Contents lists available at ScienceDirect

Catalysis Today

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

Polyoxometalate as effective catalyst for the deep desulfurization of diesel oil

Rui Wang^{*}, Gaofei Zhang, Haixia Zhao

School of Environmental Science & Engineering, Shandong University, Jinan, 250100, PR China

ARTICLE INFO

Article history: Available online 19 April 2009

Keywords: Oxidative desulfurization Hydrogen peroxide Polyoxometalate

ABSTRACT

Aiming at the deep desulfurization of the diesel oil, a comparison of the catalytic effects of several Keggin type POMs, including $H_3PW_xMo_{12-x}O_{40}$ (x = 1, 3, 6), $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, and $H_3PW_{12}O_{40}$, was made, using the solution of DBT in normal octane as simulated diesel oil, H_2O_2 as oxidant, and acetonitrile as extractant. $H_3PW_6Mo_6O_{40}$ was found to be the best catalyst, with a desulfurization efficiency of 99.79% or higher. Hence, it is promising for the deep desulfurization of actual ODS process. The role of the main factors affecting the process including temperature, O/S molar ratio, initial sulfur concentration, and catalyst dosage, was investigated, whereby the favourable operating conditions were recommended as T = 60 °C, O/S = 15, and a catalyst dosage of 6.93 g ($H_3PW_6Mo_6O_{40}$)/L (simulated diesel). With the aid of GC–MS analysis, sulfone species was confirmed to be the only product after reaction for 150 min. Furthermore, macro-kinetics of the process catalyzed by $H_3PW_6Mo_6O_{40}$ was studied, from which the reaction orders were found to be 1.02 to DBT and 0.38 to H_2O_2 , and the activation energy of the reaction was found to be 43.3 kJ/mol. Moreover, the catalyst recovered demonstrated almost the same activity as the fresh.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The presence of sulfur compounds in transportation fuels is recognized as a major source of SO_x which contributes to air pollution, acid rain and damages exhaust after-treatment devices. The global need for clean fuels requires the minimization of the sulfur level in transportation fuels. In the past decade, the specifications for sulfur in diesel have undergone dramatic revisions in many countries. According to the legislations in Japan and Europe, the sulfur content in diesel was limited to a maximum of 50 ppmw by 2005, and further to 10 ppmw by 2007 [1]. Whereas in the US, the EPA regulations had cut the highway diesel fuel sulfur from 500 ppmw down to 15 ppmw by June 2006 [2]. In the long run, these restrictions are only a milestone before the society at large stepping on the road of zero sulfur fuel.

To meet the requirements of more and more stringent legislations, clean fuels research including ultra-deep desulfurization of diesel is currently being conducted by worldwide researchers as a challenging subject. The conventional process for the removal of organosulfur is known as catalytic hydrodesulfurization (HDS). HDS is highly efficient in removing thiols, sulfides and disulfides, but less effective for dibenzothiophene (DBT) and its derivatives with steric hindrance on the sulfur atom (refractory organosulfur compounds) [3,4]. Severe operating

E-mail address: ree_wong@hotmail.com (R. Wang).

conditions of high temperature, high pressure and high hydrogen consumption, as well as the use of more active catalyst or longer residence time are inevitably required for HDS to produce ultralow sulfur fuel. However, the implementation of these alternatives requires huge capital investment. Hence, it is desirable to develop alternative more energy-efficient deep desulfurization processes.

