Catalysis Today 149 (2010) 127–131

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Characterization and catalytic performance of Au/Ti-HMS catalysts on the oxidative desulphurization using in situ H_2O_2: Effect of method catalysts preparation

Hai-Yan Song [a], Gang Li [a,*], Xiang-Sheng Wang [a], Yi-Jun Xu [b,**]

[a] Department of Catalytical Chemistry and Engineering, State Key Laboratory of Fine Chemicals, Dalian University of Technology, 158 Zhongshan Road, Dalian 116012, China
[b] Research Institute of Photocatalysis, State Key Laboratory Breeding Base of Photocatalysis, College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou 350002, China

ARTICLE INFO

Article history:
Available online 23 May 2009

Keywords:
Gold catalysts
In situ
Deposition–precipitation
Hydrogen peroxide
Oxidative desulphurization

ABSTRACT

Au/Ti-HMS was prepared by in situ method, NH_3 deposition–precipitation (NH_3 DP) and urea deposition–precipitation (Urea DP), respectively. The catalysts were characterized by a series of techniques including ICP, powder XRD, N_2 sorption, UV–visible spectroscopy, TEM and H_2-TPR. Using n-octane containing BT, DBT and 4,6-DMDBT as model compound, the performance of the catalysts in oxidative desulfurization (ODS) using in situ generated H_2O_2 from H_2 and O_2 were investigated. The results show that preparation method influences porous structure of the support and gold particles size. In situ sample has maintained the intrinsic structure of Ti-HMS, whereas, the gold particles are not as uniform and small as that of DP sample. NH_3 DP sample still possesses the wormhole structure of HMS despite the absence of typical XRD peak. The mesoporous structure of urea DP sample has been damaged seriously. Au^{3+} on outer surface of the support is easier to be reduced than that in pores, as confirmed by H_2-TPR. In addition, the three samples exhibit different catalytic activities in ODS using in situ H_2O_2 as oxidant. For the removal of BT and DBT, Au/Ti-HMS (NH_3 DP) exhibits the highest catalytic activities. Regarding the removal of 4,6-DMDBT, the optimum catalyst is Au/Ti-HMS (In situ); however, Au/Ti-HMS (Urea DP) nearly loses catalytic activity.

1. Introduction

Supported gold catalysts have been intensively studied in recent years [1–4]. There are many factors influencing the catalytic activity of gold catalyst such as gold deposition method, support, gold particles size, loading amount of gold and calcination temperature [5–7]. As the research goes forward, various supports and preparation methods have been developed. Mesoporous materials are the novel supports for gold particles due to the capacious pore channels and large specific surface areas compared with microporous zeolites. Gold with higher loading can be uniformly dispersed in mesoporous channels as nanoscale particles and catalytic performances for the selective oxidation reactions of bulky molecules can be improved. A series of mesoporous silica-supported gold catalysts including Au/SBA-15, Au/MCM-41, Au/Ti-MCM-41 and Au/HMS have been synthesized successively [8–10]. Haruta's group has prepared Au/Ti-MCM-41 to achieve the vapor phase propylene epoxidation [11]. Au/MCM-41 is also used in the selective oxidation of cyclohexane [12]. On the other hand, appropriate method should be chosen to synthesize gold catalysts and the supports have a critical effect on the morphology of gold particles. Deposition–precipitation (DP) is considered as an important method to prepare supported gold catalysts due to the average size and the excellent activity of gold particles [13–15]. Noticeably, the hydrothermal or basic conditions for gold deposition may influence the intrinsic structure of the support. As a result, it is important to exploit a special method aiming at maintaining the original characteristic of the support and improving the activity of gold catalyst.

Ti-HMS is a promising mesoporous material in petrochemical processing and green catalysis [16–18]. In our previous research, Ti-HMS exhibited excellent activity in the removal of bulky sulfur compounds such as benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) for model oil using H_2O_2 as oxidant [19–21]. Benzothiophene and its derivatives are oxidized into their corresponding sulfoxides or sulfones which are then removed by simple liquid–liquid extraction. But continuous decomposition of commercial H_2O_2 during the 333 K reaction may lower the atom economy. Recently, pilot study on the preparation of Au/Ti-HMS by DP using ammonia as the precipitator and its catalytic performance in direct synthesis of H_2O_2 in the

---

* Corresponding author. Fax: +86 411 8368 9065.
** Corresponding author.
E-mail addresses: liganghg@dlut.edu.cn (G. Li), yjxu@fzu.edu.cn (Y.-J. Xu).

