with distilled water and acetone and dried under vacuum (Scheme 1). The content of Au in MSS-SH-Au⁰ as estimated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis, was 2.50 wt%.

2.5 Catalytic tests

Olefin oxidations were carried out in a 25 ml glass reactor equipped with a reflux condenser. Typically, substrate, solvent, and catalyst were mixed in the reactor, then the system was evacuated by a vacuum pump, and then pure O_2 was introduced and sealed in the reaction system at atmosphere pressure by a three direct links. And then the mixture was stirred (1000rpm) and the temperature was increased to 373 K (the

temperature was measured with a thermometer in an oil bath). After reaction, the products were analyzed by GC (P.E. AutoSystem XL) or GC–MS (Agilent 6890 N/5973 N). The recyclability of the catalyst was tested by separating it from the reaction system with a magnet, and then, washing with large quantity of ethanol, and drying at 50 \square for 6 h, then the catalyst was reused in the next reaction.

2.6 Characterization

The morphology and chemical composition of the catalyst were characterized by Tecnai G2 F30 transmission electron microscopy (TEM). Au contents of the catalyst were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The low-temperature N₂ adsorption–desorption experiments were carried out using a Tristar II 3020. The pore diameter distributions were calculated from desorption branches using the BJH (Barrett-Joyner-Halenda) methods, and the surface areas were calculated using the BET (Brunauer-Emmett-Teller) method based on the desorption isotherms. XRD measurement was performed on a Rigaku D/max-2400 diffractometer, using CuK α radiation as the X-ray source in the 2 θ range of 10°-80°. The magnetic measurement was done using a Quantum Design vibrating sample magnetometer (VSM). X-ray photoelectron spectroscopy (XPS) was recorded on a PHI-5702 instrument and the C_{1s} line at 297.8 eV was used as the binding energy reference.

3. Results and discussion

3.1 Catalysts characterization

The morphologies and structural features of the supported material MSS and

as-synthesized catalyst MSS-SH-Au⁰ could be observed directly through TEM and HRTEM images (Fig. 1). As was shown in Fig.1a, each magnetic particle was composed of plentiful nanocrystals. Besides, the catalyst had obvious disordered mesostructure derived from CTAB-templating. The average diameter of the support spheres was about 130 nm. The TEM image in Fig. 1b revealed that the MSS-SH-Au catalyst didn't change considerably after attachment of the Au onto the surface of the MSS. In addition, Au NPs with similar sizes of 5 nm were well dispersed in the MSS. From the Fig. 1c, it could be seen that the resolved lattice fringes of (111) planes (d= 0.235 nm) detected in the HRTEM image were attributed to Au nanocrystals,[34].

The elemental composition of the MSS-SH-Au⁰ samples was determined by EDX analysis. The result shown in Fig. 2 reveals that the as-prepared products contain Fe, Si, Au, S, Cu, C and O. Among these elements, Cu C and O are generally influenced by the copper network support films and their degree of oxidation, Si, O, Fe, S and Au signals result from the MSS-SH and Au particles which form the products.

In order to obtain the structural information about the catalyst on a mesoscopic scale, N_2 adsorption-desorption was used to characterize the catalyst. The MSS had a specific surface area 694.5 m²/g and pore volume 0.73 cm³/g. The MSS-SH-Au⁰ had a specific surface area 241.5 m²/g and pore volume 0.18 cm³/g (Table 1). It was worthwhile to note that the specifc surface area and pore volume of the parent MSS underwent a significant decrease after grafting thiol group and Au nanparticles.

The XRD patterns of the prepared MSS and MSS-SH-Au were shown in Fig. 3a-b. As shown in Fig. 3a, a broad band at around $2\theta = 22^{\circ}$ (*) was derived from the

amorphous mesoporous silica spheres and the characteristic peaks of (220), (311), (400), (511) and (440) were typical of a spinel magnetite structure. As presented in Fig.3b, the new peaks with 20 at 38°, 44°, 65° and 78°, relating to the (111), (200), (220) and (311) crystal faces of Au nanoparticles respectively, and mostly corresponding to face-centered cubic metallic gold diffraction [35]. No peak was observed to be connected with gold chloride salt crystalline phase, indicating that the reduction of chloroauric acid was completed during the preparing process. This result was confirmed by XPS data.

The chemical composition of the obtained MSS-SH-Au⁰ nanomaterial was detected from the XPS spectra (Fig. 4). From the wide-scan XPS spectrum, the existence of the S2p (172.4 eV) provided an evidence for the successful introduction of thiol groups onto the surface of MSS. The XPS signature of Au 4f doublet for the Au nanoparticles supported on MSS was given in the inset figure. The Au $4f_{7/2}$ and Au $4f_{5/2}$ peaks appeared at 84.7 and 88.3 eV respectively were the characteristic peaks for the metallic Au⁰[36].

