available at www.sciencedirect.com journal homepage: www.elsevier.com/locate/chnjc

Article

Oxidative desulfurization of dibenzothiophene catalyzed by peroxotungstate on functionalized MCM-41 materials using hydrogen peroxide as oxidant

Dong Xie, Qihui He, Yangyang Su, Tongwei Wang, Renfu Xu, Baixing Hu *

Jiangsu Key Laboratory of Vehicle Emissions Control, and School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, Jiangsu, China

ARTICLE INFO

Article history:

Received 29 January 2015

Accepted 20 May 2015

Published 20 August 2015

Keywords:

Dibenzothiophene

Oxidative desulfurization

Peroxotungstate

MCM-41

ABSTRACT

Catalysts play an important role in oxidative desulfurization, a promising process for producing cleaner fossil fuels for transport. A highly efficient catalyst, $Q_4\text{-H}_2\text{Se}^{\text{IV}}\text{W}_6$, for the oxidative desulfurization of dibenzothiophene (DBT) was reported in 2011. To comprehensively evaluate this catalyst and better understand its recovery, two types of the catalyst were prepared by impregnating $Q_4\text{-H}_2\text{Se}^{\text{IV}}\text{W}_6$ on MCM-41 and functionalized MCM-41 materials. In the oxidative desulfurization process catalyzed by these supported catalysts, the conversion of DBT reached 98.7%. The catalytic activities were excellent when $Q_4\text{-H}_2\text{Se}^{\text{IV}}\text{W}_6$ was impregnated on functionalized MCM-41. The results showed that the supported catalysts had excellent reusability. In addition, a mechanism for the catalytic oxidative desulfurization was proposed.

© 2015, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Globally, crude oil continues to be a widely used and important resource, particularly, for transportation fuels [1–3]. However, crude oil-derived fuels contain a complex range of components, which themselves include various sulfur compounds. As well as deactivating catalysts that are fitted to automotive exhausts to decrease pollutant emissions, combustion of these sulfur compounds releases pollutants that contribute to acid rain [4,5]. Increasing environmental protection awareness has therefore led to an urgent need for fuel desulfurization [6,7]. Many countries have issued environmental regulations to limit fuel-sulfur concentrations to less than 10 ppm [8]. However, achieving such low concentrations with the range of complicated sulfur compounds found in petroleum makes refining more challenging [2,9].

At present, the removal of sulfur compounds from liquid fuels is achieved by hydrodesulfurization that can remove thiols, sulfides, and disulfides efficiently [10,11]. However, hydrodesulfurization is a nonselective hydrogenation process that requires high temperature and high pressure. The process also lowers the fuel's octane level and requires substantial quantities of H_2 , which is expensive [12]. Furthermore, hydrodesulfurization is a less successful method for achieving desulfurization of thiophene and benzothiophene derivatives [13–15]. Therefore, for the production of cleaner transportation fuels, supplementary approaches to achieve this deep desulfurization are required.

A number of deep desulfurization approaches have been investigated, including biodesulfurization, extractive desulfurization by ionic liquid, adsorptive desulfurization, and oxidative desulfurization [16–21]. Among them, the oxidative desulfuri-

* Corresponding author. Tel/Fax: +86-25-83592878; E-mail: hubx@nju.edu.cn

This work was supported by the National Science Fund for Talent Training in Basic Science (J1103310).

DOI: 10.1016/S1872-2067(15)60897-X | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 36, No. 8, August 2015

Scheme 1. Example of the oxidative desulfurization process.

zation is considered one of the most effective methods [22–27]. This is because in the oxidative desulfurization process dibenzothiophene (DBT) and its derivatives can be selectively oxidized to their corresponding sulfoxides and sulfones (Scheme 1) under mild reaction conditions (< 373 K and ambient pressure) using common and inexpensive oxidants [28,29]. The sulfoxides and sulfones can then be easily removed using water-soluble polar solvents as the extractant [8,24].

The oxidant plays a very important role in the oxidative desulfurization process. Many types of oxidants have been studied, such as O_2 , H_2O_2 , and organic peroxides. Among them, H_2O_2 has been widely used as it is cheap, commercially available, and relatively environmentally friendly [30–33].

Catalysts are responsible for activating the oxidants and are therefore essential in the oxidative desulfurization process [34]. Different catalytic systems have been reported for the process; these include those based on an organic acid [35], heteropolyoxometalates [36], an ionic liquid [37], a molecular sieve [38], and photocatalysts [39]. Within this group, polyoxometalates have a number of unique features that allow their processes to exhibit higher sulfur removal efficiencies [40,41].

In recent years, supporting catalysts on solid mesoporous materials have been reported as a potential solution to deep desulfurization. Li et al. [42] reported a mesoporous silicate incorporated with phosphotungstic acid for DBT oxidation that obtained 98%–99% DBT conversion in experiments with model oil. In another experiment, Li et al. [43] prepared molybdovanadophosphoric acid on functionalized SBA-15 for oxidative desulfurization and reported a 97.8% conversion of DBT in a model oil while the supported catalyst was shown to be easily recovered; an important finding given that catalyst recovery and recycling is now a significant focus of the catalytic industry. The same work also noted that immobilization of the catalyst on mesoporous materials with weak bonding led to partial leaching when reacted in a polar solvent [43]. However, this and a number of other works have shown that when the catalyst is supported on modified silica materials with electrostatic interactions it exhibits better stability [43–45].