0920-5861/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2009.04.013

presence of H_2 and O_2 has been achieved [22]. Further, using the continuously generated H_2O_2 in situ, the bulky sulfur compounds are expected to be eliminated by an oxidation process. In the present work, we report the preparation of Au/Ti-HMS by three different methods, and compare the effects of the preparation methods on the intrinsic structure of the support via a series of characterizations. In addition, the catalytic performance of the three catalysts in the oxidative desulphurization using the in situ generated H_2O_2 was investigated.

2. Experimental

2.1. Preparation of Ti-HMS and Au/Ti-HMS (In situ)

Au and Ti components of in situ sample were simultaneously introduced into HMS following Refs. [10,23]. Phase A: 14.3 g H_2O was added in the mixture of 7.6 g ethanol and 1.25 g dodecylamine (DDA); Phase B: 5.2 g tetraethylorthosilicate (TEOS) was added in the mixture of 1.55 g isopropyl alcohol (IPA) and 0.17 g tetrabutylorthotitanate (TBOT). Phase B and 20 ml ethanol solution of $HAuCl_4$ (0.024 mol/l) were simultaneously dropped into Phase A then aging for 18 h. Then the template DDA was extracted by ethanol at ambient temperature. After washing, drying and calcination at 673 K for 4 h, Au/Ti-HMS (In situ) was obtained finally. The synthesis of Ti-HMS is similar but without Au added. In addition, the template of Ti-HMS was eliminated via direct calcination at 913 K.

2.2. Preparation of Au/Ti-HMS (NH_3 DP)

Au/Ti-HMS (NH_3 DP) with 4% of target gold loading was prepared by dripping diluent ammonia (0.05%) to the mixture of $HAuCl_4 \cdot 4H_2O$ solution and prepared support Ti-HMS until pH rising to 8. The mixture was stirred for 18 h at ambient temperature, then washed using distilled water and separated. The dried powder was calcined at 573 K for 4 h.

2.3. Preparation of Au/Ti-HMS by urea DP

The mixture of Ti-HMS, diluent $HAuCl_4 \cdot 4H_2O$ solution and urea (mass ratio of Au:urea = 0.025:1) was heated at 353 K for 12 h and then aged for 6 h at ambient temperature. After washing and separation, the dried powder was calcined at 673 K for 4 h. Sample Au/Ti-HMS (Urea DP) with 4% of target gold loading was obtained finally.

2.4. Catalyst characterization

Au loadings of the catalysts were determined by ICP (Leeman Plasma-Spec-II). 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. 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. H_2 temperature programmed reduction (H_2-TPR) was carried out on GC-7890T-TCD. The flowing rate of 10% H_2/N_2 is 40 ml/min and the temperature increased at the rate of 10 K min^{-1}.

2.5. Catalytic activity

BT (1550 ppm), DBT (2700 ppm) and 4,6-DMDBT (1980 ppm) were respectively dissolved in n-octane as model oil. Catalyst testing for oxidation of benzothiophene derivatives using the in situ generated H_2O_2 was performed using a stainless steel autoclave charged with catalyst (0.14 g), solvent (10 ml methanol), model oil (10 ml), H_2/N_2 (0.3 MPa/0.2 MPa) and O_2/N_2 (0.9 MPa/0.1 MPa) under stirring. After reacting at 333 K for 0.5–4 h, the reactor was rapidly cooled to ambient temperature. Then the remnants of sulfur compounds in oil phase were analyzed by GC HP6890-FPD.

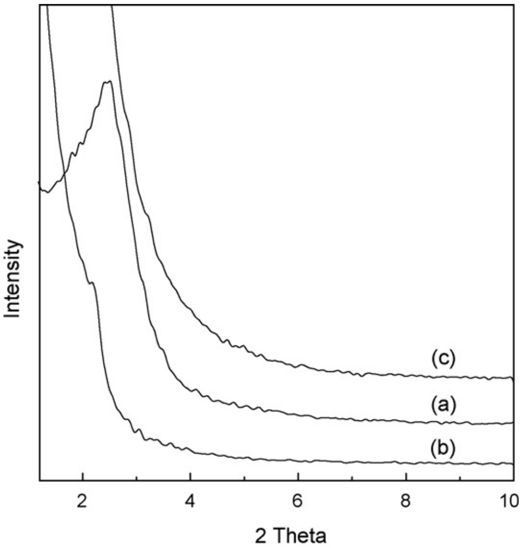

Fig. 1. Low-angle XRD patterns of (a) Au/Ti-HMS (In situ), (b) Au/Ti-HMS (NH_3 DP) and (c) Au/Ti-HMS (Urea DP).

