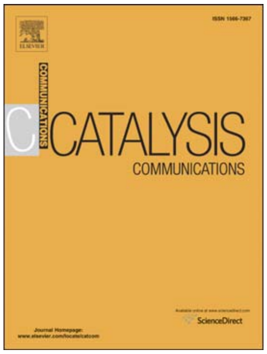

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Selective oxidation of sulfides to sulfoxides using hydrogen peroxide over Au/CTN-silica catalyst

Fang Wang[a*], Cheng Liu[b], Gui Liu[b], Wenxiu Li[b], Junhua Liu[b,c*]

[a] College of Sciences, Nanjing Tech University, Nanjing 211816, China

[b] College of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023,China

[c] Jiangsu Provincial Key Laboratory of Palygorskite Science and Applied Technology, Huaiyin Institute of Technology, Huaian 223003, China

Abstract: Chitosan (CTN) can be used as potential support to create environmentally friendly catalysts; however, chitosan's poor diffusion properties and low surface area limit its application. Direct deposition method on inorganic supports might be a feasible and simple solution, using core (silica nanosphere)-shell (chitosan) material as support, a series of Au/CTN-silica catalysts were prepared by inverse microemulsion system. These catalysts were active in catalyzing the oxidation of sulfides to sulfoxides with relative good conversion and high selectivity. This study confirms that the key factor governing catalytic performance of this catalyst should be the interaction between gold nanoparticles and N atoms.

Keywords: Chitosan; Silica nanosphere; Core-shell; Nano-gold; Oxidation of sulfides.

1. Introduction

In recent years, interest in sulfoxide chemistry is increasing; the chemoselective preparation of sulfoxides and sulfones represents an extremely important synthetic process in organic chemistry [1]. So various efforts have been made in development of new synthetic methods for sulfoxide synthesis [2-6], however, many of these procedures utilize environmentally unfavorable reagents,

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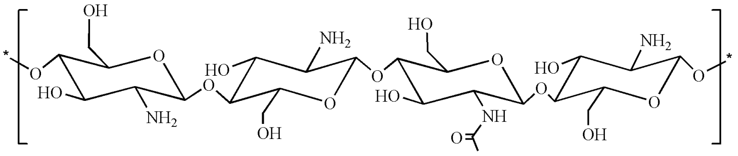
* Corresponding author. Tel: +86-25-85891767
E-mail address: liujh2007@aliyun.com (J. Liu); qufuwangfang@aliyun.com (F. Wang).

solvents and catalysts that bring out the matter of eco-efficiency in our environmentally conscious times. Hence, there is still a need for the development of new, efficient, highly selective, and widely applicable methods for this transformation under mild reaction conditions.

Nano-gold catalysis has attracted considerable attention in recent years, which showed various catalytic activities. It has been widely accepted that the catalytic performance of nano-gold is dependent on size of gold nanoparticles (GNPs) and the interaction between gold and supports. Articles have showed that some functional groups, such as $–NH_2$, -SH, -COOH etc., are necessary for the controlling of GNPs size. As the presence of these groups, some natural polysaccharides, such as alginate, carrageenan and especially chitosan (CTN), have stimulated widespread interests to use them as supports to create environmentally friendly catalysts, these materials are renewable resource, chemically stable but biodegradable [7]. Chitosan is a copolymer of linked β, (1→4), 2-amino-2-deoxy-D-glucan and 2-acetamidodeoxy-D-glucan (Scheme 1), the presence of hydroxyl and amino groups, which are excellent functional groups for the anchoring of GNPs.



Scheme 1 Chemical Structure of Chitosan

The poor diffusion properties of chitosan, its weak mechanical properties and low surface area limit its application; researchers have provided many methods to solve these problems, such as CO_2 supercritical drying method [7-9], direct deposition method on inorganic supports [10-11]. However, these methods have encountered with rigorous experimental conditions, high energy-consumptions or poor dispersion of chitosan on inorganic supports. Obviously, the good dispersion of chitosan on silica nanosphere was necessary for the deposition of GNPs. Direct deposition method might be a feasible and simple way, however, previous researchers are failed to achieve this goal by this method. In this article, we have deposited chitosan on silica nanosphere by an inverse microemulsion system and used chitosan/silica nanosphere supports to capture GNPs. Firstly, we synthesized some silica nanosphere, then a certain amount of chitosan-acetic acid solution was added dropwise to the mixture of a large amount of acetone and silica nanosphere with vigorous stirring, uniform deposition of chitosan on silica nanosphere ensured the formation of core (silica nanosphere)-shell (chitosan)-type supports, and then dispersed gold nanoparticles (GNPs) were obtained on the supports. In this catalyst, silica nanosphere as the core ensures the GNPs are dispersed equably, and improve chitosan's mechanical stability, surface area and diffusion properties. To the best of our knowledge, it is the first time to construct core-shell typed Au/CTN-silica catalyst by inverse microemulsion system, and this catalyst showed high catalytic activity and selectivity for the oxidation of sulfides to sulfoxides. Meanwhile, only a few articles present the oxidation of sulfides over gold-based catalysts so far [12-13].