In 2011, the catalyst used in this work ($Q_4-H_2Se^{IV}_3W_6$) was reported to exhibit highly efficient and selective properties in the oxidative desulfurization process with DBT conversion of more than 99% in a desulfurization test using model oil [46]. However, catalyst recovery in this case remains an unresolved topic and is the focus of this work.

Here, an optimized approach is reported whereby the peroxotungstate catalyst was impregnated in MCM-41 and MCM-41-NH₂ (functionalized by 3-aminopropyltriethoxysilane (APTES)) materials. The ability of these materials to facilitate the oxidative desulfurization process was tested using a model oil. The optimum reaction conditions were investigated, including reaction time, reaction temperature, molar ratio of

[O]/[S], and dosage of catalyst. In addition, recycling tests were carried out.

2. Experimental

2.1. Materials

DBT (99%), APTES, sodium tungstate dihydrate (AR), cetyltrimethylammonium bromide (CTABr), selenium dioxide (AR), typical tetraethyl orthosilicate (TEOS), and stearyl trimethyl ammonium chloride (STAC, 99%) were purchased from Aladdin Reagent Inc. H_2O_2 (30%, AR) and *n*-octane (CP) were obtained from Sinopharm Chemical Reagent Co. Ltd. NaOH (AR), chloroform (AR), acetonitrile (AR), toluene (AR), and HCl (37%, AR) were supplied by Nanjing Chemical Reagent Co. Ltd. All of the reagents except toluene were used as received without any further purification. The toluene was distilled to remove water and sealed in bottles to keep it dry.

The model fuels were prepared by dissolving DBT in *n*-octane to obtain three solutions with a sulfur content of 200, 500, and 800 ppm, respectively.

2.2. Synthesis of MCM-41 and MCM-41-NH₂

MCM-41 was synthesized following the procedures described in the literature [47–49]. In brief, this involved TEOS slowly being added to a vigorously stirred solution of NaOH and CTABr at room temperature. The solution was then stirred for 2 h at 353 K. Heating was stopped though stirring continued until the temperature had cooled to room temperature. The obtained gel was crystallized at 383 K for 48 h in stainless steel reactors with Teflon liners. After filtration, the crystallized gel was calcined in a muffle furnace at 823 K for 5 h and allowed to cool naturally yielding MCM-41 as a white powder.

MCM-41-NH₂ was prepared using a grafting technique [50]. Here, MCM-41 was first activated in a muffle furnace at 773 K for 4 h and cooled in a vacuum oven. One gram of activated MCM-41 was then dispersed in 50 mL of distilled toluene, and 1.5 g of APTES was added to the mixture. The mixture was magnetically stirred and refluxed at room temperature for 8 h. The resultant white solid was filtered and washed with distilled toluene. MCM-41-NH₂ powder was obtained after the white solid had been dried under vacuum at 303 K for 8 h.

2.3. Preparation of catalysts

Catalyst A, $[C_{18}H_{37}N(CH_3)_3]_4[H_2Se^{IV}_3W_6O_{34}]$ (abbreviated to $Q_4-H_2Se^{IV}_3W_6$), was synthesized according to the method described in the literature [46]. A yellow flaky solid was obtained after the crude product had been dried at room temperature under vacuum overnight.

Catalyst B, MCM-41/ $Q_4-H_2Se^{IV}_3W_6$, was prepared by the wet impregnation method [42]. A desired amount of $Q_4-H_2Se^{IV}_3W_6$ was weighed and dissolved into an aqueous solution, and a calculated amount of MCM-41 was added to the solution. As previously reported [51], to ensure that the peroxotungstate retains its structure and is well dispersed on MCM-41 materi-

als, the peroxotungstate content should be lower than the amount required for monolayer coverage. Therefore, a loading of 5 wt% was chosen. To prepare 5 wt% MCM-41/Q₄-H₂Se^{IV}W₆, 0.020 g Q₄-H₂Se^{IV}W₆, 1.550 g of deionized water, and 0.389 g of MCM-41 were mixed in a beaker with the mixture then continuously stirred overnight at room temperature. To activate MCM-41/Q₄-H₂Se^{IV}W₆, the impregnated materials were placed into a vacuum oven for 12 h at 383 K.

Catalyst C, MCM-41-NH₂/Q₄-H₂Se^{IV}W₆, was prepared following a similar method as that used for catalyst B. To prepare 5 wt% MCM-41-NH₂/Q₄-H₂Se^{IV}W₆, 0.020 g of Q₄-H₂Se^{IV}W₆, 2.680 g of deionized water, and 0.420 g of MCM-41-NH₂ were mixed. Prior to use, the sample was heated overnight in a vacuum oven at 383 K to remove gas or water trapped in the sample.

2.4. Characterization of samples

Fourier transform infrared spectra (FTIR) in the range of 500–4000 cm⁻¹ were obtained using a NEXUS 870 spectrometer (Nicolet, America) using a dried KBr pellet.

X-ray diffraction (XRD) measurements were carried out from 0.6° to 10° with a scan rate of 0.5°/min using a D8 ADVANCE system using a Cu K_α radiation source at 40 kV and 40 mA.

Images of the samples were captured by transmission electron microscopy (TEM), which was carried out using a JEOL 2100 electron microscope operating at 200 kV.