Potential deep desulfurization processes other than HDS include, but are not limited to, adsorption [2,5], extraction [1], oxidation [6-16], and bioprocesses [6]. Oxidative desulfurization (ODS) combined with extraction, carried out in biphasic system, is one of the most promising desulfurization processes [1,6,13]. Compared with conventional HDS, ODS requires very mild conditions as ambient temperature and atmospheric pressure. In the ODS process, the refractory organosulfur compounds can be readily oxidized to their corresponding sulfoxides and sulfones, which can be removed by extraction or adsorption. The commonly used oxidant in ODS is H₂O₂, since it is cheap, environmentally compatible, and commercially available. In very recent years, polyoxometalates (POMs), renowned as green catalysts in many processes, have been attracting worldwide attentions for their effectiveness in ODS with H₂O₂ [11,13,17–21]. POMs belong to a large class of nanosized metal-oxygen cluster anions, formed by a self-assembly process typically in an acidic aqueous solution [22]. Among numerous applications of POMs, catalysis is by far the most important. However, reported ODS processes catalyzed by POMs are quite limited to date.

In this paper, several Keggin type POMs were evaluated as catalysts for the oxidative removal of DBT from simulated diesel oil



^{*} Corresponding author. Tel.: +86 531 88364513.

^{0920-5861/\$ –} see front matter © 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.cattod.2009.03.011

in a biphasic system. $H_3PW_6Mo_6O_{40}$ was found to be the best catalyst, with a desulfurization efficiency of 99.79% or higher. Main factors affecting the process were investigated. Sulfone species was confirmed to be the only product after reaction for 150 min. From macro-kinetic study of the process catalyzed by $H_3PW_6Mo_6O_{40}$, values of the reaction orders and activation energy were obtained. Moreover, the catalyst recovered demonstrated almost the same effect as the fresh. As to the knowledge of the authors, no similar report can be found in open literatures.

2. Experimental

2.1. Preparation of polyoxometalates

The POMs employed in this study include phosphotungstomolybdic acids ($H_3PW_xMo_{12-x}O_{40}$, x = 1, 3, 6), cesium phosphotungstate ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) and phosphotungstic acid ($H_3PW_{12}O_{40}$). The phosphotungstic acid was purchased reagent, the rest were prepared.

Phosphotungstomolybdic acids with various W content (x = 1, 3, 6) were prepared by the following procedure. Stoichiometric amounts of Na₂WO₄, Na₂MoO₄ and H₃PO₄ were dissolved in deionized water under agitation for 30 min. After adjusting the pH value to 1.0 through the addition of 0.5 mol/L HCl solution, the resultant solution was refluxed at 100 °C for 6 h, then cooled to below 5 °C. Subsequently, an extractant of ethyl ether was added, then a favourable amount of dilute HCl solution was dripped slowly into the mixture under vigorous agitation. Thus, the desired product was extracted as an ether-coordinated complex. Adding a certain amount of dilute H₂SO₄ solution to the extracted complex, removing the ethyl ether at 80 °C in a water bath by evaporation, the phosphotungstomolybdic acids were crystallized in a drier and collected by filtration.

The preparation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ required the stoichiometric addition of Cs_2CO_3 solution drop by drop into the bulk solution of $H_3PW_{12}O_{40}$ under agitation at 50–80 °C for 1.5 h. As the reaction proceeds, a white precipitate could be observed. The resultant suspension was laid overnight, then the precipitate was separated out by centrifugation. After having been washed for several times with deionized water, the precipitate was dried first at 85 °C in a water bath, then at 105 °C in a drying oven, before stored for use.

2.2. Characterization of the prepared POMs

The $H_3PW_xMo_{12-x}O_{40}$ (x = 1, 3, 6) prepared were analysed using a Thermo Nicolet Avatar 370 FT-IR instrument and a Perkin Elmer ICP analyser, respectively. The $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ prepared was analysed using the ICP analyser only.

2.3. Experimental method

The solution of DBT in normal octane was used as simulated diesel oil, in which the sulfur content was set by fixing the dosage of DBT. The oxidation reactions were carried out in a three-necked 250 mL round-bottomed flask immersed in a thermostatically controlled water bath. The middle neck connected with a water condenser tube; the other two side necks were closed with glass stoppers. The liquid in the flask was continually and vigorously stirred at a constant speed by a magnetic agitator. The polyoxometalate was dissolved in an aqueous hydrogen peroxide with needed amount of H_2O_2 and mixed with 60 mL of acetonitrile. The oxidation reactions were started by further addition of 60 mL of the simulated diesel oil into the above mixture. During the reactions, the DBT concentrations in the normal octane phase were analysed by a GC-FID equipped with a capillary column. The

temperatures for GC-FID tests were set as 334 °C for both the injector and the detector, and 280 °C for the oven. The concentration of DBT was quantified by external standard method. The product derived from DBT oxidation by H_2O_2 was analysed using Agilent HP-6890N/MS-5793 GC-MS analyser.