2. Experimental

2.1. Materials

H_2O_2 (30% in water) and other reagents were all obtained from commercial sources without any further purification.

2.2. Catalyst preparation

2.2.1 Preparation of silica nanosphere

Silica nanosphere was prepared according to one modified procedures [14]. 0.5 g of cetyltrimethyl ammonium bromide (CTAB) was dissolved in a system composed of 70 mL of H_2O, 0.8 mL of aqueous ammonia and 20 mL ethanol. After the mixture was vigorously stirred for 0.5 h at room temperature, 2.5 mL of tetraethyl orthosilicate (TEOS) was quickly dripped into the mixture. The resulting mixture was vigorously stirred at room temperature for 6 h. A white precipitate was obtained, filtered, washed with pure water, and dried in air at 60 ℃ for 24 h.

CTAB and other organic components in the products were eventually removed by calcination in air at 550 ℃ for 5 h.

2.2.2 Preparation of Au/CTN-silica catalyst

The Au/CTN-silica catalyst was prepared as follows: Firstly, 3 g chitosan was dissolved in 100 ml 2% acetic acid solution, then 0.5 g silica nanosphere and 4 ml above solution was sequentially added into the large amounts of acetone, and 0.35 ml 4 M NaOH solution was added when the stirring time was 4h. The inverse microemulsion system was vigorous stirring for 24 h at room temperature. After drying, 0.2 g CTN-silica powder was transferred into 20 ml 9.1×10^{-7} M $HAuCl_4$ solution and refluxed at 80 ℃ for 10 h; the catalyst was filtrated, washed with ethanol and dried at 60 ℃ in vacuum (Au content: 0.15 mmol %).

2.3. Catalyst characterization

The morphologies of obtained Au/CTN-silica catalysts were examined by transmission electron microscope (TEM) (JEM-2010) and scanning electron microscopy (SEM) (JSM-7600F). The crystals of the catalysts were studied by X-ray diffraction (XRD) (X' Pert PRO PANalytical). Surface composition was determined by X-ray photoelectron spectroscopy (XPS), using a K-Alpha-surface Analysis system with X-Ray Monochromatisation. The fourier transformed-infrared spectroscopy (FT-IR) spectra of samples were obtained on a Bruker Tensor 27 spectrometer. Elemental analysis was determined by X-ray fluorescence spectrometry (XRF) (Magix PW 2403 XRF).

2.4 Catalyst test

Catalytic reactions were carried out in a batch reactor, a typical procedure was as follows: 0.02 g catalyst, 6 mmol substrate and 5 ml solvent were added into a 100 ml round-bottom flask equipped with a condenser and stirred for 5 min at room temperature, after addition of hydrogen peroxide, the reaction was started by immersing the flask in the oil bath kept at 60 ℃, then carried out with vigorous stirring for a certain time. The products were analyzed by gas chromatography (GC 9560) with a DB-1 capillary column, the nature of the products were also determined by gas chromatography-mass spectrometer (GC-MS).