N₂ adsorption-desorption isotherms were measured by an ASAP 2020 (Micromeritics). The samples were pretreated at 473 K under a high vacuum, and the pore structure was calculated from the adsorption isotherm. Specific surface areas were calculated in accordance with the BET method and pore size distributions were calculated using the desorption branch of the isotherm and employing the BJH method.

2.5. Oxidative desulfurization of DBT

In a 50 mL round-bottom flask equipped with a magnetic stirrer and a heated circulating bath, 0.5 mL of acetonitrile was mixed with 10 mL of DBT, the model fuel, to be tested. Acetonitrile was used as it is one of the most suitable solvents for the oxidation desulfurization system [52–54]. The amount of catalyst was maintained at a molar ratio of catalyst/DBT = 1:60 [46]. Following the reaction detailed in Scheme 1, the amount of H₂O₂ (30 wt%) required was determined by maintaining [O]/[S] = 2:1. After the catalyst and H₂O₂ were added, the reaction was started at atmospheric pressure and a given set temperature that depended on the test with the reaction time then recorded.

The progress of oxidation was promptly analyzed by a sulfur-specific gas chromatography system that was equipped with a flame photometric detector (GC-FPD). The specimens were sampled from the supernatant liquid at different time intervals. The GC-FPD was set as follows: capillary column SE-30 (50 mm × 0.53 mm × 0.5 μm); injector temperature 513 K; column temperature 453 K; detector temperature 493 K;

ultra-pure N₂ as carrier gas (1.0 mL/min); reagent gases air (60 mL/min) and ultra-pure H₂ (60 mL/min); injection volume 1 μL. Confidence in measurements repeatability was ensured by repeating each measurement three times.

The DBT conversion (*D*) was calculated as $D = (S_0 - S_F)/S_0 \times 100\%$, where *S*₀ and *S*_F are the concentration of sulfur (DBT) in the oil phase initially and after the reaction had completed, respectively.

3. Results and discussion

3.1. Catalyst characteristics

The FTIR spectrum of Q₄-H₂Se^{IV}W₆ (catalyst A) is shown in Fig. 1(1) and exhibits characteristic peaks at 969 cm⁻¹ (W=O stretching vibration), 911 cm⁻¹ (O–O stretching vibration), and 721 cm⁻¹ (Se–O stretching vibration). Fig. 1(2)–(5) shows the FTIR spectra of MCM-41, MCM-41/Q₄-H₂Se^{IV}W₆ (catalyst B), MCM-41-NH₂, and MCM-41-NH₂/Q₄-H₂Se^{IV}W₆ (catalyst C). The peaks at 780 and 1090 cm⁻¹ are associated with the Si–O–Si symmetric and asymmetric stretching vibrations of mesoporous silica, respectively. The band at 780 cm⁻¹ is assigned to the stretching vibration of Si–O–H. The peak at 721 cm⁻¹ shifted to 696 cm⁻¹ after Q₄-H₂Se^{IV}W₆ was impregnated on MCM-41 and MCM-41-NH₂. Significantly, compared with MCM-41 and MCM-41-NH₂, a new band appeared at approximately 1470 cm⁻¹ over catalyst B and catalyst C. These results indicate that Q₄-H₂Se^{IV}W₆ was highly dispersed on the surface of MCM-41 and MCM-41-NH₂.

Small-angle XRD patterns of four samples are depicted in Fig. 2. Both MCM-41 and MCM-41-NH₂ exhibited a strong reflection at 2θ = 2.1° because of the (100) plane and a few weak peaks because of (110) and (200) plane reflections. These peaks show highly ordered, two-dimensional, hexagonal and mesoporous channels of MCM-41 and MCM-41-NH₂. For catalysts B and C, all of these peaks were still detected but with a decreased intensity. This indicates that the ordered pore structure of mesoporous materials was retained well and that the Q₄-H₂Se^{IV}W₆ was well-dispersed across the mesoporous

Fig. 1. FTIR spectra of various samples. (1) Catalyst A; (2) MCM-41; (3) MCM-41-NH₂; (4) Catalyst B; (5) Catalyst C.

Fig. 2. Small-angle XRD patterns of MCM-41 (1), MCM-41-NH₂ (2), catalyst B (3), and catalyst C (4).

channels. The intensity of the peaks is associated with the degree of crystallinity [55]. The lower intensity demonstrates a decrease in the arrangement of ordered, two-dimensional, hexagonal and mesoporous channels of silica. It reveals that Q₄-H₂Se^{IV}₃W₆ was loaded onto the mesoporous channels successfully. This could be caused by interaction between mesoporous silica materials and Q₄-H₂Se^{IV}₃W₆. This result agrees with other reported studies [55,56].

TEM was used to image the porous structure of the synthesized materials, as shown in Fig. 3. It clearly shows the well-ordered, hexagonal arrays of the mesopores typical of MCM-41 materials. The modified samples (MCM-41-NH₂) also provide well-ordered, hexagonal array structures. The pores of catalyst B were slightly smaller than those of the MCM-41 samples and the channels were less clearly defined. This implies that the Q₄-H₂Se^{IV}₃W₆ inserted into the pores, but that the mesoporous structure of the support was retained after being impregnated by Q₄-H₂Se^{IV}₃W₆. The pore size has clearly changed following the impregnation of Q₄-H₂Se^{IV}₃W₆ in the channels of MCM-41-NH₂. The channels of catalyst C were thinner and less sharply defined than those of MCM-41-NH₂, but the mesoporous structure of the support was retained. The TEM images provide strong evidence that Q₄-H₂Se^{IV}₃W₆ was well dispersed in the channels of the mesoporous materials,

Fig. 3. TEM images of MCM-41 (a), MCM-41-NH₂ (b), catalyst B (c), and catalyst C (d).