3. Results and discussion

3.1. Characterizations of the samples

As determined by ICP, the real gold loadings of Au/Ti-HMS (In situ), Au/Ti-HMS (NH_3 DP) and Au/Ti-HMS (Urea DP) is 3.89 wt.%, 4.71 wt.% and 4.59 wt.%, respectively. The samples have the gold loadings between 3.9 wt.% and 4.7 wt.%. During in situ process, most of gold was supported on Ti-HMS. As for the other two samples, the dissolution of the prepared support in alkaline system may result in the higher gold loading amount.

Low-angle and wide-angle powder X-ray diffraction (XRD) patterns are shown in Figs. 1 and 2, respectively. In Fig. 1, only in situ sample exhibits an intense first-order ($d_{1\,0\,0}$) diffraction peak accompanied by broader unresolved higher order reflections, indicating that this material possesses a mesostructure with the lack of long-range order [24]. Contrarily, there is no peak for the

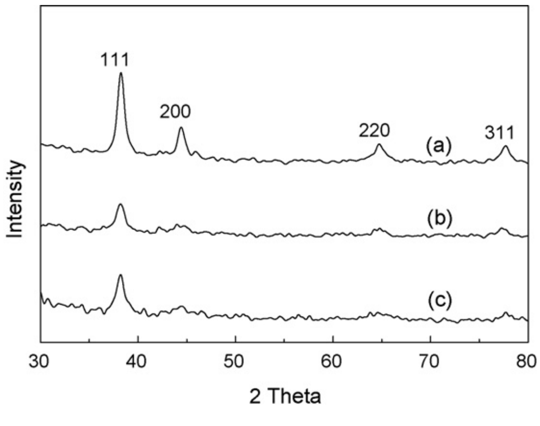

Fig. 2. Wide-angle XRD patterns of (a) Au/Ti-HMS (In situ), (b) Au/Ti-HMS (NH_3 DP) and (c) Au/Ti-HMS (Urea DP).

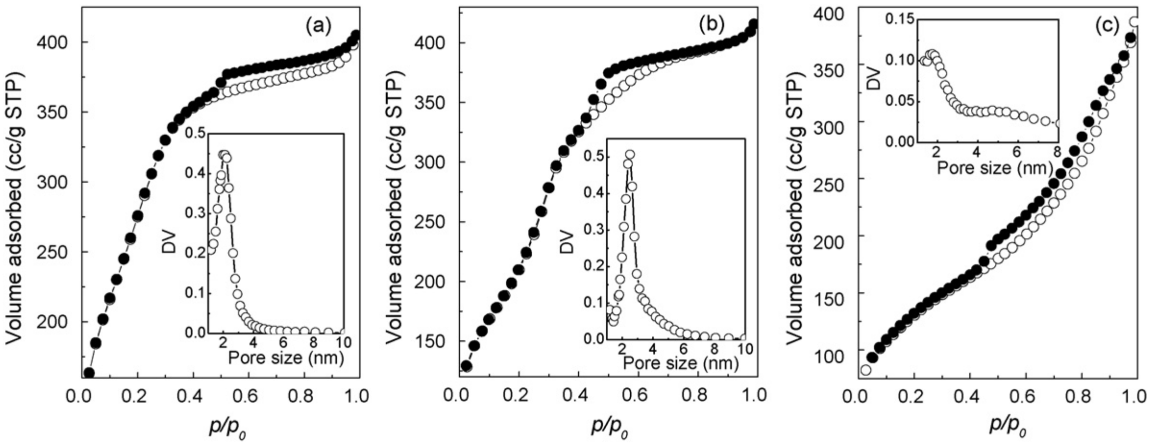

Fig. 3. Nitrogen adsorption–desorption isotherms and pore size distribution of (a) Au/Ti-HMS (In situ), (b) Au/Ti-HMS (NH_3 DP) and (c) Au/Ti-HMS (Urea DP).