3. Results and discussion

3.1. Catalyst characterization

3.1. Catalyst characterization

The XRD patterns of Au/CTN-silica catalyst showed that CTN was very well dispersed on silica nanosphere and the gold crystals were loaded on CTN-silica nanosphere (Fig.1a, b, d). For Au/CTN-silica catalyst, the 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 silica nanosphere (Fig. 1c). Fig.2 shows the qualitative identification of the structure vibration in the samples. The typical Si-O-Si bending, Si-O-Si symmetric stretching and Si-O-Si asymmetric stretching associated with the condensed silica network were present in all samples, corresponding to the vibration band at 470, 800 and 1,100 cm^{-1} [15], respectively. An absorption peak at around 970 cm^{-1} was attributed to stretching vibration of Si–OH groups. The intense band at 3430 cm^{-1} was assigned to -OH group asymmetric stretching, the peak around 1630 cm^{-1} was attributed to the stretching and bending vibrations of adsorbed H_2O [16]. The peak at 1597 and 1650 cm^{-1} was assigned for the N-H bending of the primary amine and C=O stretch of the secondary amide (Fig. 2a, c). In fact, the deformation vibration of NH group at 1597 cm^{-1} disappeared and a new band at 2036 cm^{-1} appeared after incorporation of the GNPs (Fig. 2d). This new band assigned to the NH group vibration of the amine group that shifted to higher wave numbers when interacting with the GNPs, which was contrary with the previous reports [17].

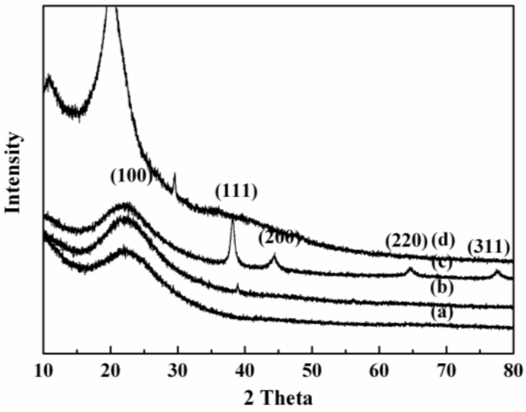


Fig.1 XRD patterns of (a) Silica nanosphere; (b) CTN-silica; (c) Au/CTN-silica catalyst; (d) CTN.

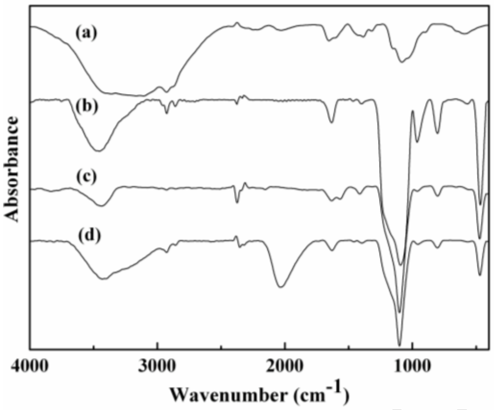
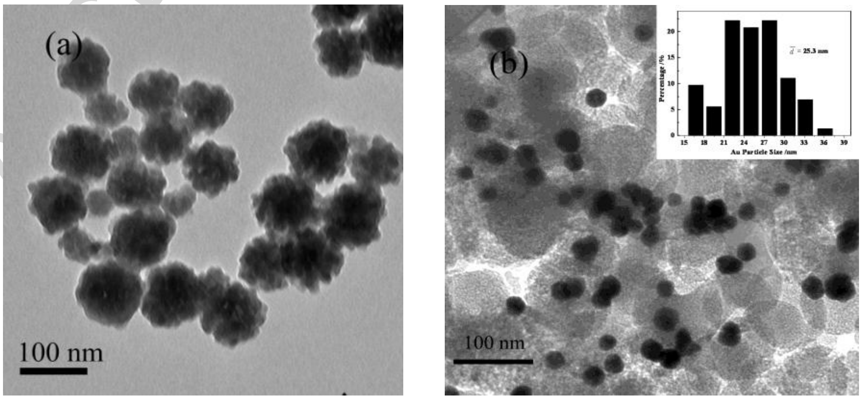


Fig.2 FT-IR spectra of (a) CTN; (b) silica nanosphere; (c) CTN-silica; (d) Au/CTN-silica catalyst.

Fig.3 shows a representative TEM picture of CTN-silica supports and Au/CTN-silica catalyst. TEM revealed that chitosan regimented equably around the silica nanosphere, and core-shell-type supports were obtained (Fig.3a). More precise information about the shape and size distribution of GNPs was obtained from TEM and HADDIF-STEM measurements, a careful analysis of the TEM images revealed that gold nanoparticles were highly dispersed in core-shell type support with the mean particle diameter of 25.3 nm (Fig.3b, c). SEM further testified that chitosan was deposited equably around the silica nanosphere (Fig.3d). BET showed that the Au-CTN-silica catalyst had a larger surface area (958 m^2/g), it was much larger than chitosan itself (0.65 m^2/g), which made it possible to exhibit high catalytic activity for organic reactions.