Table 1

Surface area and pore volume of mesoporous materials and catalysts.

Sample	A_{BET} (m ² /g)	Pore volume (cm ³ /g)
Catalyst A	< 10	0.03
MCM-41	647	0.76
MCM-41-NH ₂	324	0.31
Catalyst B	551	0.52
Catalyst C	229	0.21

agreeing well with the XRD results.

The measured values of surface area and pore volume for all catalysts are presented in Table 1. Pure Q₄-H₂Se^{IV}₃W₆ showed a limited surface area (< 10 m²/g) and a small pore volume (0.03 cm³/g). The average pore volume of MCM-41 was larger than that of MCM-41-NH₂, indicating that the MCM-41 was successfully modified by APTES. As shown in Fig. 4, the internal channels became more complex and smaller after modification. The values for both surface area and pore volume decreased after the two supports (MCM-41 and MCM-41-NH₂) were impregnated with Q₄-H₂Se^{IV}₃W₆. Considering the low surface area of Q₄-H₂Se^{IV}₃W₆ (< 10 m²/g), the decrease of surface area and pore volume was likely caused by small clusters of Q₄-H₂Se^{IV}₃W₆ forming in the channels of the mesoporous materials. The data shown in Table 1 confirmed that Q₄-H₂Se^{IV}₃W₆ was dispersed in the channels of the mesoporous materials.

As mentioned above, simple impregnation of catalyst on mesoporous materials could lead to partial leaching. Therefore, favoring the stability of catalyst, catalyst C was chosen to conduct the following tests.

3.2. Effect of reaction conditions on the conversion of DBT

3.2.1. Reaction time

DBT conversion tests were carried out for fuel samples with different sulfur contents. The results are shown in Fig. 5. It is obvious that the conversion of DBT increases with time, though the majority of the conversion completed within 30 min for each of the tests. Moreover, DBT was almost completely converted (> 99%) after 180 min. When the sulfur content was raised to 800 ppm, the conversion of DBT decreased. As seen from Fig. 5, for model fuels with 500 ppm sulfur content, the conversion of DBT was 98.7% (approximately the same as the > 99% required for deep desulfurization) after a reaction time of 120 min. These conditions (500 ppm sulfur content and 120 min reaction time) were chosen for comparative experiments for the desulfurization process using the different catalysts. A similar time was required to achieve deep desulfurization as that reported in the literature [46]. This suggested that the high

Fig. 4. MCM-41 functionalized by APTES.

Fig. 5. Influence of reaction time on DBT conversion over catalyst C. Reaction conditions: model fuels 10 mL, 318 K, $[O]/[S] = 2:1$, catalyst/DBT = 1:60.

efficiency of DBT conversion by $Q_4-H_2Se^{IV}_3W_6$ was retained following being impregnated on MCM-41- NH_2 .

3.2.2. Reaction temperature

Fig. 6 shows that at a given reaction time the conversion of DBT was improved by increasing the reaction temperature. When the reaction temperature was elevated from 298 to 318 K, the conversion of DBT reached 90% within 60 min (compared to 78% at 298 K). The variation between reaction rates at different temperatures suggests a suitable temperature for accelerating reaction needs to be found. According to the Arrhenius equation ($K = A \exp(-E_a/RT)$) the reaction rate increases exponentially as temperature rises. Although increasing the reaction temperature increases the reaction rate, a tradeoff is needed to decrease energy requirements and to account for other reactions that could occur. For example, elevating the temperature from 318 to 338 K had little impact on the DBT conversion at 100 min, with this attributed to the fact that the increased temperature could also cause decomposition of H_2O_2 . This decomposition of H_2O_2 decreases the amount of oxidant available and also dilutes the oxidant as water is one of the

Fig. 6. Effect of temperature on DBT oxidation reaction. Reaction conditions: 500 ppm model fuels 10 mL, $[O]/[S] = 2:1$, catalyst/DBT = 1:60.

decomposition products. In this study, 318 K was therefore chosen as the most suitable temperature for the desulfurization process, somewhat lower than that used in previously reported work [43].

3.2.3. $[O]/[S]$ ratio

In the oxidative system, one of the main factors impacting the conversion is the dosage of oxidant used. The effects of oxidation dosage were studied under different $[O]/[S]$ molar ratios. As seen in Fig. 7, the conversion of DBT quickly increased when $[O]/[S]$ increased to 2:1. However, increasing $[O]/[S]$ further only slightly increased DBT conversion.

According to the stoichiometry of the reaction, 1 mol DBT would consume 2 mol H_2O_2 and produce 1 mol sulfone (DBTO₂). As reported elsewhere [57–60], the H_2O_2 /sulfur molar ratio is usually > 2 in the actual reaction process because both oxidation of DBT by H_2O_2 and decomposition of H_2O_2 simultaneously occur. When $[O]/[S] > 2$, the diminishing marginal increase in reactivity is attributed to an increase in the thermal decomposition of H_2O_2 and dilution effects from water produced from the oxidative reaction. Hence, an excess of H_2O_2 was deemed unnecessary and $[O]/[S] = 2$ was chosen for this experiment.

