Styrene Epoxidation over Carbon Nanotube-Supported Gold Catalysts

Junhua Liu · Fang Wang · Tan Xu · Zhenggui Gu

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Abstract Carbon nanotube supported gold catalysts prepared by deposition–precipitation with urea (DP urea) were characterized by various techniques. Its catalytic activity was examined for the oxidation of styrene using *t*-butylhydroperoxide as oxidant. This system showed good epoxide selectivity. The other factors, such as solvent, reaction time, concentrations of oxidant and catalyst, have also been investigated and reaction conditions are optimized. It is a novel highly active/selective and reusable heterogeneous catalyst for styrene epoxidation.

Keywords Carbon nanotubes (CNTs) \cdot Epoxidation \cdot Gold \cdot Styrene

1 Introduction

Olefin epoxidation, especially styrene, is a subject of great interest from both academic and industrial points of view; the oxirane group is highly reactive which makes epoxides an essential group of organic intermediates [1].

J. Liu (⊠) · T. Xu · Z. Gu College of Chemistry and Environmental Science, Nanjing Normal University, 210097 Nanjing, China e-mail: liujh2010@yahoo.cn

F. Wang (⊠)
College of Sciences, Nanjing University of Technology, 210009 Nanjing, China
e-mail: qufuwangfang@yahoo.com.cn

Consequently, there is a growing interest in the synthesis of fine chemicals via this versatile reaction.

The gold-based catalysts have demonstrated a very interesting and promising activity, and different types of gold-based homogeneous and heterogeneous catalysts in the form of metal complex or nano-particles have been developed for the oxidation of olefins. Choudhary et al. [2–4] and subsequently Yin et al. [5] have shown that gold nanoparticles (Au–NPs) supported on a range of oxides are active for the epoxidation of styrene using tertiary butylhydroperoxide (TBHP) in greater than stoichiometric amounts. Selectivities to styrene oxide of *ca*. 50% are readily achieved using this approach.

Generally, the catalytic properties of heterogeneous gold catalysts strongly depend on the particle size. The use of gold as a catalyst requires careful preparation of the gold particles focusing on achieving a very small particle size. Recent trends in this area have fallen into two broad categories: (1) modulation of nano-size gold particles prepared by different preparation methods [6, 7]; (2) application of new nano material as carrier to control the nano-size of gold particles. Much attention was paid to the latter. Some new catalytic materials, such as meso-micro sieves [8, 9], nanotubes [10] and polymers [11], have been used to prepare gold-based catalysts. However, carbon nanotubes (CNTs) were extensively studied due to their unique chemical and mechanical properties for different potential applications. CNTs are resistant to acid/base media and precious metals can easily be recovered by burning off the support. The material also provides high dispersion of the metals. Herein, we present a strategy for the design of high-performance heterogeneous catalysts utilizing the carbon nanotube supported Au-NPs by deposition-precipitation (DP) method, which exhibits high styrene conversion and epoxide selectivity.

2 Experimental

2.1 Materials

CNTs were purchased from Chengdu Times Nano Company, TBHP(70% mass concentration in water) and H_2O_2 (50% mass concentration in water) were purchased from Beijing Chemical Reagents Company. Other chemicals and reagents used in the present study were of analytical grade and purchased from Sinopharm Chemical Reagent Company and used without any further purification.

2.2 Catalyst Preparation

Au/CNTs catalysts were prepared by DP with urea, in the so-called standard preparation procedures: 1 g CNTs was added into 25 ml of an aqueous HAuCl₄ solution $(4.2 \times 10^{-3} \text{ M})$ and 0.63 g urea (0.42 M). The initial pH was about 2. The suspension thermostated at 80 °C, was vigorously stirred for 8 h (pH increases) and then centrifuged, washed and dried (Au content: 0.3 wt%).

2.3 Catalyst Characterization

The morphologies of obtained carbon nanotube and Au/CNTs catalyst were examined by transmission electron microscope (TEM) (JEM-1200EX) and scanning electron microscope (SEM) (JSM-5600 LV). The crystals of the catalysts were studied by X-ray diffraction (XRD) (X' Pert PRO). Surface composition was determined by X-ray photoelectron spectroscopy (XPS), using an ESCALAB 210 XPS system with a Mg K α source. BET surface areas were obtained by physisorption of nitrogen at 77 K using a Micromeritics ASAP2010 instrument. Elemental analysis was determined by the Panalytical Company with a Magix PW 2403 XRF Spectrometer.

