

Synthesis, Characteristic and Application of PAM Catalysts for Oxidative Desulfurization

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Abstract: Oxidative desulfurization has been widely used in the desulfurization process for petroleum production. But conventional oxidative desulfurization catalyst was low desulfurization efficiency, low recycle use, and the mechanism was unclear. In this work, polyacrylamide (PAM) was first used in the loading of heteropolyacids and was used in oxidative desulfurization, which was prepared by simple reaction of each of the heteropolyacids and PAM. The optimal process condition for the catalyst was chosen by the single factor experiment. The optimal condition was as follows: the temperature was 60 °C, the amount of the catalyst was 0.2 g, the oxygen to sulfur ratio was 16, and the reaction time is 100 minutes. Besides, the cycle use experiment indicated the desulfurization efficiency was high after 10 times. In the end, the oxidative desulfurization mechanism was put forward. The catalyst had a good industrial development prospect.

Keywords: PAM, Desulfurization, Heteropolyacid

1. Introduction

In recent years, the progress of industrialization caused serious pollution to the environment. Petroleum has been widely used as the conventional energy sources. When the petroleum was used as the fuel, sulfur compounds in petroleum are troublesome substances, which was due to the fact that sulfur-containing substances are mixed into the air after combustion to produce SOX. When combined with water vapor, acid rain is generated, so it is important removed sulfur compounds from petroleum. Traditional hydrodesulphurization [7-12] (HDS) has been considered as the most effective method for removing mercaptans and thioethers. However, the HDS process was limited to the strict process conditions, besides, it was difficult for HDS to remove aromatic sulfides. In order to solve the HDS shortcomings, some non-HDS methods have been widely studied in recent years, such as oxidative desulfurization (ODS) [13-18], extractive desulfurization (EDS) [19-24], adsorption desulfurization (ADS) [25-30]. Among them, the ODS has many advantages than other methods. Researchers have been trying to find the mild conditions for the ODS process.

Bokare et al. explored the oxidative desulfurization of a series of aromatic thiophene model oils by hydrogen carbonate to activate hydrogen peroxide under mild conditions. [31] Bicarbonate ions can be combined with decomposed oxygen and transported in a limited manner, and DBT (dibenzothiophene) can be easily oxidized under suitable reaction conditions. Moreover, the inorganic metal carbonate is inexpensive and easily available. Shi et al. successfully synthesized a novel porous catalyst by a simple synthesis method. [32] Moreover, the hydroxide ions were added until pH was neutral. The porous catalyst had a high oxidative desulfurization efficiency under different conditions. Xun et al. designed a novel sheet-like catalyst with high thermal/chemical stability by sol-gel method. [33] The efficiency of removing dibenzothiophene (DBT) by the novel catalyst reached 99.9%.

In recent years, many researchers focused on high desulfurization efficiency catalyst for ODS process [34-36, 37-39]. Researchers are working to find different carriers such as SiO₂ [34-36], graphene [37-39], polyionic liquids [40-42], MnO₂ [43-45], and molecular sponges [46-48]. Among these different carriers, polyacrylamide was an ideal polymer carrier, which was due to the fact the synthesis polyacrylamide method was easy, and quantities of amine functional groups help disperse heteropoly acids. In recent years, many experiments on polyamide desulfurization have been reported. Yen et al. studied some characteristics of flue gas desulfurization (FGD) in polyamide membranes [49]. Meichsner et al.

produced hydrogen by a polyamide as an additive to produce water with a hydrate of a metal borate, and then the desulfuration was done by calcium cyanamide and hydrogen at the molten metal temperature [50]. Yu et al. used polyamide compounds to prepare a high-performance membrane and tested the desulfurization effect [51].

In this paper, a linear polymer was synthesized by combining polyacrylamide with phosphomolybdic acid. The polyacrylamide has quantities of amide groups in its main chain, which has high chemical activity. Besides, the amine group can react with heteropoly acid to form a salt, so that the heteropoly acids have high desulfurization efficiency.

2. Experimental

2.1 Materials

Dibenzothiophene (Shandong West Asia Chemical Industry Co., Ltd.); polyacrylamide (Aladdin); phosphotungstic acid (Aladdin); n-octane (Shanghai Mike Lin Biochemical Technology); 30% hydrogen peroxide (Shanghai Mike Lin Biochemical Technology); Benzenethiophene (Shanghai Mike Lin Biochemical Technology); 4,6-dibenzothiophene (Aladdin), All the reagents used in the present case are of analytical grade.