3. Results and discussion

3.1. POMs confirmation

As to the $H_3PWMo_{11}O_{40}$, $H_3PW_3Mo_9O_{40}$ and $H_3PW_6Mo_6O_{40}$ prepared, excluding the presence of Na⁺ by ICP analyses, the cations were confirmed to be $\operatorname{H}^{\!\!+}$ only. Furthermore, the molar ratios of P, W, Mo were confirmed to agree with the desired ratios. In polyoxometalate chemistry, the IR spectroscopy is extensively used for the purpose of finger printing and structural elucidation [23]. The most characteristic region of the spectrum is 1100– 700 cm⁻¹ where adsorptions due to metal-oxygen stretching vibrations occur. In the IR spectra of the $H_3PW_xMo_{12-x}O_{40}$ (x = 1, 3, 6) prepared as shown in Fig. 1, broad peaks can be observed in the region 3600-3100 cm⁻¹ and 1650-1550 cm⁻¹. These peak regions correspond to those of water. Assignments for other peaks are 1070 cm^{-1} for P–O, 965 cm⁻¹ due to Mo=O, 873, 788 cm⁻¹ due to Mo-O-Mo. The W-O adsorption peak is masked by that of the Mo-O adsorption peak [24]. Hence, the desired phosphotungstomolybdic acids with Keggin structure can be confirmed according to the presence of these adsorption peaks as fingerprint. Similar to many literature methods [22] for the preparation of mixedaddenda POMs, each of the mixed-addenda POMs prepared in this study is not pure substance but a mixture of Keggin heteropoly acids, in which the species with the desired formula predominates.

The prepared $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ retains the anion portion of the parent compound used, i.e. $H_3PW_{12}O_{40}$, and therefore possesses the same Keggin structure. According to the ICP analysis results, the Cs/P molar ratio was 2.5, therefore the desired product was obtained.

3.2. Comparison of the POMs as desulfurization catalyst

A comparison of the catalytic effects of the prepared POMs on the oxidation of DBT by H_2O_2 was made according to the experiments carried out at 60 °C for 60 min, using the abovementioned experiment system with an initial sulfur concentration of 500 ppmw and an O/S molar ratio of 15. The O/S molar ratio, viz. the ratio of the number of moles of oxygen atom in H_2O_2 to that of sulfur atom in sulfur compound, can be calculated as $2[H_2O_2]/[S]$, where molar concentration is used. For all the experiments, unless



Fig. 1. IR spectra of the $H_3PW_xMo_{12-x}O_{40}$ (x = 1, 3, 6) prepared: (a) $H_3PMo_{12}O_{40}$ (purchased), (b) $H_3PWMo_{11}O_{40}$, (c) $H_3PW_3Mo_9O_{40}$, (d) $H_3PW_6Mo_6O_{40}$.

Table 1

Catalytic effects of POMs on the oxidation of DBT by H₂O₂.

Desulfurization efficiency (%)
99.23
70.50
98.80
99.22
99.79

otherwise specified, the amount of catalyst used was 1% the mass of normal octane. The desulfurization efficiency in this study refers to the percentage ratio of sulfur concentration decrease in the normal octane phase to its initial sulfur concentration.