The magnetization curves for MSS and MSS-SH-Au⁰ were compared in Fig. 5. There was no hysteresis in the magnetization for the two types of nanoparticles. Neither coercivity nor remanence was observed, which suggested that these nanoparticles were superparamagnetic. It could be seen that the magnetic saturation values of MSS and MSS-SH-Au were 9 and 3 emu/g, respectively. The decrease in saturation magnetization of MSS-SH-Au⁰ could be attributed to the increase of organic matter and Au. Even with this reduction in the saturation magnetization, the

solid catalyst could still be efficiently separated from solution with a permanent magnet. Meanwhile, the inset figure also showed the photograph of the catalyst was pulled magnetically.

3.2 Catalytic reaction

The MSS-SH-Au⁰ was used as a catalyst for the oxidantions of styrene and cyclohexene. Table 2 presented catalytic data in cyclohexene oxidation by oxygen at atmospheric pressure using various solvents. In toluene solvent, the catalyst showed conversion at 61% (Table 2, entry 1). In N,N-dimethylformamide solvent, the catalyst showed conversion at 44% (Table 2, entry 2). In acetonitrile solvent, it gave low activity (28%, Table 2, entry 3). In addition, it was also observed that the solvent strongly influences the catalytic activity. When different oxidants were used, TBHP gave reasonably good performance for the oxidantion of cyclohexene, the conversion was 87% and the selectivity for cyclohexene epoxide reached to 21% (Table 2, entry 4), while low conversion was observed when H_2O_2 was used as oxidant (Table 2, entry 5).

Table 3 showed the catalytic performances for the oxidantions of styrene with different solvents, oxidants, and amount of catalyst. Generally, styrene is not easy to be oxidized using molecular oxygen on Au catalysts [37]. In the case of O_2 , the catalyst exhibited the conversion at 35% (Table 3, entry 1). If t-butyl hydroperoxide (TBHP) was present, the catalyst exhibited the conversion at 85% (Table 3, entry 2). Low conversion was observed when the reaction was carried out using hydrogen peroxide as oxidants (Table 3, entry 3). The rapid decomposition of H_2O_2 into O_2 over the catalysts at the initial stage would be the main reason for the lower activity. As

same as cyclohexene oxidation, in toluene solvent, the catalyst exhibited the good performance while in acetonitrile solvent, the catalyst showed conversion at zero (Table 3, entry 4). There were many factors that may cause the low conversion. We considered that the active centre was poisoned by coordination of the hydroperoxides, which may be the most important factor. In order to verify this speculation, the catalyst was separated from the reaction after the oxidation of styrene in acetonitrile solvent, and washed with acetone and ethanol thoroughly. And then, the product was dried under vacuum at 50°C overnight. IR spectroscopy was used to investigate it. Fig. 7 gave the FT-IR spectra of the catalyst before and after use. The characteristic bands of Fe-O at 590.5 and 456.6 cm⁻¹ were attributed to the Fe-O stretch bands. The data were consistent with the values reported for Fe_3O_4 in the literature [38]. Two strong bands at about 1084.4 and 802.3 cm⁻¹ were assigned to v_{as} (Si–O–Si) and v_s (Si–O–Si), respectively [39]. Two strong bands at 3428.2 and 1635.2 cm⁻¹were assigned to water stretches and bends[40]. 3-mercaptopropyltrimethoxysilane (MPS) displayed characteristic -CH₂ stretching bands at 2935.8 cm⁻¹. After the oxidation of styrene in acetonitrile solvent, the new band at 2358.8 cm^{-1} appears which was assigned to the C=N stretching. This result indicated that acetonitrile irreversibly adsorb on the surface of catalyst even after careful washing. The catalytic active sites were occupied by the cyanogroup, which lead to the catalyst was poisoned. Thus, the catalyst gave unsatisfactory performance in acetonitrile solvent.

Meanwhile, it could be seen, the use of solvent in styrene oxidation not only influences the activity but also changes the product selectivity. For example, in toluene solvent, the selectivity for styrene epoxide is 14% (Table 3, entry 2). When N,N-dimethylformamide solvent was used, the selectivity for styrene epoxide reaches

to 16% (Table 3, entry 5).

The effects of the amount of catalyst were shown in Table 3 (entry 6). Increasing the amount of catalyst from 40 to 70 mg enhanced the conversion from 55% to 87%. As can be seen, with the increase of the amount from 60 to 70 mg, there was no obvious increase of the conversion. Therefore, all epoxidation reactions were carried out using 60 mg of catalyst.