2.2 Methods

2.2.1 FTIR Measurement

The bulk potassium bromide solid was placed in an agate crucible and ground, and an appropriate amount of the sample was placed therein and ground again. After mixing, the mixture is placed on the carrier, and the mixture was tableted by a tableting machine. And then, the mixture was put in the Nexus 470 infrared spectroscopy instrument for detection.

2.2.2 SEM Measurement

Place the conductive paste on the copper table and attach the sample to the conductive paste to ensure that it will not fall. Place the copper table on the air compressor, vacuum, and the vacuum reaches 5×10^{-4} . Adjust the pressure to 20kv, adjust the contrast and brightness. Measurement with JSM-7100F (JEOL, Ltd) instrument. After finding the corresponding sample, adjust different magnifications, take photos, save the map

2.3 Synthesis of HPW/PAM-n

PAM and phosphotungstic acid were dispersed in deionized water, and the phosphotungstic acid solution was added dropwise to the PAM solution and stirred for 1 hour after the addition of the phosphotungstic acid was completed. After the reaction is completed, it is filtered, washed and dried, the product is HPW/PAM-n (n represents the molar ratio of polyacrylamide to heteropolyacid). The yield of the obtained product was 95%.

2.4 Oxidative Desulfurization Experiment

The thiophene compound and n-octane were mixed in an amount to prepare a certain ppm of the simulated oil, 10 ml of the simulated oil (500ppm) was taken, and 0.2 g of the catalyst was placed in the flask. After the set temperature was stabilized, hydrogen peroxide was added to cause the reaction. After 100min, the oil layer was analyzed by a fluorescence analyzer and the desulfurization rate was calculated. (Initial sulfur content C_0 minus the sulfur content C_t after the reaction divided by the initial sulfur content C_0 , the final result is the desulfurization rate).

The reaction flask was charged with 1 ml of 1-octyl imidazolium tetrafluoroborate to extract sulfur oxides, the oil layer was in the upper layer, and the ionic liquid was extracted in the lower layer. The sulfur remove (desulfurization efficiency) was calculated by initial sulfur minus reaction sulfur and then divided by initial sulfur.

3. Results

3.1. Characterizations of Catalysts

3.1.1 FTIR

Figure 1 indicated the polymer catalyst has been successfully synthesized. The infrared spectrum showed two different peaks of about 1417 cm^{-1} and 1647.7 cm^{-1} , of which 1647 cm^{-1} is the bending vibration peak of N-H, and 1417 cm^{-1} is the absorption peak of the methylene group corresponding to the amide portion of the polymer. The peak of about 1100 cm^{-1} should have the stretching vibration of C-H. The peak appearing in Figure 1 is in the range of $500\text{--}1200\text{ cm}^{-1}$, which clearly indicates that this is a typical heteropoly acid structure peak [52-57] at 3200 cm^{-1} . There is a broad peak near, which is a hydrated molecular O-H bond of heteropoly acid. From the figure we did not see that the vibration peak of -NH_2 may be due to the vibration peak of the hydrated molecule in the heteropoly acid obscuring the vibration peak of the amine group. In summary, successful synthesis of the polymer catalyst can be determined from infrared images and the structure and properties of the catalyst do not change during synthesis.

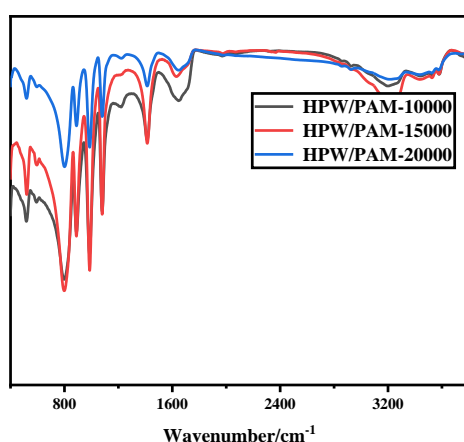


Figure 1: FT-IR spectra of HPW/PAM-10000, HPW/PAM-15000, HPW /PAM-20000.

3.1.2 SEM

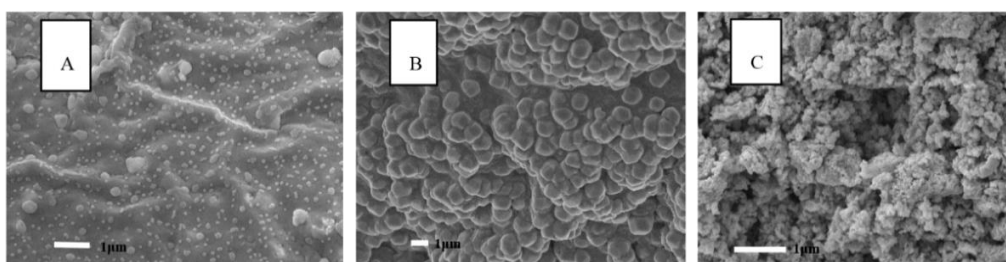


Figure 2 : SEM images of (A) HPW/PAM-10000, (B) HPW/PAM-15000, (C) HPW/PAM-20000.