samples prepared by DP with ammonia or urea, because the pseudo-order, which HMS mesoporous possesses, is possible to be damaged in alkali or hydrothermal circumstance. Generally, the low-angle XRD patterns of DP samples can only demonstrate that the ordering of the mesoporous was disturbed, however, the mesoporous structure of the support may be undamaged. The wide-angle (XRD) patterns are shown in Fig. 2 to demonstrate the formation of gold nanoparticles. The four peaks appear near 38.3°, 44.5°, 64.7° and 77.7°, which can be assigned to the diffractions of (1 1 1), (2 0 0), (2 2 0) and (3 1 1) structure, demonstrating the face-centered cubic metal gold structure is formed [25]. In addition, the intensity of wide-angle peaks also reflects the order of gold particles size obtained using different methods. The gold nanoparticles prepared by in situ method may be larger than that prepared by DP, as shown via the stronger gold diffraction peaks in the wide-angle region, and NH_3 DP is possible to generate the smallest gold particles.

The nitrogen adsorption–desorption isotherms of the samples are shown in Fig. 3. Both Au/Ti-HMS (In situ) and Au/Ti-HMS (NH_3 DP) exhibit type IV isotherms according to the IUPAC classification, with a typical H1 hysteresis loop typical of mesoporous solids. This type of hysteresis loop indicates that materials possess uniform pore size and shapes [26]. Each slope with a sharp step at P/P_0 of 0.2–0.4 indicates the capillary condensation in mesopores [27]. Whereas, the Au/Ti-HMS (Urea DP) sample exhibits no sharp slope in this field. Therefore, the sample prepared by NH_3 DP still possesses mesoporous volume despite that there is no typical XRD peak of Ti-HMS. As for the sample prepared by urea DP, its mesopores was seriously damaged during the preparation because of the poor hydrothermal stability of Ti-HMS. In Fig. 3, both Au/Ti-HMS (In situ) and Au/Ti-HMS (NH_3 DP) exhibit uniform pore size distribution which show well-defined maximum around 2.1 nm and 2.5 nm, respectively. As shown in Table 1, the mean pore size of NH_3 DP sample is enlarged to a certain extent comparing with that of support Ti-HMS without any post-treatment. In addition, the specific surface area of in situ sample can exceed 1020 m^2/g comparing with other samples.

Fig. 4 shows the UV–visible spectra of the samples. The 210–220 nm peaks of the three samples prove the existence of framework Ti species with tetrahedral coordination, which are the active centers of the samples. Although Au/Ti-HMS (Urea DP) possesses no typical mesoporous structure of HMS, the framework Ti still exists in this sample. For all the samples, no absorption at 330 nm indicates the absence of anatase phase. A strong resonance at 520–550 nm, which is attributed to the absorption of surface plasmon vibration in gold nanoparticles, is seen in each spectrum [28]. For NH_3 DP sample, the broadening of gold absorption peak is resulted from the increasing of gold containing as well as the uniform dispersion of gold particles. The gold absorption band of Urea DP sample is sharper and narrower than that of NH_3 DP sample, indicating the gold existing as a bigger size. As for In situ sample, the incomplete reduction and load of gold results in the weaker adsorption. The UV–vis result of gold particles well agrees with the observation in TEM.

The TEM images shown in Fig. 5 provide insights into the porosity framework structure of Ti-HMS after modification by gold. Typical wormhole-like pores of HMS materials exist in both in situ sample and NH_3 DP sample. The network channels and pore

Table 1
Structural properties of Au/Ti-HMS samples.

Sample	Pore size[a] (nm)	BET surface area (m^2/g)	Total pore volume[b] (cm^3/g)
Ti-HMS [19]	2.3	829.7	0.69
Au/Ti-HMS (In situ)	2.1	1024	0.62
Au/Ti-HMS (NH_3 DP)	2.5	770.1	0.64
Au/Ti-HMS (Urea DP)	–	466.7	0.60

[a] Calculated from adsorption branch of nitrogen isotherm using BJH model.
[b] Calculated from the volume adsorbed of P/P_0 at 0.99.