2.4 Styrene Epoxidation

In a typical run, a mixture of catalyst (0.05 g), substrate (4 mmol) and acetonitrile (5 ml) was stirred in a 25 ml round-bottom flask equipped with a condenser at room temperature for 30 min. After the addition of oxidant

(3 ml), the reaction was started by immersing the flask in an oil bath kept at the reaction temperature (82 °C). The resulting mixture was then refluxed for 10 h. After filtration and extraction, the filtrate was concentrated by rotary evaporator then analyzed by gas chromatography, the nature of the products was also determined by GC–MS.

3 Results and Discussion

3.1 Catalyst Characterization

SEM micrographs show the morphologies of CNTs and Au/CNTs catalyst (Fig. 1a, b). The diameter of CNTs is distributed between 20 and 30 nm. A TEM image of CNTs with 0.3 wt% deposited Au-NPs is shown in Fig. 1c. One bundle of nanotube is covered with ca. 5 nm Au-NPs with a very high particle density. The progressive decomposition of urea in solution at temperatures above 60 °C releases OH⁻ ions, which gradually increase the medium pH. This method facilitates the slow precipitation of hydroxides onto the support, and avoids a brutal and local increase of pH, which could induce precipitation in solution. The small size of the gold particles for the Au/CNTs sample prepared by DP urea implies that an interaction occurs between the carbon nanotube and the gold precipitate, which leads to a high dispersion of Au-NPs. Thus, their channels will not be blocked and the Au-NPs may not sinter under reaction conditions, which can provide an excellent catalytic activity for styrene epoxidation.

The CNTs and Au/CNTs catalyst were also characterized by XRD (Fig. 2). It could be observed that the typical peak located at a 2θ value of about 26.0° was referred to (0 0 2) reflection of CNTs supports, and the characteristic peaks assigned to CNTs become weaker after loading Au. The other featured four peaks were indexed to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) reflection of face centered cubic (fcc) crystalline Au (JCPDS, Card no. 7440-57-5), which indicated the formation of gold crystal loaded on CNTs.

To obtain information on the surface state of gold in Au/CNTs catalysts, XPS study was carried out, as can be seen from Fig. 3. Two distinct peaks appeared at 84.6 and

Fig. 1 SEM images of **a** CNTs **b** Au/CNTs catalyst and **c** TEM image of Au/CNTs catalyst





Fig. 2 XRD patterns of a CNTs; b Au/CNTs



Fig. 3 XPS of Au 4f region of Au/CNTs catalyst

88.3 eV, which were close to the Au 4f binding energies of oxidized Au(III) [12]. A lot of efforts have been spent to study the nature of the "active sites" in the oxidative reactions over gold-catalysts. Some authors suggest that the activity of gold supported catalysts depends on the size of the gold particles with a maximum of activity usually observed for a particle size of 3 nm; some argue that the effect of the oxidation state of gold is at least as important as that of the particle size of metallic gold. However, the state of the gold in active catalysts is unclear, most of them have accepted that metallic gold generated by high calcination temperature favors a high catalytic activity [13]. Hoflund and co-workers claimed that part of the gold supported on α -Fe₂O₃ and Co₃O₄ is nonmetallic, and that it may be responsible for the low-temperature activity [14], while Visco et al. [15] found much larger catalytic activity in uncalcined samples than in calcined ones and proposed that oxidized gold species are the most active sites for lowtemperature CO oxidation for Au/Fe_2O_3 catalysts. In our case, the Au/CNTs catalysts were obtained just by desiccation, without any high-temperature process, so there should be no the formation of metallic gold particles. Combining the XPS data, we concluded that the ionic Au(III) formed the true active sites, in agreement with the hypothesis proposed by Visco.

3.2 Catalytic Test

The oxidations of styrene to styrene oxide (SO) on a series of Au/CNTs catalysts were investigated. Phenyl-acetaldehyde (PA) and benzaldehyde (BA) have been the main by-products during the oxidation of styrene on these catalysts.