3.2.4. Catalyst dosage

To investigate the effect of catalyst amount on the conversion of DBT, a series of experiments with varying amounts of catalyst C were carried out under the same reaction conditions. The results shown in Fig. 8 indicate that the conversion of DBT sharply increased from 8.3% to 99.7% as the molar ratio of catalyst/DBT ranged from 0 to 0.020. It was found that 98.7% DBT conversion was obtained when catalyst/DBT = 0.015. However, further increasing catalyst/DBT up to 0.025 little improved the conversion of DBT. The catalyst/DBT = 0.015 was the point at which sufficient catalytic sites were available to drive the reaction to completion, and was chosen for further experiments. This catalyst dosage was much lower than that reported elsewhere [43,46], perhaps because the channel structure in the current work increased the number reactive sites.

Fig. 7. Impact of $[O]/[S]$ molar ratio on DBT conversion. Reaction conditions: 500 ppm model fuels 10 mL, 318 K, catalyst/DBT = 1:60.

Fig. 8. Effect of catalyst C dosage on DBT conversion. Reaction conditions: 500 ppm model fuels 10 mL, 318 K, [O]/[S] = 2:1.

3.3. Activity and reusability of the catalysts

The activity of various catalysts applied to the oxidative desulfurization reaction is compared in Fig. 9. Results for MCM-41 and MCM-41-NH₂ were similar to the control, demonstrating that the mesoporous materials make no or very limited contributions to catalytic activity. Similar results were found in the literature [61,62]. Catalysts A, B, and C all exhibited high and similar catalytic activity with conversion in the range 98.3%–99.1%.

Catalysts B and C can be recovered and reused in subsequent catalytic oxidative desulfurization runs. Following the end of a reaction, the used catalysts were separated from the reaction solution, mixed with acetonitrile and stirred for 10 min before being filtered out. This washing was carried out three times, and the catalysts were then pretreated in vacuum oven at 383 K for 12 h before being used again.

As seen in Fig. 10, the catalytic efficiency of catalyst C was higher than that of catalyst B through four reaction cycles. This could be due to increased leaching of unstable immobilized Q₄-H₂Se^{IV}₃W₆, causing a reduction in active sites for catalyst B. The activity loss in subsequent reaction cycles could also be attributed to the inactivation of some active sites during the oxidation or recovery processes, which was also more pronounced for catalyst B. The more durable nature of catalyst C in

Fig. 9. Performance of three kinds of catalyst on DBT conversion. Reaction conditions: 500 ppm model fuels 10 mL, 318 K, [O]/[S] = 2:1, catalyst/DBT = 1:60.

Fig. 10. Impact of recycling supported catalysts on DBT conversion. Reaction conditions: 500 ppm model fuels 10 mL, 318 K, [O]/[S] = 2:1, catalyst/DBT = 1:60.

the oxidative desulfurization process can be explained as follows. The silanol groups, which are present at the surface and inside the channels of the mesoporous MCM-41, reacted with aminosilane molecules forming $\equiv\text{Si}(\text{CH}_2)_3\text{NH}_3^+$ [63]. However, after Q₄-H₂Se^{IV}₃W₆ was impregnated on MCM-41-NH₂, the salt $\equiv\text{Si}(\text{CH}_2)_3\text{NH}_3^+\cdot\text{H}_2\text{Se}^{\text{IV}}_3\text{W}_6\text{-Q}_4$ was formed instead [64], with the chemical interaction between $\equiv\text{Si}(\text{CH}_2)_3\text{NH}_3^+$ and Q₄-H₂Se^{IV}₃W₆ enhancing the stability of catalyst C.

3.4. Analysis of oxidation products

After the reaction, GC-MS and FTIR analysis were carried out on solid products that were formed on the wall of the vessel. GC-MS analysis (Fig. 11) registered M⁺ at m/z = 216 confirming the presence of the sulfone of DBT. The intense m/z peaks appeared at 187.1 and 168.1 and were attributed to the C₁₁H₇SO and C₁₂H₈O moieties of DBT *S,S*-dioxide, respectively [65].

As the FTIR results in Fig. 12 show, peaks appeared at 1164 and 1288 cm⁻¹ and were associated with the O–S–O symmetric and asymmetric stretching vibrations of DBTO₂, respectively.

The acetonitrile phase and the solid product (first dissolved in acetonitrile) were analyzed by GC-FPD. The results shown in

Fig. 11. GC-MS spectrogram for oxidation products present in *n*-octane.

Fig. 12. FTIR spectrum of the solid products formed by the desulfurization reaction.

Fig. 13 demonstrate that the final products in this reaction were mainly DBTO₂.

3.5. Proposed mechanism of the catalytic oxidation

The results shown in Fig. 7 demonstrate that DBT could be oxidized by the catalyst alone (i.e. without H₂O₂) with DBT oxidized into sulfoxide or sulfone. In this study, no sulfoxide was detected by GC analysis under reaction conditions. The oxidation of sulfide to sulfoxide is considered fast. So, the mechanism of DBT oxidation in the presence of catalyst C can be described as the process shown in Fig. 14 and described below.