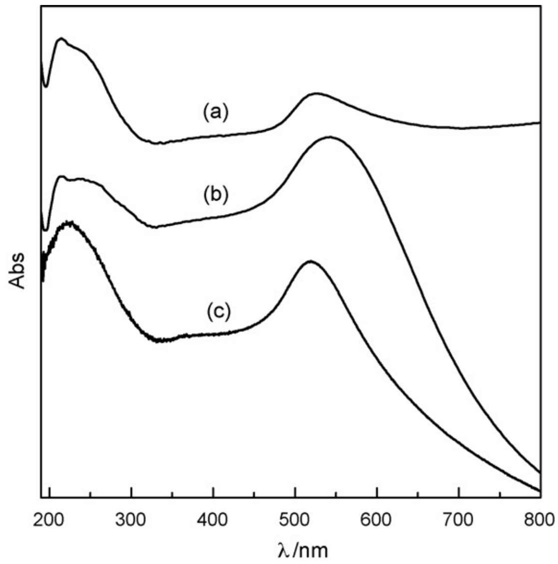

Fig. 4. UV–visible spectra of (a) Au/Ti-HMS (In situ), (b) Au/Ti-HMS (NH_3 DP) and (c) Au/Ti-HMS (Urea DP).

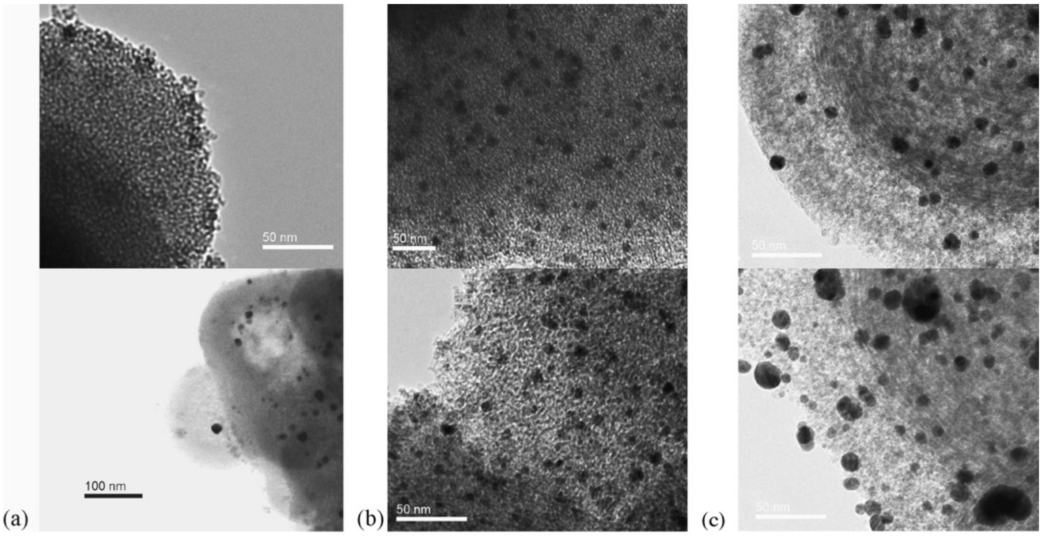

Fig. 5. TEM images of (a) Au/Ti-HMS (In situ), (b) Au/Ti-HMS (NH_3 DP) and (c) Au/Ti-HMS (Urea DP).

size are uniform, although long rang order is absent. Contrarily, there is no typical wormhole structure existing in urea DP sample. Uniform and small gold particles (about 5 nm) can be prepared by NH_3 DP method. Whereas, the gold particles prepared by urea DP method are non-uniform. The density of observable gold particles prepared by in situ method is rather low.

H_2-TPR profiles obtained from the uncalcined samples are shown in Fig. 6. Both NH_3 DP sample and urea DP sample contain a remarkable reduction peak near 450 K, which is assigned to the reduction of Au^{3+} distributed on the outer surface of the support. The TCD signal of H_2 consumption at 450 K shows that most of the Au^{3+} species can be easily reduced to metallic gold at a low temperature. In addition, there is another intense reduction peak near 850 K for Au/Ti-HMS (NH_3 DP), which is possibly attributed to the H_2 consumption for the difficult reduction of Au^{3+} species existing in the pores of the support. The 850 K peak of urea DP sample seems rather weaker, because the damaged or enlarged pores result in the easy reduction of Au^{3+}. Contrarily, the absence of reduction peak shows that no Au^{3+} exists in the uncalcined in situ sample, the reason of which can be explained as the formation of metallic gold during the extraction of template using the pseudo-reducer ethanol [29].

