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In situ synthesis of Au/Ti-HMS and its catalytic performance in oxidation of bulky sulfur compounds using *in situ* generated H_2O_2 in the presence of H_2/O_2

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ABSTRACT

Gold particles are supported on Ti-containing mesoporous silica (Ti-HMS) through an in situ process. The obtained samples were characterized by a series of techniques including ICP, powder X-ray diffraction, N_2 sorption, UV-visible spectroscopy and transmission electron microscopy. The performance of the catalyst in direct synthesis of H_2O_2 from H_2/O_2 in methanol solvent and oxidative desulphurization using the in situ generated H_2O_2 have been systematically investigated. The results show that in situ synthesized Au/Ti-HMS, the organic template of which is eliminated via extraction with ethanol, successfully maintains the typical wormhole structure of HMS and possesses uniform mesopores, which is confirmed by N_2 sorption and TEM. UV-visible spectroscopy result confirms the simultaneous existence of Au and Ti active centers in this bifunctional catalyst. Gold particles supported on Ti-HMS show high activity in the direct synthesis of H_2O_2 from H_2 and O_2 in methanol solvent. Furthermore, high removal rate of bulky sulfur compounds can be obtained using the in situ generated H_2O_2 over Au/Ti-HMS. Final conversion rate of the substrates confirms the dominant role of the in situ H_2O_2 oxidation in deep desulphurization. In addition, this bifunctional catalyst can avoid the insufficiency of H_2O_2 caused by the decomposition comparing with the Ti-HMS/commercial H_2O_2 system.

1. Introduction

Oxidative desulphurization (ODS) for fuel oil has received increasing attention primarily for environmental reasons [1,2]. In this technology, bulky sulfur compounds such as benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) can be oxidized into their corresponding sulfoxides or sulfones, which are then removed by simple liquid–liquid extraction [3]. Using H_2O_2 as the green oxidant, bulky sulfur compounds in model oil can be effectively eliminated over Ti-HMS under mild conditions due to the capacious Ti framework channel [4–6]. However, the atom economy is depressed because of the continuous decomposition of commercial H_2O_2 during the 333 K reaction. Direct synthesis of hydrogen peroxide from H_2 and O_2 has been studied for many years. Investigations of the catalyst for this reaction are focused on Pd, which is designed to be combined with active supports for the generated hydrogen peroxide being used in situ [7–9], but many side reactions may become dominant in the absence of additives such as halide anions [10]. Recently, the supported gold catalysts also show high activity in direct synthesis of H_2O_2 from H_2 and O_2 [11–13]. To be worth mentioning, there are less side reactions with a gold catalyst being used instead of costly Pd. To sum up, oxidations of organic substrates over supported gold catalyst can be achieved in the absence of commercial H_2O_2 as H_2O_2 directly generating in situ.

Supported gold catalysts have been intensively studied in recent years. Supports and preparation methods are two of the main factors that influence the size and the activity of gold particles. Mesoporous silicas, which possess large pore size and high specific surface and show excellent performance for the conversion of bulky reactants, are notable supports for gold loading. The mesoporous materials supported gold catalysts, including Au/MCM-41 [14], Au/Ti-MCM-41 [15], Au/HMS [16], Au/MCM-48 [17], and Au/Ti-SBA-15 [18], etc have already been prepared successively. On the other hand, deposition–precipitation (DP) is considered as an effective method to prepare supported gold catalysts due to the uniform size and excellent activity of the gold particles [19,20]. However, the mesoporous material such as HMS has poor hydrothermal stability [21,22]. As a result, the intrinsic mesoporous structure is possible to be damaged under the conditions of DP approach, which is confirmed in this paper.

Herein, we report an in situ method to prepare the Au/Ti-HMS catalyst, and in particular, the intact HMS structure has been maintained successfully. In addition, performance of the as-obtained catalyst in oxidative removal of bulky sulfur compounds for model oil using the in situ generated H_2O_2 has been systematically investigated.

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2. Experimental section

2.1. Materials

Tetraethylorthosilicate (TEOS), ethanol, isopropyl alcohol (IPA), *n*-octane, urea and H_2O_2 (30 wt%) were purchased from Tianjin Kermel Chemical Co. $HAuCl_4 \cdot 4H_2O$, Tetrabutylorthotitanate (TBOT) and dodecylamine (DDA) were purchased from Shanghai Chemical Co. Benzothiophene (BT), dibenzothiophene (DBT), and 4,6-dimethyl dibenzothiophene (4,6-DMDBT) were purchased from Acros Organics Co.

2.2. Preparation of catalysts

Au/Ti-HMS was synthesized through an in situ process based on the preparation of Au/HMS [16] and Ti-HMS [23]. The first solution (solution A) was prepared by slowly adding 14.3 g H_2O in the mixture of 7.6 g ethanol and 1.25 g dodecylamine (DDA) while stirring. The second solution (solution B) was prepared by adding 5.2 g tetraethylorthosilicate (TEOS) in the mixture of 1.55 g isopropyl alcohol (IPA) and 0.17 g tetrabutylorthotitanate (TBOT). Solution B and 20 ml ethanol solution of $HAuCl_4$ (0.024 M) were simultaneously dropped into solution A then aged for 18 h with vigorous stirring. The product with theoretical molar ratios of $SiO_2/TiO_2/DDA/Au^{3+}$ at 1.0/0.02/0.27/0.02 was filtered and washed, then dried at 333 K. Gold particles are easy to sinter in the case of template DDA being eliminated via calcination at high temperature. Therefore, DDA was extracted by ethanol at ambient temperature. Then the dried powder was calcined at desired temperature for 4 h. The samples extracted with ethanol, 913 K directly calcined and extracted then 673 K calcined are labeled as Au/HMS-a, Au/HMS-b, and Au/HMS-c, respectively. Ti-HMS was prepared following the same process with no ethanol solution of $HAuCl_4$ added. In addition, the template of Ti-HMS was eliminated via direct calcination at 913 K. Au/Ti-HMS-DP was prepared by heating the mixture of 1 g Ti-HMS, 10 ml $HAuCl_4 \cdot 4H_2O$ solution (0.024 M) and 0.8 g urea at 353 K for 12 h and then ageing for 6 h at ambient temperature. After washing, separation, drying and 673 K calcination for 4 h, a DP sample with 4% gold loading was obtained. The detailed compositions for the materials are presented in Table 1.