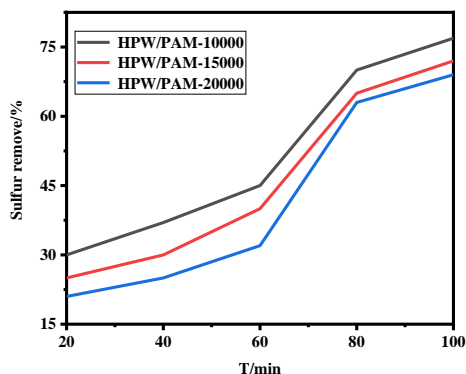


Figure 3: Desulfurization efficiency of different catalysts.

As was shown in Figure 2, the catalyst morphology was different under different loading amount. Figure 2A indicated the polymer acted like a large curtain with specific properties when the loading amount was low. The heteropoly acid can be uniformly distributed on the polymer and the morphology of the heteropoly acid is complete. When the load was larger, the amount of heteropoly acid was larger, and the distributed curtain state was much more uniform. Besides, more heteropoly acids were closely attached, which caused agglomeration. In other words, and catalyst stability would decrease with high load amount. Figure 2(c) indicated that HPW/PAM-20000 catalyst was amorphous state, and then the effective contact area of the catalyst was greatly reduced, it accords with the results in Figure 3.

3.2. Desulfurization Performance of Catalysts

HPW/PAM-n was used as catalyst to obtain the optimal desulfurization process conditions by single factor experiment. The initial sulfur content in the experiment is 500ppm. As was shown in Figure 3, the desulfurization efficiency of different catalysts were different. The catalytic efficiency decreased with the increase of load, which was due to the fact increase of n value lead to the fusion of heterozygosis, and then reduce the exposed contact sites. Therefore, desulfurization efficiency increased under low n value. The DBT removal rate by HPW/PAM-10000 reached 76.9% after 100 minutes. The desulfurization rate increased with the increase of reaction time. HPW/PAM-10000, HPW/PAM-15000 and HPW/PAM-20000 showed the highest efficiency among the three catalysts within 100 minutes. Therefore, HPW/PAM-10000 was chosen as the catalyst for the next single factor experiment. The single factor experiment explored the different oxygen to sulfur ratio, initial sulfur content, temperature and sulfur compounds influence on desulfurization rate by HPW/PAM-10000.

As shown in Figure 4, the desulfurization rate increased with the increase of mole ratio of O/S, and the optimal O/S ratio was 16(128ul). When O/S was 18, the desulfurization rate would not change significantly. It could be explained by the theory that hydrogen peroxide decomposing increased, and liquid sealing hindered the reaction under high water content.

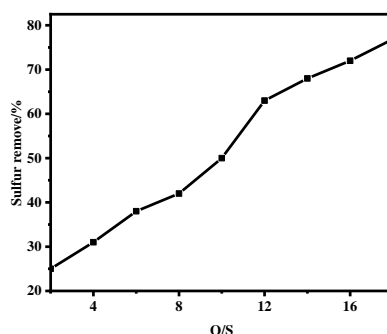


Figure 4: Desulfurization efficiency of different oxygen to sulfur ratio.

As the initial sulfur content increased from 100ppm to 250ppm (Figure 5), the desulfurization rate increased, which was due to the fact that the contact area between oxygen molecules and sulfur compounds increased with high sulfur content and then desulfurization rate increased.

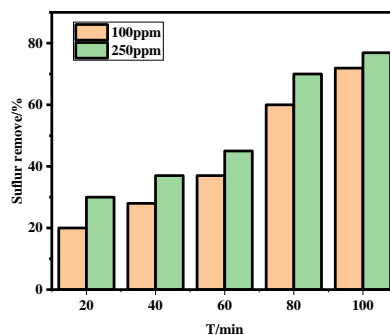


Figure 5: Desulfurization efficiency of different initial sulfur content.

As can was shown in Figure 6, when the temperature increased from 30°C to 60°C, the removal rate of DBT increased from 37.5% to 76.9%. It was due to the fact that the decomposition rate of hydrogen peroxide increased with high temperature, and oxygen molecules can effectively react with sulfur compounds.

Figure 7 indicated the desulfurization efficiency was $DBT > BT > 4,6\text{-DMDBT}$ for different sulfur compounds. Different sulfur compounds have different electron clouds densities and spatial resistances, and then the reaction rate between sulfur and oxygen molecules was different.