From the results listed in Table 1, it can be seen that the catalytic performance of $H_3PW_xMo_{12-x}O_{40}$ (x = 1, 3, 6) follows the order of $H_3PWMo_{11}O_{40} < H_3PW_3Mo_9O_{40} < H_3PW_6Mo_6O_{40}$. The catalytic performance of H₃PW₆Mo₆O₄₀ is superior to that of H₃PW₁₂O₄₀. The transformation of phosphotungstic acid to its cesium salt sharply weakens the catalytic effect, as verified by $Cs_{2.5}H_{0.5}PW_{12}O_{40} < H_3PW_{12}O_{40}$. The substitution of W for Mo in the phosphomolybdic acid results in the enhancement of the Bronsted acidity, and H₃PW₆Mo₆O₄₀ possesses the highest oxidation capacity among all W-Mo ratios of the same series, with the addition of H₃PW₁₂O₄₀ [23]. The best catalytic effect of H₃PW₆Mo₆O₄₀ can be attributed to its high Bronsted acidity as well as the highest oxidation capacity it has, under which the POM-H₂O₂ complex in form of peroxo-POM intermediate [22] possesses the highest oxidative capacity, namely the highest catalytic activity for the oxidation of DBT. Compared to H₃PW₁₂O₄₀, the insolubility of Cs_{2.5}H_{0.5}PW₁₂O₄₀ significantly limits its catalytic activity.

Based on the results gained herein, $H_3PW_6Mo_6O_{40}$ was chosen for further experiments on the effects of several operation factors, including temperature, O/S molar ratio, initial sulfur concentration and the dosage of catalyst.

3.3. Role of main factors affecting the process

Using the same experiment system, the effect of temperature was investigated under otherwise identical conditions as mentioned above. The oxidation of DBT by H_2O_2 was found to show an apparent dependence on temperature (Fig. 2). Within the temperature increase from 40 °C to 70 °C, the desulfurization efficiency increases from 98.8% to nearly 100% after reaction for 20 min, and an identical efficiency of 99.7–100% can be achieved after 120 min. From the results, the favourable temperature can be recommended as 60 °C.



Fig. 2. The temperature dependence of the process. Experimental conditions: initial sulfur concentration, 500 ppmw; O/S molar ratio, 15; catalyst dosage, 1% the mass of normal octane.



Fig. 3. The effect of O/S molar ratio. Experimental conditions: temperature, $60 \,^{\circ}$ C; initial sulfur concentration, 500 ppmw; catalyst dosage, 1% the mass of normal octane.

As a predominant factor, O/S molar ratio significantly affects the oxidation of DBT by H_2O_2 (Fig. 3). Under otherwise identical conditions, an increase of O/S molar ratio from 1 to 18 results in the sharp increase of the desulfurization efficiency from 77.0% to 99.5% after reaction for 30 min. In Fig. 3, corresponding to cases where the O/S molar ratio exceeds 9, the desulfurization efficiencies were found to be nearly identical as 99.5% or higher after reaction for 20 min.

In literatures [22,25], peroxo-POM has been widely recognized as active intermediate for POM-catalyzed oxidations of many organic compounds by H₂O₂, such as epoxidation of alkenes and oxidation of organosulfur (e.g. DBT and thioether). In our experiments carried out according to the above-mentioned procedures, H₃PW₆Mo₆O₄₀ was dissolved in H₂O₂ solution before mixing with acetonitrile and simulated diesel oil, resulting in a good activity on the oxidation of DBT. However, no activity was observed when mixing all the reagents simultaneously. This is in agreement with the phenomena reported by Bregeault and coworkers [26]. Hence, it can be concluded that, the quick oxidation of DBT lies in the formation of an active peroxo-POM intermediate, i.e. peroxo-phosphotungstomolybdic acid, upon pre-dissolving of H₃PW₆Mo₆O₄₀ in H₂O₂ solution. With the increase of the O/S molar ratio under fixed initial sulfur concentration, more and more excess H₂O₂ were added into the reaction system, leading to the enhancement in DBT conversion by direct oxidation. From the results, the favourable O/S molar ratio can be recommended as 15.