The effect of solvents on styrene epoxidation was examined and the results are shown in Table 1. The Au/CNTs catalyst exhibited the highest catalytic activity and selectivity for styrene oxide in acetonitrile. 1, 2-dichloroethane also was found to be a favorable solvent for this reaction (Table 1, entry 2), but its styrene conversion and epoxide selectivity were lower than that in acetonitrile. The reaction, however, showed low activity in toluene or N,N-dimethylacetamide (DMA) despite of their moderate epoxide selectivity (Table 1, entries 3-4). The results showed that the conversion and epoxide selectivity was relative to the polarity of solvents: the epoxidation vields increased gradually with increasing polarity of solvents except DMA (the polarity of solvent was determined by dielectric constant ε : acetonitrile (ε : 37.5) > dichloroethane (ε : 10.4) > DMA (ε : 6.4) > toluene (ε : 2.4)). Different oxidants, such as air and hydrogen peroxide have also been used for styrene epoxidation over this catalyst (Table 1, entries 5–6), although very poor yields of styrene oxide were obtained.

The effect of the amount of catalyst on styrene epoxidation was thereafter examined (Table 2). When the substrate/catalyst ratio was between 80:1 and 120:1, the reaction rate decreased considerably with the reduction in catalyst concentration; however, increasing the substrate/ catalyst ratio from 20:1 to 80:1 had little effect on the reaction rate of this reaction. According to this study, whatever the substrate/catalyst ratio, no significant effect was found with respect to the epoxide selectivity, in other words, the epoxide selectivity of this oxidation reaction is independent of the catalyst concentration.

The change of styrene epoxidation was monitored and plotted with respect to the time. The results are shown in Fig. 4. It was seen that the conversion of styrene increased continuously when the reaction time increased and was close to complete conversion ultimately after 22 h. The epoxide

Selectivity (%)^a TON^b Entry Solvent Time (h) Conversion (%)^b SO ΒZ PA 1 Acetonitrile 10 67.2 77.5 13.1 9.4 2733 2 Dichloroethane 10 71.1 48.5 15.5 13.4 1811 3 Toluene 20.9 1609 10 45.0 68.1 11.0 223 4 N,N-dimethylacetamide 10 6.9 614 38.6 _ 5^c Acetonitrile 10 2.3 74.7 10.0 15.3 90 6^d Acetonitrile 10 10.2 100 0 _

Table 1 Oxidations of styrene on Au/CNTs catalyst using different solvents/oxidants

Reaction conditions Au/CNTs catalyst 0.05 g, styrene 4 mmol, solvent 5 mL, TBHP 3 mL, 82 °C

^a Determined by GC

^b TON = moles of styrene oxides/moles of gold in the catalyst

^c Air bubbling, without TBHP

^d H₂O₂ as oxidant, without TBHP

Table 2 Styrene epoxidation at different concentrations of Au/CNTs catalyst

Entry	Substrate/Au–CNTs (mmol/g)	Time (h)	Conversion (%) ^a	Selectivity (%) ^b			TON ^b
				SO	BZ	PA	
1	20/1	10	73.1	74.5	12.8	12.7	715
2	50/1	10	71.8	75.6	13.6	10.8	1781
3	80/1	10	67.2	77.5	13.1	9.4	2733
4	100/1	10	51.6	76.1	11.8	12.1	2578
5	120/1	10	42.7	74.6	13.2	12.2	2509

Reaction conditions Au/CNTs catalyst, CH3CN 5 mL, TBHP 3 mL, 82 °C

^a Determined by GC

^b TON = moles of styrene oxides/moles of gold in the catalyst



Fig. 4 Styrene epoxidation on Au/CNTs catalyst at different time. *Reaction conditions:* Au/CNTs catalyst 0.05 g, styrene 4 mmol, CH_3CN 5 mL, TBHP 3 mL, 82 °C

selectivity was nearly steady at all times (72.1–77.5%). Although there have been several reports on the development of heterogeneous gold catalysts for this reaction, the

higher catalytic activity and epoxide selectivity over Au/ CNTs catalyst are obtained among these gold-contained catalysts to the best of our knowledge. Furthermore, when the reaction time was 22 h, the recycled catalyst could be used for epoxidation of styrene without changes in conversion and selectivity values, producing a 67.2% yield for the second use and a 66.7% yield for the third use. It was confirmed by induced coupled plasma techniques (ICP) that the gold content of recycled Au/CNTs catalyst was almost the same as that of the fresh ones.