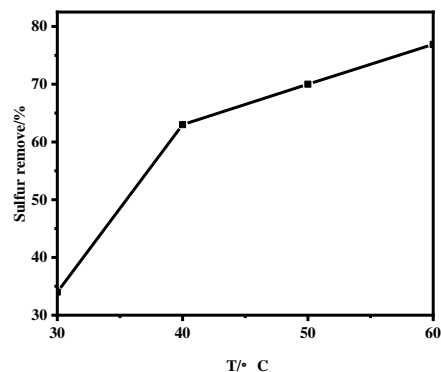


Figure 6: Desulfurization efficiency at different temperature.

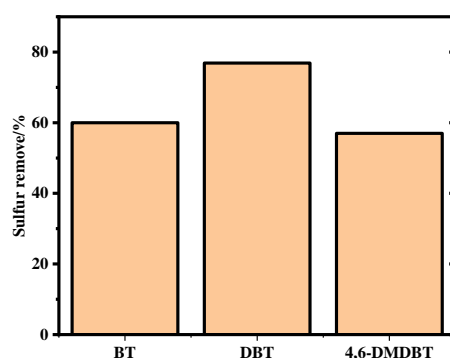


Figure 7: Desulfurization efficiency of different sulfur compounds.

3.3 Catalyst Recycling

Catalyst recovery is an important property for industrialization [58-61]. The number of cycles is large, the reaction efficiency is constant, and the time for synthesizing the catalyst can be saved multiple times. HPW/PAM-10000 catalyst was used to study the recycling efficiency (Figure 8), and the catalyst was found to be effective. The sulfur remove efficiency was stable after ten times. A slight decrease in chemical efficiency was due to a small amount of active site detachment during multiple uses, and a slight loss of catalyst in operational process.

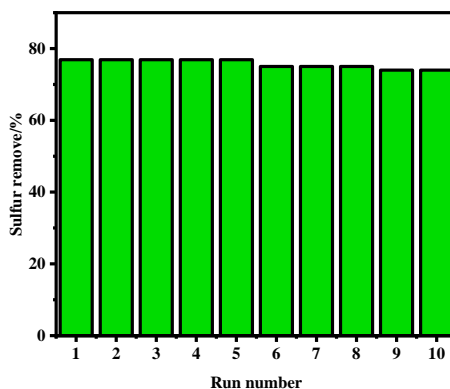


Figure 8: Recycling of catalyst.

4. Reaction Mechanism

As can be seen from Figure 9, phosphotungstic acid is a good catalyst for oxidative desulfurization. Its active center can decompose hydrogen peroxide to produce water and oxygen, and then its active

center W can act to transport oxygen molecules, transporting oxygen molecules to specific locations for reaction. Of course, the W valence state of the event center will also change [62-65]. When an oxygen molecule is successfully transported and reacts with a sulfur compound, its valence returns to its original valence state, and the process is repeated until all oxygen molecules are transported. At this time, the sulfur compound is also oxidized to a sulfone or a sulfoxide. The polarity of the sulfone or sulfoxide is greatly different from the polarity of the aromatic sulfur compound, and the sulfur oxide can be easily extracted.

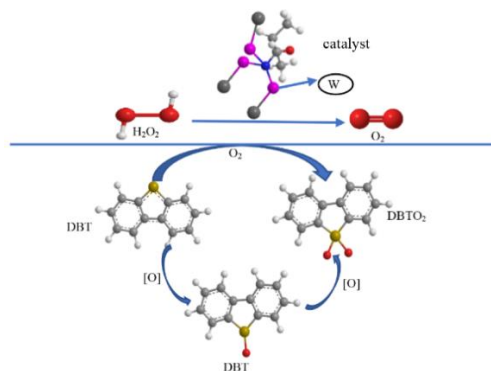


Figure 9: Oxidation mechanism diagram.

5. Conclusions

The star-like catalyst was successfully synthesized by a simple synthesis method. The catalyst was used for oxidative desulfurization, and the oxidative desulfurization efficiency was high after 10 times. The detailed conclusions were as follows. The optimal condition for the catalyst was as follows. The temperature was 60 °C, the amount of the catalyst was 0.2 g, the oxygen to sulfur ratio was 16, and the reaction time is 100 minutes. The catalyst had high desulfurization efficiency after recycle use 10 times, so the catalyst stability was suitable for the industrial application. The mechanism for the oxidative desulfurization process was put forward. Hydrogen peroxide could produce water and oxygen and then after a series of reaction the desulfurization process occurred.

Acknowledgement

This work was financially supported by the Start-up funding for high-level talents introduction and research of Dali University.

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