Initial sulfur concentration also plays an important role in the oxidation of DBT. Under otherwise identical conditions, increasing



Fig. 4. The effect of initial sulfur concentration. Experimental conditions: temperature, $60 \,^{\circ}$ C; O/S molar ratio, 15; catalyst dosage, 1% the mass of normal octane.



Fig. 5. The effect of catalyst dosage. Experimental conditions: temperature, 60 °C; initial sulfur concentration, 500 ppmw; O/S molar ratio, 15.

initial sulfur concentration from 100 ppmw to 500 ppmw and further to 800 ppmw, the desulfurization efficiency was found to increase from 96.5% to 99.5% and further to 99.7% at a reaction time of 10 min, and maintained 99.8% or higher 40 min later (Fig. 4). As a whole, both the effects of the O/S molar ratio and that of the initial sulfur concentration fall in with the law of mass action.

The effect of catalyst lies mainly in the formation of peroxo-POM intermediate, which possesses much higher oxidation capacity than H_2O_2 , and therefore facilitates the oxidation of DBT. Consequently, knowledge on the effect of catalyst dosage is very important to the process optimization. From the results as shown in Fig. 5, it is evident that higher catalyst dosage leads to higher desulfurization efficiency. Under otherwise identical conditions, after reaction for 60 min, a higher desulfurization efficiency of 99.8% can be achieved at the catalyst dosage of ca. 1% the mass of normal octane, compared to that of 99.1% achieved at the catalyst dosage in half. Hence, the favourable catalyst dosage can be recommended as 1% the mass of normal octane, equivalent to 6.93 g ($H_3PW_6Mo_6O_{40}$)/L (simulated diesel).

3.4. Reaction product

With the aid of GC–MS analysis, the product of DBT oxidation by H_2O_2 after 150 min was confirmed to contain the corresponding sulfone species only, regardless of the POM catalyst used. Hence, the overall reaction equation can be expressed as



3.5. Catalyst recovery

The used catalyst can be recovered and reused with almost the same effect as the fresh. When the reaction was finished, the resultant mixture was kept still for 20 min. Then the acetonitrile phase was separated out and distilled at 85 °C to recover acetonitrile (with some water) at the top of the distillator by cooling. The remaining in the distillator, i.e. a mixture of sulfone, water and $H_3PW_6Mo_6O_{40}$, was withdrawn and put into a beaker. With the addition of KCl aqueous solution, a precipitate of $K_3PW_6Mo_6O_{40}$ can be observed in the beaker. The precipitate was isolated by decantation, and washed twice with deionized water. Then, the precipitate was treated by mixing with a favourable amount of H-type cation exchange resin particles in deionized water under mild and continuous agitation at 70 °C. When the precipitate dissolved completely, conversion of $K_3PW_6Mo_6O_{40}$ to

 $H_3PW_6Mo_6O_{40}$ was finished accordingly. Filtering off the cation exchange resin, the $H_3PW_6Mo_6O_{40}$ solution was retrieved as filter liquor. The $H_3PW_6Mo_6O_{40}$ can be extracted from solution with ethyl ether and recovered as solid by evaporating ethyl ether at 60 °C. Using the recovered $H_3PW_6Mo_6O_{40}$ for the same experiment as Table 1, a desulfurization efficiency of 99.61% was achieved in 60 min, which is quite close to that obtained with the fresh catalyst.

3.6. Macro-kinetics of the process

Based on the experimental data, the overall process comprising mass transfer and chemical reaction can be simplified and described as follows:

In the moment of the start of the mixing of the two liquid phases, due to the vigorous agitation and the comparatively higher solubility of DBT in acetonitrile, the mass transfer of DBT extraction from *n*-octane phase to acetonitrile phase is significantly fast, and the resultant concentration of DBT in acetonitrile phase can be considered as closing to its equilibrium value. As a result, a large portion of DBT is extracted into the acetonitrile phase, leading to the quick drop of the mass transfer rate, meanwhile, the $H_3PW_6Mo_6O_{40}$ catalyzed oxidation of DBT by H_2O_2 initiates at a considerable high rate in acetonitrile phase. Consequently, the rate of the chemical reaction process reaches that of the mass transfer process is thereupon achieved and maintained till the completion of the chemical reaction.