3.3 Magnetically recoverable gold-based catalyst

To further investigate the stability of MSS-SH-Au⁰ catalyst, a series of catalyst recycle and reuse experiments for the cyclohexene and styrene oxidation were conducted, the catalyst could be easily recycled for further use because of its magnetism. After recycles for five times, the catalyst still remained its activity, indicating its excellent recyclability (Fig. 6).

4. Conclusion

In conclusion, a novel gold-based catalyst supported on thiol-functionalized mesoporous silica-coated magnetite nanoparticles was successfully prepared and Au nanoparticles are highly dispersed in the mesopores of MSS-SH-Au⁰. These ligand-modified Au MNPs are highly efficient and stable heterogeneous catalyst for oxidantions of cyclohexene and styrene by molecular oxygen at atmospheric pressure. Moreover, the catalyst could be recovered in a facile manner from the reaction mixture without any significant loss in activity, which was mainly attributed to the small size of Au nanoparticles and the thiol groups onto the surface of MSS nanospheres.

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Figure Captions

Scheme 1. Synthesis of the catalyst MSS-SH-Au⁰.

Fig. 1 TEM images of (a) MSS, (b) MSS-SH-Au⁰ and (c) HRTEM image of the Au nanoparticles crystal structure in detail on MSS.

Fig. 2 EDX spectrum of the MSS-SH-Au 0 .

Fig. 3 XRD patterns of (a) MMS and (b) MSS-SH-Au 0 .

Fig. 4 XPS wide-scan spectrum of the MSS-SH-Au⁰ (inset: high-resolution spectrum of Au 4f).

Fig. 5 Magnetic curves of MSS (a) and MSS-SH-Au 0 (b).

Fig. 6 Recyclable data in: (a) cyclohexene and (b) styrene oxidations over $MSS-SH-Au^0$ catalyst.

Fig. 7 FT-IR spectras of (a) MSS-SH-Au 0 and (b) MSS-SH-Au 0 after use in acetonitrile solvent.

Table 1 Textural Parameters of MMS and MSS-SH-Au⁰ samples^a.

 Table 2 Catalytic date in cyclohexene oxidation by molecular oxygen over

MSS-SH-Au⁰ catalyst.^a

Table 3 Catalytic date in styrene oxidation by molecular oxygen over MSS-SH-Au⁰ catalyst.^a

17



Fig. 1

25







Fig. 3





 $^aS_{BET}$ the BET surface area, V the total pore volume, D the average

porediameter calculated using the BJH method.

Table 1



^a 6 mmol of cyclohexene, 10 ml of solvent, 60 mg of catalyst, time for 8 h, temperature of oil bath at 373 K. Oxidant amount, t-butyl hydroperoxide (TBHP, 3 mol% based on substrate) ; hydrogen peroxide (H_2O_2 , 3 mol% based on substrate).

^b P1, cyclohexene epoxide; P2, 2-cyclohexen-1-ol; P3, 2-cyclohexen-1-one; P4, CO₂ and other organic products with less than six C atoms.

Table 2

		2, solven u catalyst			_0]			
stryene			stryene epoxide	benzaldehyde		acetophenone		
			1	2			3	
Entry	Solvent	Oxidant	Amout of catalyst	Conversion	Proc	Product selectivity ^b (%)		
			(mg)	(%)	P1	P2	P3	P4
1	Toluene	O ₂	60	35	3	71	20	6
2	Toluene	TBHP	60	85	14	55	9	22
3	Toluene	$\mathrm{H}_2\mathrm{O}_2$	60	23	7	66	11	16
4	MeCN	TBHP	60	0	-	-	-	-
5	DMF	TBHP	60	43	16	34	22	28
6	Toluene	TBHP	40	55	9	40	10	41
7	Toluene	TBHP	50	71	12	49	7	32
8	Toluene	ТВНР	70	87	13	53	13	21

^a 6 mmol of styrene, 10 ml of solvent, time for 8 h, temperature of oil bath at 373 K. Oxidant amount, t-butyl hydroperoxide (TBHP, 3 mol% based on substrate) ; hydrogen peroxide (H_2O_2 , 3 mol% based on substrate).

^b P1, styrene epoxide; P2, benzaldehyde; P3, acetophenone; P4, phenylacetic acid, benzoic acid, ester, and some others.

Table 3



Highlights

(1) A facile method was put forward to prepare the catalyst $MSS-SH-Au^0$.

(2) The catalyst had <u>mesoporous structure</u> and Au NPs were well dispersed in the MSS.

(3) The catalyst showed high activity in oxidations of cyclohexene and styrene by oxygen.

(4) The catalyst was easily recovered with external magnetic field.

(5) The catalytic could be reused for five times without any obvious loss of activity.