



Original article

A new green system of HPW@MOFs catalyzed desulfurization using O₂ as oxidantJian-Wei Ding^a, Rui Wang^{b,*}^aSchool of Environmental Science & Engineering, Shandong University, Jinan 250199, China^bDepartment of Environmental Science and Engineering, Shandong University, Jinan 250199, China

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ABSTRACT

A series of crystalline compounds were obtained from simple one-step hydrothermal reaction of copper nitrate, benzenetricarboxylate and different Keggin polyoxometalates. Phosphotungstic acid immobilized in host matrix was selected for the first time as a recyclable and efficient catalyst in oxidative desulfurization process, under eco-sustainable conditions supported by the green oxidant O₂ and the green extracting agent distilled water. The efficiency of desulfurization with air was studied and it is possible to use air as green oxidant in desulfurization. Moreover, the catalyst is effective for the desulfurization of real diesel.

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1. Introduction

The strict regulations of fuel specifications recently implemented in many countries for environmental protection have promoted the research demand of optimizing deep desulfurization technologies. Oil desulfurization technology can be simply divided into hydrodesulfurization (HDS) and non-hydrodesulfurization (NHDS). HDS is highly efficient in removing thiols, sulfides and disulfides, however, its investment and operation costs are both very high. Moreover, it is less successful for removing refractory sulfur species, such as dibenzothiophene (DBT) and its derivatives [1]. Oxidative desulfurization process (ODS) applied as one kind of NHDS methods, has shown to be one of the most promising techniques as it avoids use of hydrogen and can be conducted under mild condition. Different oxidants, such as hydrogen peroxide [2], molecular oxygen [3], and ozone [4], were used in the process to reduce sulfur in fuel.

The polyoxometalates (POMs) having strong Brønsted acidity enable them to be utilized as solid-acid catalysts in chemical reactions. The most obvious drawback is the relatively poor surface area for heterogeneous process, which confined the application of POMs as solid catalysts. Thus materials with high surface area are utilized to act as supports to improve the

dispersion of POMs. Metal organic frameworks (MOFs) have emerged as a particular class of functional solid-state materials, owing to their large surface area, adjustable chemical composition and tunable pore structure. Recently, investigations relevant to applications of MOFs in gas storage, separation, catalysis and drug delivery have been widely reported [5–8]. Consequently, MOFs have been found to be suitable supports capable of incorporating POMs to form efficient heterogeneous catalysts. However, at present, only a few examples can be found in literatures involving the use of POM@MOFs as catalysts for oxidative desulfurization, and the oxidant used was H₂O₂ [9,10]. Taking environmental and economic concerns into account, the utilization of O₂ as the oxidant for ODS is most desirable, especially the advantages of air has received a universal attention. At present, O₂ has been used for ODS with catalysts like metal oxides and salts [11–13], but these methods can only achieve low desulfurization efficiency. Murata reported a highly efficient oxidation of sulfur compounds with O₂ by using cobalt salts as catalysts and aldehydes as sacrificial materials, respectively [14]. However, use of sacrificial materials is not economical in most cases and seeking new efficient way of achieving low sulfur fuel is therefore desirable to date.

Unprecedentedly, using O₂ as oxidant, our present work developed a new and green POM@MOFs catalyzed system to realize deep desulfurization of refractory sulfur compounds from fuel oil, which should provide a new pathway for efficient oxidative desulfurization under eco-sustainable conditions.

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2. Experimental

Preparation of the materials: The preparation of the catalysts was conducted according to the literature method [15]. The $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, $\text{H}_7[\text{P}(\text{W}_2\text{O}_7)_6(\text{Mo}_2\text{O}_7)_6]$, threphthalic acid (H_3BTC) and $(\text{CH}_3)_4\text{NOH}$ were obtained commercially from Tianjin Kermel Chemical Reagent Co., (Tianjin, China), $\text{Cu}(\text{NO}_3)_2$ was purchased from Tianjin Fuyu Fine Chemistry Co., (Tianjin, China). Water was redistilled after deionisation. The heteropolyacid were dried under $230\text{ }^\circ\text{C}$ for 3 h before use. The mixture of $\text{Cu}(\text{NO}_3)_2$ (0.96 g) and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (HPMo, 0.8 g) for HPMo@MOFs, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW, 0.8 g) for HPW@MOFs, $\text{H}_7[\text{P}(\text{W}_2\text{O}_7)_6(\text{Mo}_2\text{O}_7)_6]$ (HPWMo, 0.8 g) for HPWMo@MOFs and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (HSiW, 0.8 g) for HSiW@MOFs in distilled water (40 mL) were stirred for 20 min, followed by the addition of H_3BTC (0.84 g) and $(\text{CH}_3)_4\text{NOH}$ (0.36 g), respectively. After that, continuous stirring of the mixture was performed for about 30 min at r.t. The turbid mixture (pH 2–3) was sealed in a Teflon-lined autoclave and heated at $180\text{ }^\circ\text{C}$ for 24 h, and then was slowly cooled to room temperature. Blue or green crystals were then collected.

The O_2 driven oxidative desulfurization process: A certain amount (0.123 g) of dibenzothiophene (DBT, 99%) was dissolved in 60 mL octane contained in a three-necked flask to obtain the simulated oil with 500 mg/L (500 ppm) sulfur content, 60 mL distilled water was then added as extraction agent. Using thermostate water bath to stir the mixture at $90\text{ }^\circ\text{C}$ for 10 min, then oxygen was bubbled into the mixed liquid (the flow rate of O_2 was 90 mL/min), followed by the addition of catalyst. Catalyst dosage is 1% of the mass of normal octane (0.421 g). Reaction liquids in octane phase were sampled, respectively at a series of reflux condensation reaction time within 180 min and analyzed afterwards with a micro coulometer (WK-2E).