In the light of the above assumptions, using the equilibrium formula, we have

$$K = \frac{y_A}{x_A} \tag{1}$$

where *K* is the equilibrium constant, and x_A , y_A , the mole fractions of DBT in *n*-octane phase and acetonitrile phase, respectively.

With the transformation of x_A , y_A into X_A , Y_A through the following Eqs. (2) and (3), we can finally turn Eq. (1) into a new form, i.e. Eq. (4).

$$X_{\rm A} = \frac{n_{\rm A,1}}{n_{\rm n-o}} = \frac{x_{\rm A}}{1 - x_{\rm A}} \tag{2}$$

where n_{n-0} and $n_{A,1}$ are the mole amount of *n*-octane and that of DBT in *n*-octane phase, respectively.

$$Y_{\rm A} = \frac{n_{\rm A,2}}{n_{\rm ac}} = \frac{y_{\rm A}}{1 - y_{\rm A}}$$
(3)

where n_{ac} and $n_{A,2}$ are the mole amount of acetonitrile and that of DBT in acetonitrile phase, respectively.

$$Y_{\rm A} = \frac{KX_{\rm A}}{1 + (1 - K)X_{\rm A}}$$
(4)

As X_A is very small, Eq. (4) can be approximately expressed as

$$Y_{A} = K X_{A} \tag{5}$$

Since acetonitrile and *n*-octane are mutually unsoluble, forming a distinct biphase system, and $H_3PW_6Mo_6O_{40}$ and H_2O_2 exist merely in acetonitrile phase [13], so, what we need is the distribution of DBT in the biphase system. In the absence of $H_3PW_6Mo_6O_{40}$ and H_2O_2 , no chemical reaction occurs, and the total amount of DBT remains the original of n_{A0} . That is

$$n_{\rm A,1} + n_{\rm A,2} = n_{\rm A0} \tag{6}$$

Combining Eqs. (2), (3) and (5) yields

$$n_{\rm A,2} = K \frac{n_{\rm ac}}{n_{\rm n-o}} n_{\rm A,1} \tag{7}$$

Further combination of the above two equations leads to

$$n_{\rm A,2} = \frac{\varphi}{1+\varphi} n_{\rm A0} \tag{8}$$

where

$$\varphi = K \frac{n_{\rm ac}}{n_{\rm n-o}} \tag{9}$$

The constant K is slight dependant on temperature within the temperature range of the experiment conditions and can therefore be regarded as fixed. As for n_{ac} and n_{n-o} , the amounts of acetonitrile and *n*-octane are identical for all the experiments. Hence φ can be regarded as an identical constant for all the experiments.

Owing to the equal volume of *n*-octane and acetonitrile used in all the experiments, according to Eq. (8), the concentration of DBT in acetonitrile phase can be written as

$$C_{\rm A,2} = \frac{\varphi}{1+\varphi} C_{\rm A0} \tag{10}$$

where C_{A0} is the initial concentration of DBT in *n*-octane phase. From the experimental test, the value of φ was determined as 1.17.

In the presence of $H_3PW_6Mo_6O_{40}$ and H_2O_2 (B) in acetonitrile phase, the irreversible oxidation of DBT will proceed at the initial rate of

$$r_i = k C_{A,2}^m C_B^n \tag{11}$$

where the kinetic factor k can be expressed in terms of activation energy E and temperature T as the well-known Arrhenius equation

$$k = A \exp\left(-\frac{E}{RT}\right) \tag{12}$$

Combining Eqs. (10)-(12) yields

$$r_i = A' \exp\left(-\frac{E}{RT}\right) C_{A0}^m C_B^m \tag{13}$$

where

$$A' = A \left(\frac{\varphi}{1+\varphi}\right)^m \tag{14}$$

In the light of above assumptions, since the steady state of the overall process can be achieved instantaneously, the initial rate of the overall process can be represented by Eq. (13).