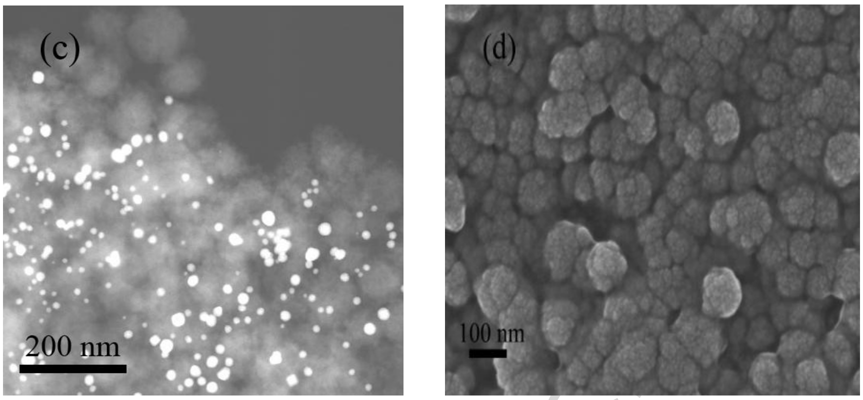


Fig.3 TEM images of (a) CTN (shell)-Silica (core), (b) Au/CTN-silica catalyst and (c) HADIFF-STEM, (d) SEM of Au/CTN-silica catalyst.

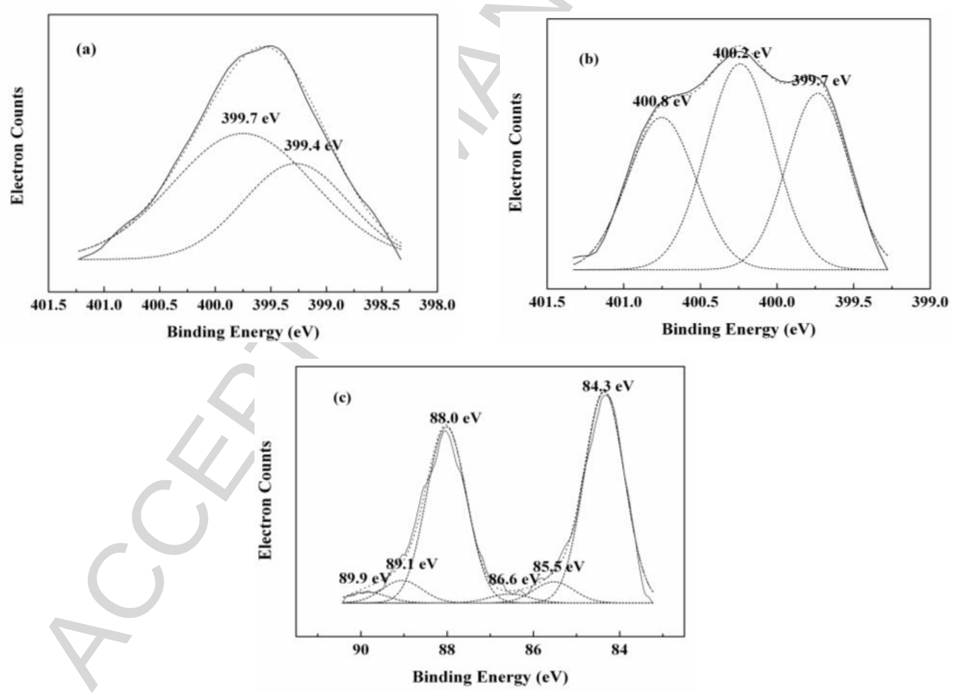


Fig.4 XPS spectra of N1s of (a) CTN-silica, (b) Au/CTN-silica and (c) Au 4f of Au/CTN-silica.