It could be suggested that the catalyst on the surface of mesoporous silica samples acted as the catalytic active sites in the oxidative desulfurization. However, the oxidation of DBT actually contains two steps. First, the sulfur atom of dibenzothiophene stages a nucleophilic attack on the specific oxygen atom in the catalyst, two protons shift, and the oxygen atom transfers from the catalyst to the dibenzothiophene molecule, forming DBTO or DBTO₂ (Fig. 14(i)). Second, the catalyst that lost the oxygen atom contacts with H₂O₂, and the peroxide bond regenerates (Fig. 14(ii)). Together these two half reactions complete the oxidation of DBT [66–68].

Fig. 14. Mechanism of DBT oxidation.

4. Conclusions

Mesoporous materials impregnated with Q₄-H₂Se^{IV}W₆ show effective performance in the oxidative desulfurization at mild reaction conditions. The catalyst MCM-41-NH₂/Q₄-H₂Se^{IV}W₆ showed excellent properties when MCM-41 functionalized by APTES was used as the support structure. The desulfurization reaction achieved a high conversion of DBT at mild conditions (318 K) with almost all hydrogen peroxide used in the oxidative reaction ([O]/[S] = 2:1). Furthermore, only a small amount of catalyst (catalyst/DBT = 0.015) was required to achieve a high conversion of DBT (98.7%). The catalyst activity slightly decreased following subsequent reaction cycles though the conversion of DBT remained around 90% after four rounds of recycling.

Taken together these results demonstrate that the mesoporous material of MCM-41-NH₂ impregnated with Q₄-H₂Se^{IV}W₆ is an excellent catalyst for the oxidative desulfurization system. The present work on the most economical and efficient conditions for the use of Q₄-H₂Se^{IV}W₆ not only solves the problem of recovery and reuse of Q₄-H₂Se^{IV}W₆, but also provides a reference for future work in oxidative desulfurization.

Acknowledgments

The authors wish to acknowledge the financial support provided by the School of Chemistry and Chemical Engineering, Nanjing University.

Fig. 13. The megascopic GC-FPD traces of post-reaction acetonitrile phase (a) and the solution of the solid products formed by the desulfurization reaction dissolved in acetonitrile (b).

References

- [1] Palomino J M, Tran D T, Hauser J L, Dong H, Oliver S R J. *J Mater Chem A*, 2014, 2: 14890
- [2] Srivastava V C. *RSC Adv*, 2012, 2: 759
- [3] Liu C H, He Q H, Zhang Z, Su Y Y, Xu R F, Hu B X. *Chin J Chem*, 2014, 32: 410
- [4] Tang N F, Zhao X P, Jiang Z X, Li C. *Chin J Catal* (唐南方, 赵小平, 蒋宗轩, 李灿. 催化学报), 2014, 35: 1433
- [5] Huang C P, Chen B H, Zhang J, Liu Z C, Li Y X. *Energy Fuels*, 2004, 18: 1862
- [6] Ali S H, Hamad D M, Albusairi B H, Fahim M A. *Energy Fuels*, 2009, 23: 5986
- [7] Xiong J, Zhu W S, Ding W J, Yang L, Chao Y H, Li H P, Zhu F X, Li H M. *Ind Eng Chem Res*, 2014, 53: 19895
- [8] Stanislaus A, Marafi A, Rana M S. *Catal Today*, 2010, 153: 1
- [9] Song C S. *Catal Today*, 2003, 86: 211
- [10] Ma X L, Sakanishi K, Mochida I. *Ind Eng Chem Res*, 1994, 33: 218
- [11] Ribeiro S, Barbosa A D S, Gomes A C, Pillinger M, Goncalves I S, Cunha-Silva L, Balula S S. *Fuel Process Technol*, 2013, 116: 350
- [12] Xiao J, Song C S, Ma X L, Li Z. *Ind Eng Chem Res*, 2012, 51: 3436
- [13] García-Gutiérrez J L, Laredo G C, García-Gutiérrez P, Jiménez-Cruz F. *Fuel*, 2014, 138: 118
- [14] Zhu W S, Li H M, Jiang X, Yan Y S, Lu J D, Xia J X. *Energy Fuels*, 2007, 21: 2514
- [15] Zhao D S, Sun Z M, Li F T, Liu R, Shan H D. *Energy Fuels*, 2008, 22: 3065
- [16] Song H, Wan X, Dai M, Zhang J J, Li F, Song H L. *Fuel Process Technol*, 2013, 116: 52
- [17] Derikvand P, Etemadifar Z, Biria D. *Int Biodeter Biodegr*, 2014, 86: 343
- [18] Shu C H, Sun T H, Zhang H B, Jia J P, Lou Z Y. *Fuel*, 2014, 121: 72
- [19] Imtiaz A, Waqas A, Muhammad I. *Chin J Catal* (催化学报), 2013, 34: 1839
- [20] Ban L L, Liu P, Ma C H, Dai B. *Chin Chem Lett*, 2013, 24: 755
- [21] Chamack M, Mahjoub A R, Aghayan H. *Chem Eng J*, 2014, 255: 686
- [22] Fang D W, Wang Q, Liu Y, Xia L X, Zang S L. *Energy Fuels*, 2014, 28: 6677
- [23] Jiang Z X, Lü H Y, Zhang Y N, Li C. *Chin J Catal* (蒋宗轩, 吕宏纓, 张永娜, 李灿. 催化学报), 2011, 32: 707
- [24] Zhang G F, Yu F L, Wang R. *Petroleum Coal*, 2009, 51: 196
- [25] Campos-Martin J M, Capel-Sanchez M C, Perez-Presas P, Fierro J L G. *J Chem Technol Biotechnol*, 2010, 85: 879
- [26] Zheng H W, Sun Z, Chen X L, Zhao Q, Wang X H, Jiang Z J. *Appl Catal A*, 2013, 467: 26
- [27] Chan N Y, Lin T Y, Yen T F. *Energy Fuels*, 2008, 22: 3326
- [28] Sundararaman R, Ma X L, Song C S. *Ind Eng Chem Res*, 2010, 49: 5561
- [29] Xiao J, Wu L M, Wu Y, Liu B, Dai L, Li Z, Xia Q B, Xi H X. *Appl Energy*, 2014, 113: 78
- [30] Abdalla Z E A, Li B S. *Chem Eng J*, 2012, 200-202: 113
- [31] Te M, Fairbridge C, Ring Z. *Appl Catal A*, 2001, 219: 267
- [32] Zhang J, Wang A J, Wang Y J, Wang H Y, Gui J Z. *Chem Eng J*, 2014, 245: 65
- [33] Li C, Jiang Z X, Gao J B, Yang Y X, Wang S J, Tian F P, Sun F X, Sun X P, Ying P L, Han C R. *Chem Eur J*, 2004, 10: 2277
- [34] Mei H, Mei B W, Yen T F. *Fuel*, 2003, 82: 405
- [35] Wan M W, Yen T F. *Appl Catal A*, 2007, 319: 237
- [36] Zhang M, Zhu W S, Xun S H, Li H M, Gu Q Q, Zhao Z, Wang Q. *Chem Eng J*, 2013, 220: 328
- [37] Zhu W S, Wu P W, Yang L, Chang Y H, Chao Y H, Li H M, Jiang Y Q, Jiang W, Xun S H. *Chem Eng J*, 2013, 229: 250
- [38] Shan J H, Chen L, Sun L B, Liu X Q. *Energy Fuels*, 2011, 25: 3093
- [39] Zhu W S, Xu Y H, Li H M, Dai B L, Xu H, Wang C, Chao Y H, Liu H. *Korean J Chem Eng*, 2014, 31: 211
- [40] Luo G Q, Kang L H, Zhu M Y, Dai B. *Fuel Process Technol*, 2014, 118: 20
- [41] Zhu W S, Zhu G P, Li H M, Chao Y H, Zhang M, Du D L, Wang Q, Zhao Z. *Fuel Process Technol*, 2013, 106: 70
- [42] Li B S, Ma W, Liu J J, Han C Y, Zuo S L, Li X F. *Catal Commun*, 2011, 13: 101
- [43] Li J L, Hu B, Tan J J, Zhuang J Z. *Transit Metal Chem*, 2013, 38: 495
- [44] Nowińska K, Kaleta W. *Appl Catal A*, 2000, 203: 91
- [45] Verhoef M J, Kooyman P J, Peters J A, Van Bekkum H. *Microporous Mesoporous Mater*, 1999, 27: 365
- [46] Hu Y W, He Q H, Zhang Z, Ding N D, Hu B X. *Chem Commun*, 2011,