The value of r_i in Eq. (13) can be calculated as the mean slope of the initial stage of the concentration-time curve of DBT in noctane. It should be noted that, owing to the instant attainment of equilibrium through mass transfer, the starting point at time zero for determining the mean slope of the above curve corresponds to a DBT concentration of C_{A0} - $C_{A,2}$, rather than C_{A0} .

In the above experimental results, by means of variable isolation, i.e. leaving only one changeable variable while fixing the rest, the pattern of the effects of each variable has been obtained. Based on these results, setting Eq. (13) as objective function, through successive least-squares regressions of $\ln r_i$ against $C_{A,2}$, $\ln r_i$ against $C_{A,2}$, and further $\ln r_i$ against 1/T, the values of *m*, *n*, *E* in Eq. (13) were determined as follows:

m = 1.02 (R = 0.996)

$$n = 0.38 \ (R = 0.989)$$

E = 43.3 kJ/mol (R = 0.992)

Meanwhile, the value of A' was determined as $(1.01\pm 0.06)\times 10^7\,(mol/L)^{-0.40}\,min^{-1}.$

Hence, the H₃PW₆Mo₆O₄₀ catalyzed oxidation of DBT by H₂O₂ is 1st order to DBT and 0.4th order to H₂O₂. Therefore, it can be drawn from this study that, when high O/S molar ratio are used, the reaction can simply be taken as a pseudo-1st order reaction. The activation energy of 43.3 kJ/mol indicates that the reaction process is quite fast in the presence of the H₃PW₆Mo₆O₄₀ catalyst. Hence, the macrokinetic results derived from this study should lay a solid foundation for better understanding and optimum design of the overall process.

4. Conclusions

The catalytic performance of $H_3PW_xMo_{12-x}O_{40}$ (x = 1, 3, 6) was found to follow the order of $H_3PWMo_{11}O_{40} < H_3PW_3Mo_9O_{40} <$ $H_3PW_6Mo_6O_{40}.$ Moreover, $H_3PW_6Mo_6O_{40}$ was also found to be superior to H₃PW₁₂O₄₀. The transformation of phosphotungstic acid to its cesium salt sharply weakens the catalytic effect, as verified by $Cs_{2.5}H_{0.5}PW_{12}O_{40} < H_3PW_{12}O_{40}$. Under the simulated system with an initial sulfur concentration of 500 ppmw, the ODS process catalyzed by H₃PW₆Mo₆O₄₀ can proceed very efficiently at 60 °C and an O/S molar ratio of 15. achieving a desulfurization efficiency of 99.79% or higher after 60 min. Hence, H₃PW₆Mo₆O₄₀ is promising for the deep desulfurization of actual ODS process. The process efficiency can be improved by an increase in any of the factors including temperature, O/S molar ratio, and catalyst dosage, whereby the favourable operating conditions were recommended as $T = 60 \degree C, O/C$ S = 15, and a catalyst dosage of 6.93 g $(H_3PW_6Mo_6O_{40})/L$ (simulated diesel). The effects of both the O/S molar ratio and the initial sulfur concentration conform to the law of mass action. With the aid of GC-MS analysis, sulfone species was confirmed to be the only product after reaction for 150 min. Furthermore, macro-kinetics of the process catalyzed by H₃PW₆Mo₆O₄₀ was studied, from which the reaction orders were found to be 1.02 to DBT and 0.38 to H₂O₂, and the activation energy of the reaction was found to be 43.3 kJ/mol. Moreover, the used catalyst can be recovered and reused with almost the same activity as the fresh.

Acknowledgement

Financial support from the Ministry of Education of China under New Century Excellent Talents Project (NCET-05-0584) is gratefully acknowledged.