Fig.4 shows N 1s and Au 4f XPS spectra of Au/CTN-silica sample. In general, the banding energy at 399.1-399.7 eV in N 1s is attributed to sp^3 nitrogen [18], the peak at energy 399.4 eV are associated with -NH$_2$ [19], so the peak at 399.7 eV is assigned to -NH-C=O-. In Au/CTN-silica catalyst, the N 1s signal could be deconvoluted into three peaks at 399.7 eV, 400.2 eV and 400.8 eV, which were assigned to the to -NH-C=O- groups, GNPs bonded NH$_2$ and NH-C=O- groups, there were with 0.8 eV and 1.1 eV positive shift corresponding to the CTN-silica, respectively (Fig. 4a, b), it might due to the presence of an interaction between Au NPs and the N atoms. Clearly, the positive shift of the N 1s binding energy suggested that the electron of N atoms was transferred to gold atoms. Most of articles concluded that Au $4f_{7/2}$ at 84.0 eV was assigned to the metallic Au [20, 21], in the Au 4f region of Au/CTN-silica catalyst, six peaks could be observed mainly due to the Au $4f_{7/2}$ and Au $4f_{5/2}$ transitions. The signal at 84.3 eV indicated the presence of metallic gold species. Similarly, the peaks at 85.5 eV and 86.6 eV were assigned to Au^+ and Au^{3+}, respectively. From the XPS quantitative report, the atomic percentage of gold was estimated to be 0.5%, corresponding to 87.9% of Au^0, 3.6% of Au^{3+} and 8.5% of Au^+ (Fig. 4c), the reduction in valence state of gold was due to the electron transfer of N atoms, which further testified the interaction between Au NPs and N atoms.

3.2. Catalytic activity

The oxidation of sulfides to sulfoxides on Au/CTN-silica catalysts were investigated, sulfones has been the main by-products during the oxidation of sulfides. Initially, the oxidation of diphenyl sulfide was examined as a model reaction under different conditions; the results are shown in Table 1. The Au/CTN-silica catalyst showed the highest catalytic activity and selectivity for diphenyl sulfoxide in methanol, diphenyl sulfone was primary byproducts. Protic and aprotic solvents have different polarity (i.e. different dielectric constants), these solvents are chosen to form a single phase with organic substrates and hydrogen peroxide solution, so that the mass transfer problems associated with dissolubility are avoided. The solvents used in the experiments are CH_3OH, CH_3CN, $ClCH_2CH_2Cl$ and toluene, of which CH_3OH and H_2O are protic solvents; the other solvents are aprotic. The decrease order of dielectric constants is for protic solvents: MeOH (32.7) < H_2O (78.5), and for aprotic solvents: toluene (2.4) < $ClCH_2CH_2Cl$ (10.4) < CH_3CN (37.5), respectively. Obviously, for the aprotic solvents, the yield of diphenyl sulfoxide increased gradually with increasing polarity of solvents, polarity of solvent was a crucial factor to the activity and selectivity of catalyst, so only acetonitrile gave satisfactory results among these solvents (Table 1, entries 1-3). However, the protic solvents obviously were in favor of oxidation of sulfides, the conversion of diphenyl sulfide was 96.2% and the selectivity of diphenyl sulfoxide was 81.4% when the methanol was used as solvent (Table 1, entry 4). Meanwhile, the existence of Au/CTN-silica catalyst was crucial because no product was found without catalyst (Table 1, entry 5). Considering the cost of the solvent, we chose methanol as solvent and hydrogen peroxide as oxidant in next experiments.

Table 1. Selective oxidation of diphenyl sulfide using different solvents[a]

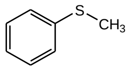
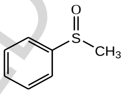
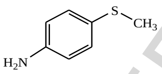
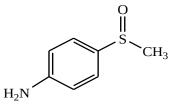
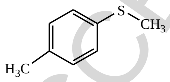
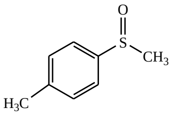
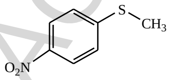
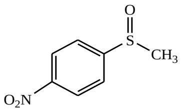
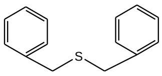
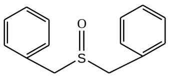
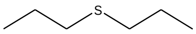
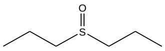
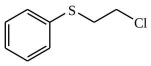
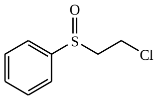
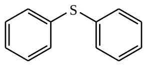
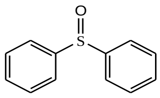
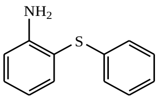
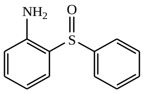
Entry	Solvent	Conversion (%)[b]	Product Selectivity (%)[b]	
			Sulfoxide	Sulfone
1	Toluene	0.7	100	0
2	Dichloroethane	12.4	86.7	13.3
3	Acetonitrile	87.1	70.6	29.4
4	Methanol	96.2	81.4	18.6
5[c]	Methanol	N.R.[d]	-	-
6	H_2O	7.2	96.2	3.8

[a] *Reaction conditions:* Au/CTN-silica catalyst 0.02 g, diphenyl sulfide 6 mmol, solvent 5 mL, H_2O_2 3 mL (30% in water), 60℃, 3 h. [b] Determined by GC. [c] Blank experiment, without catalyst. [d] N.R.: Reaction did not occur.