3. Results and discussion

The results are shown in Fig. 1. During the catalytic ODS process, under the same condition, the efficiencies of oxidative desulfurization decrease in the order of $\text{HPW@MOFs} > \text{HPMo@MOFs} > \text{HPWMo@MOFs} > \text{HSiW@MOFs}$. The DBT removal rate can reach 83% in 180 min with HPW@MOFs. The result is influenced by the Brønsted acidity sites on POMs. It is important to protect the acid sites to allow the reactant molecules

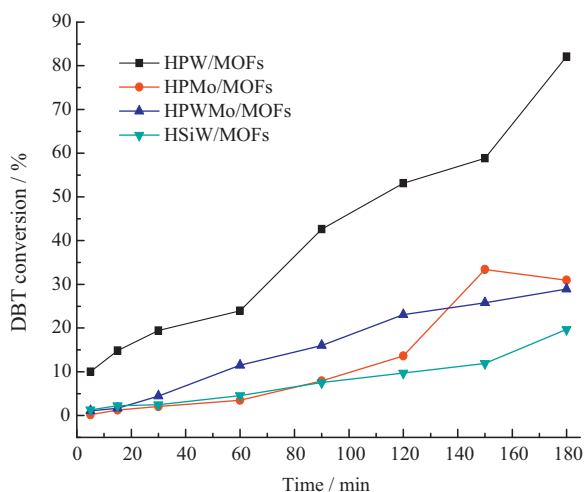


Fig. 1. Oxidative desulfurization effects of the composite catalysts from different polyoxometalates and same MOFs, using O_2 as oxidant. Conditions: reaction temperature, $90\text{ }^\circ\text{C}$; the flow rate of O_2 , 90 mL/min; catalyst dosage; 1% the mass of normal octane; extracting agent, distilled water; reaction time, 180 min.

access the acidic sites on POMs, which is responsible for their highly catalytic activity. HPW@MOFs shows a higher catalytic activity than other catalysts, which is attributed to $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW) species' strongest Brønsted acid among the Keggin series [16]. From Fig. 1, the desulfurization reaction over HPW@MOFs shows a rising trend in 180 min. Therefore we prolonged the reaction time to 240 min in subsequent experiments and investigated the effects of oxygen flow rate and the amount of catalyst on the DBT conversion over HPW@MOFs.

Characterizations of the HPW@MOFs were conducted by XRD and IR to confirm the structures of HPW@MOFs. Comparison of the HPW and HPW@MOFs powder XRD patterns (Fig. 2). There are several peaks which emerge mainly at 6° , 9° , 12° , 17° , 23° , 24° , 26° and 28° , showing that the polyoxometalate anion was retained after immobilization. The strongest peak appears at 6° , according to the literature [16,17], the reflection at $2\theta = 6^\circ$ is a typical feature of the Keggin structure. The IR spectrum (Fig. 3) contains bands at $800\text{--}1100\text{ cm}^{-1}$, which matches those exhibited by heteropolyacid. The HPW anion contains the typical bands [18] of $\text{W-O}_c\text{-W}$ at 813 cm^{-1} , $\text{W-O}_b\text{-W}$ at 893 cm^{-1} , W=O_d at 981 cm^{-1} , P-O_a at 1079 cm^{-1} . The XRD and IR characterizations of the HPW@MOFs confirm the presence of HPW in the cavities of the crystalline skeleton support, which is in line with the previous literature [15]. From the TG analysis (Fig. 4), an obvious plateau of $200\text{--}250\text{ }^\circ\text{C}$ can be observed for HPW@MOFs, indicating its high thermal

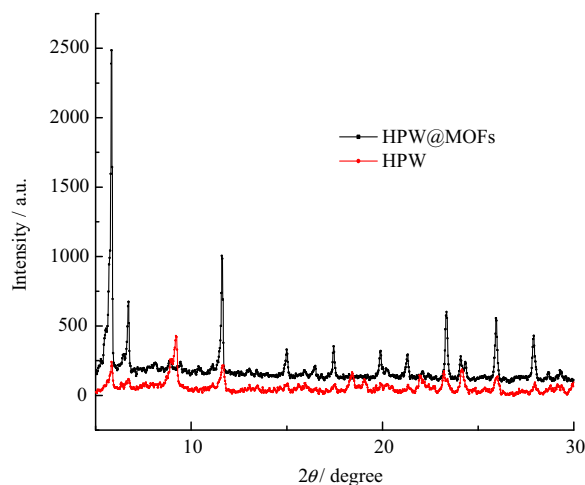


Fig. 2. Powder XRD patterns of pure HPW and HPW@MOFs.

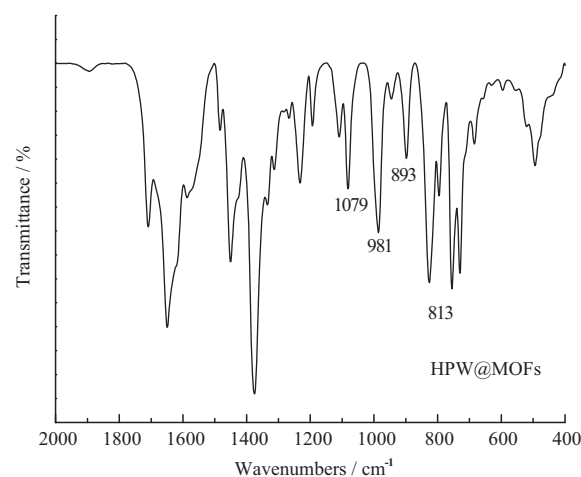


Fig. 3. IR spectra of HPW@MOFs.

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