References

- [1] E.W. Qian, J. Jpn. Petrol. Inst. 51 (2008) 14.
- [2] C. Song, Catal. Today 86 (2003) 211.
- A. Röthlishberger, R. Prins, J. Catal. 235 (2005) 229.
- [4] I.V. Babich, J.A. Moulijn, Fuel 82 (2003) 607.
- R.T. Yang, A.J. Hernández-Maldonado, F.H. Yang, Science 301 (2003) 79.
- S. Mondal, Y. Hangun-Balkir, L. Alexandrova, D. Link, B. Howard, P. Zandhuis, A. [6] Cugini, C.P. Horwitz, T.J. Collins, Catal. Today 116 (2006) 554.
- S. Liu, B. Wang, B. Cui, L. Sun, Fuel 87 (2008) 422.
- L. Cedeno-Caero, H. Gomez-Bernal, A. Fraustro-Cuevas, H.D. Guerra-Gomez, R. Cuevas-Garcia, Catal. Today 133-135 (2008) 244.
- A. Chica, A. Corma, M.E. Domine, J. Catal. 242 (2006) 299.
- [10] J.L. Garcia-Gutierrez, G.A. Fuentes, M.E. Hernandez-Teran, P. Garcia, F. Murrieta-Guevara, F. Jimenez-Cruz, Appl. Catal. A: Gen. 334 (2008) 366.
- [11] H. Lü, J. Gao, Z. Jiang, F. Jing, Y. Yang, G. Wang, C. Li, J. Catal. 239 (2006) 369.
 [12] G. Yu, S. Lu, H. Chen, Z. Zhu, Carbon 43 (2005) 2285.
- [13] K. Yazu, Y. Yamamoto, T. Furuya, K. Miki, K. Ukegawa, Energy Fuels 15 (2001) 1535. [14] J.L. Garcia-Gutierrez, G.A. Fuentes, M.E. Hernandez-Teran, F. Murrieta, J. Navar-
- rete, F. Jimenez-Cruz, Appl. Catal. A: Gen. 305 (2006) 15.
- [15] F. Al-Shahrani, T. Xiao, S.A. Liewellyn, S. Barri, Z. Jiang, H. Shi, G. Martinie, M.L.H. Green, Appl. Catal. B: Environ. 73 (2007) 311.
- [16] B. Zapata, F. Pedraza, M.A. Valenzuela, Catal. Today 106 (2005) 219.
- [17] F.M. Collins, A.R. Lucy, C. Sharp, J. Mol. Catal. A: Chem. 117 (1997) 397.
- [18] M.T.C. Fairbridge, Z. Ring, Appl. Catal. A: Gen. 219 (2001) 267
- [19] C. Li, J. Gao, Z. Jiang, S. Wang, H. Lu, Y. Yang, F. Jing, Top. Catal. 35 (2005) 169.
- [20] K. Yazu, T. Furuya, K. Miki, J. Jpn. Petrol. Inst. 46 (2003) 379.
- [21] C. Li, Z. Jiang, J. Gao, Y. Yang, S. Wang, F. Tian, F. Sun, X. Sun, P. Ying, C. Han, Chem. Eur. I. 10 (2004) 2277.
- I.V. Kozhevnikov, Catalysts for Fine Chemical Synthesis, vol. 2: Catalysis by [22] Polyoxometalates, John Wiley & Sons., Chichester, 2002.
- [23] M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer, Berlin, 1983. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, John [24]
- Wilev & Sons, London, 1963. [25] O.A. Kholdeeva, L.A. Kovaleva, R.I. Maksimovskaya, G.M. Maksimov, J. Mol. Catal.
- A: Chem. 158 (2000) 223.
- [26] C. Aubry, G. Chottard, N. Platzer, J.M. Bregeault, R. Thouvenot, F. Chauveau, C. Huet, H. Ledon, Inorg. Chem. 30 (1991) 4409.