Next, we carried out oxidation of various sulfides under optimum conditions, the results are listed in Table 2.

As shown in Table 2, various sulfides showed good reaction activities and selectivities for the oxidation to corresponding sulfoxides. Obviously, methyl phenyl sulfide gave much higher yields (94.2% yield) than diphenyl sulfide (Table 2, entries 1), meanwhile，we observed the significant effects of electronic and steric factors of the substrates on the conversion of sulfide and selectivity for sulfoxide. Generally, sulfides with electron-rich side groups (hence, higher electron density on the -S- atom of the sulfide), such as 4-(methylthio)benzenamine and 4-methylthioanisole, were oxidized at a higher conversion than the electron-deficient 4-nitrothioanisole (Table 2, entries 3–5). In contrast, sulfides with greater steric hindrance showed lower conversion than those with less steric hindrance (Table 2, entries 7–8 vs. entry 6). Some straight-chain sulfides, such as dibenzylsulfane, showed good catalytic results for the corresponding sulfoxides. Meanwhile, it is interesting to note that both the conversion and selectivity for the oxidation of diphenyl sulfide and 2-(phenylthio) benzenamine (Table 2, entry 10) are much lower than those of other sulfides, which should be caused by the p system of this particular substrate [22]. Because the GNPs in Au/CTN-silica catalyst were anchored by dispersed Si-OHs, so the catalyst was easily separated from the reaction mixture, ICP analysis of filtrate confirmed that no leaching of Au species occurred. It was shown that the recovered Au/CTN-silica catalyst could be reused (Table 2, entry 2), meanwhile, the catalyst was filtered off after ca. 50% conversion at the reaction temperature, further treatment of the filtrate under similar reaction conditions did not afford to any products.

Table 2. Selective oxidation of various sulfides to sulfoxides over Au/CTN-silica catalyst[a]

Entry	Substrate	Product	Time (h)	Conversion[b] (%)	Selectivity[b] (%)
1			2	100	94.2
2[c]			2	100	93.7
3			1	97.6	100
4			2	100	96.7
5			6	81.5	100
6			4	96.8	100
7			2	100	99.2
8			1	88.5	100
9			3	96.2	81.4
10			3	66.5	92.9

[a] *Reaction conditions:* Au/CTN-silica catalyst 0.02 g, sulfide 6 mmol, methanol 5 mL, H_2O_2 3 mL (30% in water), 60℃. [b] Determined by GC. [c] Recycled experiment.

4. Conclusions

In this article, Au/CTN-silica catalyst was prepared by one-pot synthesis method, this catalyst showed high catalytic activity and good sulfoxide selectivity for the oxidation of sulfides using H_2O_2 as oxidant. The interactions between the GNPs and Si-OH groups guaranteed good dispersions of GNPs, and resulted in excellent catalytic performance. It is an environmental friendly, recycled and economical catalytic system.

Acknowledgements

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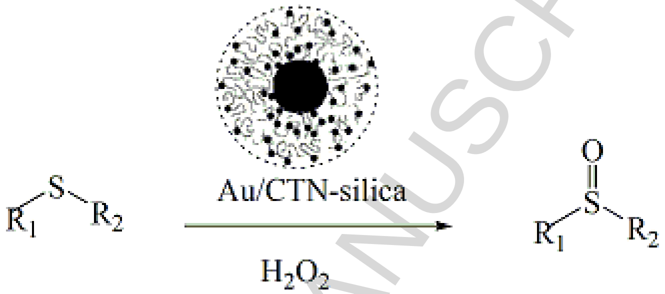
Selective oxidation of sulfides to sulfoxides using hydrogen peroxide over Au/CTN-silica catalyst

Fang Wang, Cheng Liu, Gui Liu, Wenxiu Li, Junhua Liu



Graphical abstract

Research Highlights

▸ Core (silica)-shell (chitosan) materials were constructed by the inverse microemulsion system. ▸ Au/CTN-silica catalyst was prepared using above core-shell materials as supports. ▸ This catalyst showed good catalytic activity and selectivity for the oxidations of sulfides to sulfoxides. ▸ Key factor governing catalytic property was Au NPs-support interactions.