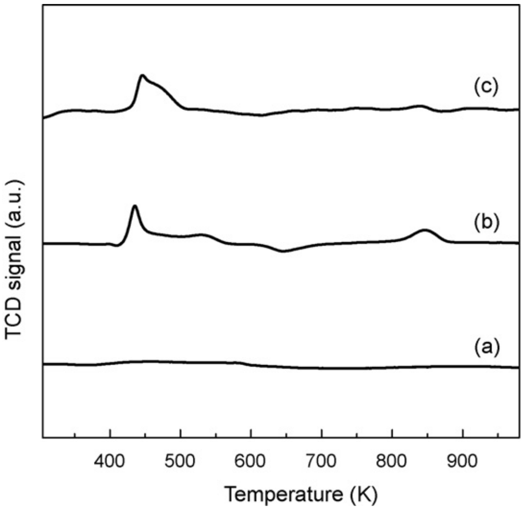

Fig. 6. H_2-TPR profiles of 0.05 g uncalcined (a) Au/Ti-HMS (In situ), (b) Au/Ti-HMS (NH_3 DP) and (c) Au/Ti-HMS (Urea DP) treated at 373 K for 1 h.

3.2. Catalytic tests of the samples

In our previous study, direct synthesis of H_2O_2 in the presence of H_2 and O_2 over Au/Ti-HMS prepared by NH_3 DP has been investigated [22]. However, our final target is in situ using the H_2O_2 in the oxidative desulphurization. Therefore, oxidation of BT, DBT and 4,6-DMDBT using in situ generated H_2O_2 with different catalysts has been investigated and the results are shown in Figs. 7–9, respectively. Successful oxidation of these bulky sulfur compounds is decided by three important factors: sufficient in situ H_2O_2 yield, electron density on the sulfur atom and enough pore size of the catalyst [19,29,30]. For the removal of BT and DBT (Figs. 7c and 8c), although Au/Ti-HMS (Urea DP) loses typical mesoporous structure of HMS, it still gives high final removal rate because of the existence of framework Ti, as shown in the UV–visible spectra (Fig. 4c). Both Au/Ti-HMS (NH_3 DP) and Au/Ti-HMS (In situ) can give final removal rate of 100% for BT and DBT, which is a little higher than that with urea DP sample (Figs. 7 and 8). NH_3 DP sample, which possesses uniform and small gold nanoparticles, is possible to generate high concentration of H_2O_2 in situ. Therefore, the removal rate of BT at 2 h over Au/Ti-HMS (NH_3 DP) is a little higher than that over Au/Ti-HMS (In situ). As reported, the oxidative elimination for 4,6-DMDBT is the most difficult in the three compounds, because the oxidation of 4,6-DMDBT with the substituents at the fourth and sixth position requires more molecular accessibility and capacious space

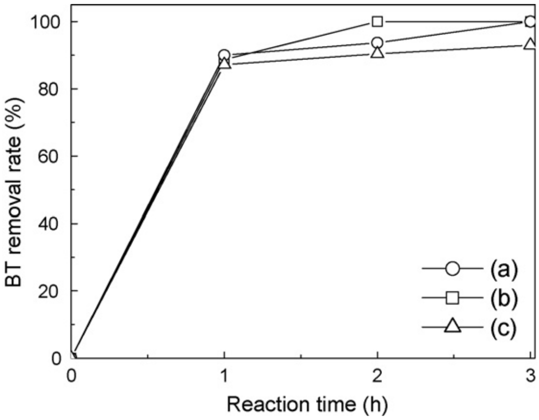

Fig. 7. Oxidation of BT using in situ generated H_2O_2 over (a) Au/Ti-HMS (In situ), (b) Au/Ti-HMS (NH_3 DP) and (c) Au/Ti-HMS (Urea DP).

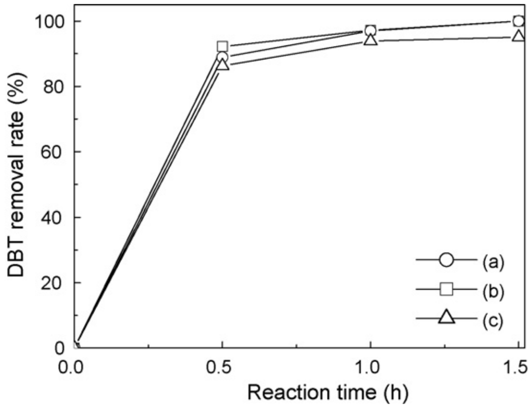

Fig. 8. Oxidation of DBT using in situ generated H_2O_2 over (a) Au/Ti-HMS (In situ), (b) Au/Ti-HMS (NH_3 DP) and (c) Au/Ti-HMS (Urea DP).