Graphical Abstract

Chin. J. Catal., 2015, 36: 1205–1213 doi: 10.1016/S1872-2067(15)60897-X

Oxidative desulfurization of dibenzothiophene catalyzed by peroxotungstate on functionalized MCM-41 materials using hydrogen peroxide as oxidant

Dong Xie, Qihui He, Yangyang Su, Tongwei Wang, Renfu Xu, Baixing Hu*
Nanjing University

In the oxidative desulfurization of dibenzothiophene (DBT), peroxotungstate was supported on functionalized MCM-41 mesoporous molecular sieves. The supported catalyst shows a highly catalytic ability and it also has a good reusability.

- 47: 12194
- [47] Kresge C T, Leonowicz M E, Roth W J, Vartuli J C, Beck J S. *Nature*, 1992, 359: 710
- [48] Roik N V, Belyakova L A. *J Solid State Chem*, 2014, 215: 284
- [49] Corma A. *Chem Rev*, 1997, 97: 2373
- [50] Johnson B J S, Stein A. *Inorg Chem*, 2001, 40: 801
- [51] Marme F, Coudurier G, Védrine J C. *Microporous Mesoporous Mater*, 1998, 22: 151
- [52] Ishimoto R, Kamata K, Mizuno N. *Angew Chem Int Ed*, 2009, 48: 8900
- [53] Hulea V, Fajula F, Bousquet J. *J Catal*, 2001, 198: 179
- [54] Lü H Y, Gao J B, Jiang Z X, Yang Y X, Song B, Li C. *Chem Commun*, 2007: 150
- [55] Blasco T, Corma A, Martínez A, Martínez-Escolano P. *J Catal*, 1998, 177: 306
- [56] Lim M H, Blanford C F, Stein A. *Chem Mater*, 1998, 10: 467
- [57] Xiong J, Zhu W S, Ding W J, Yang L, Zhang M, Jiang W, Zhao Z, Li H M. *RSC Adv*, 2015, 5: 16847
- [58] Li H M, Zhu W S, Wang Y, Zhang J T, Lu J D, Yan Y S. *Green Chem*, 2009, 11: 810
- [59] Ding W J, Zhu W S, Xiong J, Yang L, Wei A M, Zhang M, Li H M. *Chem Eng J*, 2015, 266: 213
- [60] Zhu W S, Li H M, Jiang X, Yan Y S, Lu J D, Xia J X. *Energy Fuels*, 2007, 21: 2514
- [61] Al-Shahrani F, Xiao T C, Llewellyn S A, Barri S, Jiang Z, Shi H H, Martinie G, Green M L H. *Appl Catal B*, 2007, 73: 311
- [62] Jiang X, Li H M, Zhu W S, He L N, Shu H M, Lu J D. *Fuel*, 2009, 88: 431
- [63] Bordoloi A, Lefebvre F, Halligudi S B. *J Catal*, 2007, 247: 166
- [64] Kaleta W, Nowińska K. *Chem Commun*, 2001: 535
- [65] Bowie J H, Williams D H, Lawesson S O, Madsen J, Nolde C, Schroll G. *Tetrahedron*, 1966, 22: 3515
- [66] Duncan D C, Chambers R C, Hecht E, Hill C L. *J Am Chem Soc*, 1995, 117: 681
- [67] Antonova N S, Carbó J J, Kortz U, Kholdeeva O A, Poblet J M. *J Am Chem Soc*, 2010, 132: 7488
- [68] Kamata K, Hirano T, Ishimoto R, Mizuno N. *Dalton Trans*, 2010, 39: 5509