The effect of oxidant concentrations on styrene oxidation was plotted in Fig. 5. An increase of oxidant concentration enhanced the rate of styrene oxidation, and epoxide selectivity was increased firstly then decreased with increased concentration of oxidant. The conversion of styrene was 55.4% and the epoxide selectivity was 59.8% at 2 ml oxidant, then a maximum styrene conversion (78.0%) and high epoxide selectivity (77.3%) were obtained at 3 ml. The catalytic activity was found to increase slightly and the epoxide selectivity decreased gradually when the oxidant exceeded 3 ml, so an optimal concentration of oxidant should be 3 ml.



Fig. 5 Styrene epoxidation on Au/CNTs catalyst with different concentrations of oxidant. *Reaction conditions:* Au/CNTs catalyst 0.05 g, styrene 4 mmol, CH₃CN 5 mL, 82 °C, 14 h



Scheme 1

3.3 Mechanism Investigation

Mechanistic issues most often addressed have been the roles of oxygen and of promoters in olefin epoxidation reactions. It is typically reported that atomic, rather than molecular, adsorbed oxygen reacts with ethylene [16], styrene [17], and norbornene [18] in the rate-determining step. Moreover, in our experiments, the data showed that the key factors governing the activity and selectivity of catalyst are highly dispersed Au(III) species. Based on the above description, a possible mechanism was proposed (Scheme 1). Initial complex formation between metal catalyst and TBHP renders the peroxidic oxygen more electrophilic and hence more labile to attack by an olefinic double bond.

The free radical mechanism involves the interaction of TBHP with the Au(III) species 1 in catalyst to form a hydroperoxy species 2 in a preequilibrium step. Species 2, being unstable, undergoes one-electron reduction with a loss of water molecule and rearranges to give the Au(III)– O_{ad} (peroxo) species 3. In another preequilibrium step,

species 3 interacts with styrene to form a π -bonded transient species 4. The transfer of oxygen to olefinic bond in a rate-determining step forms a metalloepoxy intermediate species 5, which dissociate to form products, while regenerating the active species.

4 Conclusions

Au/CNTs catalyst is active in catalyzing the oxidation of styrene with relative good conversion and high epoxide selectivity using TBHP as oxidant. This study confirms that the key factors governing the activity and selectivity of Au/CNTs are highly dispersed Au(III) species. Further work is in progress for the oxidation of other olefins, and details of the experiments will be given in a forthcoming paper.

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References

- Ullmann's Encyclopedia of Industrial Chemistry (1998) 6th edn (Electronic Release). Wiley/VCH, New York
- 2. Choudhary VR, Durnbre DK (2009) Catal Commun 10:1738
- 3. Patil NS, Uphade BS, Jana P, Bharagava SK, Choudhary VR (2004) J Catal 223:236
- Patil NS, Uphade BS, Jana P, Sonawane RS, Bharagava SK, Choudhary VR (2004) Catal Lett 94:89
- 5. Yin D, Qin L, Liu J, Jin CLY (2005) J Mol Catal A Chem 240:40
- 6. Eustis S, Hsu H-Y, El-Sayed MA (2005) J Phys Chem B 109:4811
- 7. Liu Y, Lin L, Chiu W (2004) J Phys Chem B 108:19237
- Kónya Z, Puntes VF, Kiricsi I, Zhu J, Ager JW, Ko MK, Frei H, Alivisatos P, Somorjai GA (2003) Chem Mater 15:1242
- 9. Hu J, Chen L, Zhu K, Suchopar A, Richards R (2007) Catal Today 122:277
- Bavykin DV, Lapkin AA, Plucinski PK, Murciano LT, Friedrich JM, Walsh FC (2006) Top Catal 39:151
- 11. Tsunoyama H, Sakurai H, Tsukuda T (2006) Chem Phys Lett 429:528
- Cattaruzza E, Battaglin G, Canton P, Sada C (2005) J Non-Cryst Solids 351:1932
- Zanella R, Giorgio S, Shin CH, Henry CR, Louis C (2004) J Catal 222:357
- Epling WE, Hoflund GB, Weaver J, Tsubota S, Haruta M (1996) J Phys Chem 100:9929
- 15. Visco AM, Neri F, Neri G, Milone C, Galvagno S (1999) Phys Chem Chem Phys 1:2869
- 16. Grant RB, Lambert RM (1985) J Catal 92:364
- Hawker S, Mukoid C, Badyal JPS, Lambert RM (1989) Surf Sci 219:L615
- 18. Roberts JT, Madix RJ (1988) J Am Chem Soc 110:8540