2.3. Characterization methods

The real Au loadings of the catalysts were determined by ICP (Leeman Plasma-Spec-II). The compositions of the samples were obtained on a Bruker SRS-3400 sequential X-ray spectrometer (XRF). Powder X-ray diffraction (XRD) patterns were recorded using Rigaku D/Max 2400 diffractometer employing Cu Kα radiation. N_2 adsorption isotherm was measured using a Quantachrome Autosorb-1 physical adsorption apparatus. The pore size distribution was calculated according to the Barrett–Joyner–Halenda (BJH) model. UV-vis spectra were obtained on a JASCO UV550 spectrometer with $BaSO_4$ as the internal standard. Transmission electron microscopy (TEM) images were taken on Tecnai G^2 20 S-twin instrument (FEI Company) with an acceleration voltage of 200 kV.

2.4. Catalytic performance

Catalyst testing for direct synthesis of H_2O_2 was performed using a stainless steel autoclave charged with catalyst (0.13 g), solvent (10 ml methanol), H_2/N_2 (0.3/0.2 MPa) and O_2/N_2 (0.9/0.1 MPa) while stirring. H_2O_2 yield was determined by iodometric titration. BT (1550 ppm), DBT (2700 ppm) and 4,6-DMDBT (1980 ppm) were, respectively, dissolved in *n*-octane as the model oil. ODS using the in situ generated H_2O_2 was tested under the same conditions with 10 ml model oil added, which was heated by a water bath. ODS using the commercial H_2O_2 was performed at 333 K in a three neck glass flask charged with catalyst (0.13 g), solvent (10 ml methanol), model oil (10 ml) and 30% H_2O_2 (H_2O_2:S mol ratio = 2:1) while stirring. The oil phase and the methanol phase were analyzed using GC HP6890-FPD. The removal rate (R) of sulfur compounds is expressed as in Eq. (1) and the conversion rate (C) of sulfur compounds is expressed as Eq. (2).

$$R = \frac{M_0C_0 - M_0C_{t,1}}{M_0C_0} \times 100\% = \frac{C_0 - C_{t,1}}{C_0} \times 100\% \quad (1)$$

$$C = \frac{M_0C_0 - M_0C_{t,1} - M_1C_{t,2}}{M_0C_0} \times 100\% \quad (2)$$

M_0 is the mass of model oil (*n*-octane); M_1 is the mass of solvent (methanol); C_0 is the initial mass concentration of sulfur compounds; $C_{t,1}$ is the mass concentration of sulfur compounds in model oil after reacting *t, h*, $C_{t,2}$ is the mass concentration of sulfur compounds in solvent after reacting *t, h*.

3. Results and discussion

The in situ synthesis of Au/Ti-HMS includes three main phases: stabilization of Au^{3+} by organic template, self-assembly of Si–Ti species and extraction of template using ethanol. In order to check the mesoporous structure of the support and the gold loading state, a series of characterization results for the samples are listed. Fig. 1 presents low-angle powder XRD patterns of the samples using different treatment processes and the sample prepared by DP using urea as the precipitator. Each sample prepared by the in situ method exhibits a diffraction peak at 2.4°, which is a characteristic of HMS materials [23]. Contrarily, the intrinsic ordered structure of Ti-HMS was seriously damaged during DP of gold with urea, which resulted in the absence of 2.4° peak. In Fig. 1, the similar peaks of HMS type indicate that Au/Ti-HMS-c possesses almost the same pseudo-ordered pores as Au/Ti-HMS-b. Therefore, to avoid the sintering of gold, the organic template can be eliminated via extraction with ethanol and further 673 K calcination instead of direct calcination at high temperature. As for Au/Ti-HMS-a, which is uncalcined, the peak intensity is possibly affected by residual water or template in pores. The four Bragg reflections at 38.2°, 44.4°, 64.6°, 77.5° which correspond to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) faces of Au crystal at wide-angle region [24] show that the gold nanoparticles have formed on the support (Fig. 2). As shown in gold peaks of Au/Ti-HMS-a, Au^{3+} species has already started to be reduced to Au^0 during extraction of the organic template dodecylamine. On the other hand, the size of gold particles enlarges evidently as the sample calcined at 913 K, which can be deduced from the four intense gold peaks of Au/Ti-HMS-b. In

Table 1
Compositions of Ti-HMS and Au/Ti-HMS samples.

Sample	Theoretical gold loading (wt%)	Product gold loading (wt%)	Gel SiO_2/TiO_2 (mol/mol)	Product SiO_2/TiO_2 (mol/mol)
Ti-HMS	0	0	50	41
Au/Ti-HMS-DP	4	4.6	50	42
Au/Ti-HMS-c	4	3.9	50	41