MCM-41分子筛负载亚硒核过氧钨酸盐催化剂催化二苯并噻吩氧化脱硫

谢 东, 何其慧, 苏阳洋, 王童薇, 许仁富, 胡柏星*

南京大学化学化工学院, 江苏省机动车尾气污染控制重点实验室, 江苏南京210093

摘要: 石油在作为燃料使用过程中常常产生各种污染, 特别是油品中的含硫化合物不仅会降低油品品质, 而且燃烧后产生的硫氧化物可污染大气, 形成酸雨, 危害人类健康。因此, 油品深度脱硫是一项十分重要而紧迫的工作。

目前油品脱硫方法有很多种, 主要分为加氢脱硫与非加氢脱硫。加氢脱硫反应条件苛刻, 脱硫效率低, 对设备要求高, 因而非加氢脱硫正在被广泛研究。其中氧化脱硫反应条件温和, 脱硫效率高, 对设备要求不高, 有望实现规模化应用。在氧化脱硫反应中, 催化剂是研究重点, 尤其是催化剂效率及可回收能力。本课题组合成的亚硒核过氧钨酸盐是一种具有高选择性和高催化活性的催化剂, 但它在反应后无法实现回收再利用, 从而限制了其广泛应用。为了提高该催化剂的可回收能力, 本文尝试制备负载型亚硒核过氧钨酸盐用于氧化脱硫反应中, 考察其催化效率及可回收能力。

分子筛具有孔结构, 比表面积大且较为稳定, 是理想的催化剂载体。本文采用浸渍法制备了MCM-41分子筛负载的亚硒核过氧钨酸盐, 为了提高负载能力, 减少催化剂溶脱, 还制备了MCM-41-NH₂分子筛负载的亚硒核过氧钨酸盐, 并运用红外光谱、X射线衍射、N₂吸附-脱附和透射电镜对它们进行了表征。结果显示, 亚硒核过氧钨酸盐在MCM-41和MCM-41-NH₂分子筛内分散均匀, 表明负载成功。将负载型亚硒核过氧钨酸盐催化剂用于模拟油样二苯并噻吩(DBT)氧化脱硫实验, 并用气相-火焰光度检测仪跟踪实验。结果表明, 负载型和非负载型催化剂均具有较高的催化性能。模拟油样在负载型催化剂作用下氧化脱硫反应2 h后, DBT转化率达98.7%, 实现了深度脱硫。此外, 还优化了反应时间、反应温度及氧化剂和催化剂用量。与其它催化剂相比, 在相似脱硫效率情况下, 负载型催化剂的催化效率更高, 反应条件更加温和, 催化剂用量更少, 因而更加环保和节能。对反应产物进行了红外光谱、气相-质谱联用分析以及气相色谱保留时间对比分析, 结果表明DBT脱硫反应产物为DBTO₂。结合相关文献, 对该催化剂上DBT氧化脱硫提出了一种可能的催化氧化反应机理。

反应后将负载型催化剂回收过滤, 洗涤和干燥后, 进行下一轮氧化脱硫反应。结果表明, MCM-41分子筛负载的亚硒核过氧钨酸盐在循环使用过程中, DBT转化率下降较快, 循环使用4次后, DBT转化率降至80%, 而MCM-41-NH₂分子筛负载的催化剂在循环使用4次后, DBT转化率仍达90%。这表明MCM-41-NH₂分子筛负载的亚硒核过氧钨酸盐催化剂具有更好的稳定性和回收使用性能。

综上所述, 负载型亚硒核过氧钨酸盐是一种高效的氧化脱硫催化剂, 在较为温和的反应条件下即可实现深度催化氧化脱硫, 其循环使用性能也得到明显提高。本结果可为该催化剂未来在工业上广泛应用提供一定参考。

关键词: 二苯并噻吩; 氧化脱硫; 亚硒核过氧钨酸盐; MCM-41分子筛

收稿日期: 2015-01-29. 接受日期: 2015-05-20. 出版日期: 2015-08-20.

*通讯联系人. 电话/传真: (025)83592878; 电子信箱: hubx@nju.edu.cn

基金来源: 国家基础科学人才培养基金(J1103310).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).