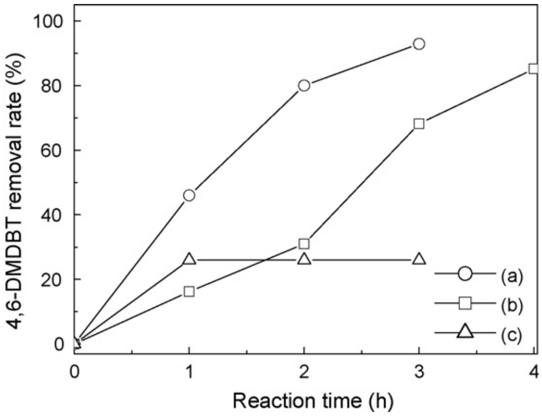

Fig. 9. Oxidation of 4,6-DMDBT using in situ generated H_2O_2 over (a) Au/Ti-HMS (In situ), (b) Au/Ti-HMS (NH_3 DP) and (c) Au/Ti-HMS (Urea DP).

[19,21,30]. The removal rate of 4,6-DMDBT can only reach 26% with Au/Ti-HMS (Urea DP) which possesses no obvious mesoporous structure, and it no longer increases as the reaction time increasing. As using Au/Ti-HMS (In situ) or Au/Ti-HMS (NH_3 DP), two oxidation products, 4,6-DMDBTO and 4,6-$DMDBTO_2$, can be detected by GC. But there are no products when using Au/Ti-HMS (Urea DP) for 3 h. On the other hand, the blank test using only extractant methanol without catalyst and oxidant shows the same removal rate as Fig. 9c. Therefore, the main contribution of 4,6-DMDBT removal is from methanol extraction and no oxidation reaction happened using Urea DP sample (Fig. 9c). Although NH_3 DP sample possesses more uniform and smaller gold particles on the support, the removal rate of 4,6-DMDBT is much lower than that of in situ sample. The main reasons are that Au/Ti-HMS (In situ) maintains entire structure of HMS and possesses larger surface area than other samples, as confirmed by the above characterization results. To sum up, the concentration of in situ generated H_2O_2 is possibly the main factor that decides the final removal rate of BT. But that influences the removal of DBT unremarkably. Effective removal of DBT can be achieved just as the simultaneous existence of gold particles and framework Ti in HMS, because DBT is easy to be oxidized by H_2O_2. In addition, successful maintenance of HMS mesoporous obviously contributes to effective removal of 4,6-DMDBT which is more difficult to be oxidized. Therefore, the sample with absolute mesoporous and high specific surface area can obtain a high removal rate of 4,6-DMDBT finally.

4. Conclusions

Effective gold loading can be obtained by three methods and each sample contains Au and framework Ti active centers simultaneously. Whereas the mesoporous structure of urea DP sample has been seriously damaged in the hydrothermal system. On the other hand, the temperature of Au^{3+} being reduced to Au^0 is decided by the form of Au species existing in Ti-HMS support. Uniform and small gold nanoparticles can be prepared by DP method using NH_3 as the precipitator.

Using the in situ generated H_2O_2 from H_2 and O_2, all the samples can achieve almost complete removal of BT and DBT. And NH_3 DP sample exhibits a little superiority. For the removal of 4,6-DMDBT, in situ sample with large surface area shows excellent activity comparing with DP samples. The urea DP sample with no intact mesopores has lost the catalytic activity to oxidize 4,6-DMDBT. These samples could have high sulphur removal ability for real diesel oil using the in situ generated H_2O_2. In addition, further research on deactivation and regeneration of these catalysts is in progress.

Acknowledgements

The Project is sponsored by the Foundation for the Author of National Excellent Doctoral Dissertation of PR China (No. 200346), Program for New Century Excellent Talents in University (NCET-04-0270), National Natural Science Foundation of China (No. 20406005) and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry. Yi-Jun Xu thanks the Award Program of Minjiang River Scholar Professorship and Support by Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT0818).

References

[1] M. Haruta, Catal. Today 36 (1997) 153.
[2] G. Li, J. Edwards, A.F. Carley, G.J. Hutchings, Catal. Today 114 (2006) 369.
[3] Z.Y. Zhong, J.Y. Lin, S.-P. The, J. Teo, F.M. Dautzenberg, Adv. Funct. Mater. 17 (2007) 1402.
[4] F. Moreau, G.C. Bond, Catal. Today 122 (2007) 260.
[5] A.K. Sinha, S. Seelana, S. Tsubota, M. Haruta, Top. Catal. 29 (2004) 96.
[6] R. Zanella, C. Louis, Catal. Today 107–108 (2005) 768.
[7] F. Moreau, G.C. Bond, Catal. Today 122 (2007) 215.
[8] E. Sacaliuc, A.M. Beale, B.M. Weckhuysen, T.A. Nijhuis, J. Catal. 248 (2007) 235.
[9] I. Sobczak, A. Kusior, J. Grams, M. Ziolek, J. Catal. 245 (2007) 259.
[10] B. Lee, H.G. Zhu, Z.T. Zhang, S.H. Overbury, S. Dai, Micropor. Mesopor. Mater. 70 (2004) 71.
[11] A.K. Sinha, S. Seelan, T. Akita, S. Tsubota, M. Haruta, Appl. Catal. A 240 (2003) 243.
[12] G.M. Lu, R. Zhao, G. Qian, Y.X. Qi, X.L. Wang, J.S. Suo, Catal. Lett. 97 (2004) 115.
[13] R. Zanella, S. Giorgio, C.R. Henry, C. Louis, J. Phys. Chem. B 106 (2002) 7634.
[14] N.S. Patil, B.S. Uphade, D.G. McCulloh, S.K. Bhargava, V.R. Choudhary, Catal. Commun. 5 (2004) 681.
[15] R. Zanella, S. Giorgio, C.-H. Shin, C.R. Henry, C. Louis, J. Catal. 222 (2004) 357.
[16] G. Li, X.S. Wang, C.Z. Jin, G.M. Li, Chin. J. Catal. 25 (2004) 315.
[17] B. Pawelec, J.L.G. Fierro, A. Montesinos, T.A. Zepeda, Appl. Catal. B 80 (2008) 1.
[18] T.A. Zepeda, B. Pawelec, J.L.G. Fierro, T. Halachev, J. Catal. 242 (2006) 254.
[19] C.Z. Jin, G. Li, X.S. Wang, L.X. Zhao, L.P. Liu, H.O. Liu, Y. Liu, W.P. Zhang, X.W. Han, X.H. Bao, Chem. Mater. 19 (2007) 1664.
[20] Y. Wang, G. Li, X.S. Wang, C.Z. Jin, Energy Fuels 21 (2007) 1415.
[21] Y. Wang, G. Li, X.S. Wang, C.Z. Jin, Chin. J. Catal. 26 (2005) 567.
[22] H.Y. Song, G. Li, X.S. Wang, S.Q. Ma, C.Z. Jin, D.W. Sun, Prepr. Pap. Am. Chem. Soc., Div. Petr. Chem. 52 (2007) 297.
[23] P.T. Tanev, M. Chibwe, T.J. Pinnavaia, Nature 368 (1994) 321.
[24] P.T. Tanev, T.J. Pinnavaia, Science 267 (1995) 865.
[25] J. Li, X.Q. Lin, Sens. Actuators B 126 (2007) 527.
[26] T.A. Zepeda, B. Pawelec, J.L.G. Fierro, A. Montesinos, A. Olivas, S. Fuentes, T. Halachev, Micropor. Mesopor. Mater. 111 (2008) 493.
[27] T.A. Zepeda, J.L.G. Fierro, B. Pawelec, R. Nava, T. Klimova, G.A. Fuentes, T. Halachev, Chem. Mater. 17 (2005) 4062.
[28] A. Kumar, S. Mandal, P.R. Selvakannan, R. Pasricha, A.B. Mandale, M. Sastry, Langmuir 19 (2003) 6277.
[29] H.Y. Song, G. Li, X.S. Wang, Micropor. Mesopor. Mater. 120 (2009) 346.
[30] T.A. Zepeda, Appl. Catal. A 347 (2008) 148.