PERFORMANCE EVALUATION OF "SHIP-IN-THE-BOTTLE" TYPE HETEROPOLY ACID ENCAGED Y-TYPE ZEOLITE AS CATALYST FOR OXIDATIVE DESULFURIZATION

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Clean fuel and clean production technologies, including desulfurization, have become a subject of concern in environmental catalysis studies. One of the most promising desulfurization processes is oxidative desulfurization combined with extraction. Keggin-type heteropoly acids encaged Y-type zeolite were studied as promising catalytic agents for the oxidation of dibenzothiophene with hydrogen peroxide in a normal octane/acetonitrile biphasic system. The key factors affecting the reaction, including the catalyst amount, O/S molar ratio and contact time between oxidant and catalyst, were investigated. The conditions favourable to the reaction were also determined. Moreover, the reused encaged type catalyst exhibited good catalytic activity in recovery experiments and can be effectively applied to diesel oil.
Keywords: Oxidative desulfurization; Heteropoly acid; Ship-in-the-bottle; Encagement; Clean fuel; Heterogeneous catalysis.

Removing sulfur compounds in fuel oil is a beneficial method to reduce the total emission of SO_x in the air. Environmental specification and legal requirements are globally well-established to promote clean fuels. In conventional catalytic hydrodesulfurization (HDS), aliphatic and acyclic thiols, sulfides, and disulfides have high reactivity to be converted into H_2S, while aromatic compounds with steric hindrance on the sulfur atom are difficult to remove in hydrogenation reaction[1]. To obtain ultra-low sulfur fuels, severe process conditions with higher temperature and pressure and longer residence time are required to bring high investment and operating cost. It is desirable to develop more energy-efficient technology.

Potential deep desulfurization processes include, but are not limited to, adsorption[2], extraction[3], oxidation[4], and bioprocesses[5]. Oxidative desulfurization (ODS) combined with extraction is one of the most promising desulfurization processes. Compared with conventional HDS, ODS can be

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carried out under mild conditions as ambient temperature and atmospheric pressure. In the ODS process, organosulfur compounds can be oxidized to corresponding sulfoxide and sulfone by electrophilic addition reaction. The products can be removed by extraction or adsorption.

Heteropoly compounds (HPCs), renowned as green catalysts, are regarded as potentially effective catalysts in the ODS process with hydrogen peroxide (H_2O_2). The Keggin-type heteropoly acids (HPAs) are composed of a tetrahedral or octahedral oxygen-metal cluster, and have a regular hexahedron cage structure. The symmetrical structure and the large molecule bulk determined catalysis efficiency and selectivity[6]. However, HPAs are difficult to recover because they are soluble in water and polar organic solvents. A beneficial solution to this problem is immobilising Keggin-type HPAs in supports with high specific surface areas. The shape of the anion of Keggin-type HPA is similar to a sphere, whose diameter is about 1 nm. The supercages of Y-type zeolites have a diameter of 1.3 nm and are interconnected by windows 0.74 nm in diameter. Therefore, zeolite is regarded as an ideal material for the encagement of HPA molecules having a Keggin structure[7].

The encaged catalysts, called "ship-in-the-bottle" catalysts, can potentially serve as alternative solid catalysts to conventional homogeneous or heterogenous catalysts[7]. Sulikowski et al.[8] encapsulated Keggin-type phosphotungstic acid (PW) in the supercages of Y-type zeolite and the highly active catalysts were exemplified in the isomerisation and disproportionation of *m*-xylene. Mukai et al.[9] succeeded in immobilising phosphomolybdic acid (PMo) in a dealuminated Y-type zeolite crystal. The obtained catalysts showed high activity for the esterification of acetic acid with ethanol. Tran et al.[10] encaged molybdenum oxide into the supercages of US-Y using a hydrothermal synthesis technique. The dispersion of phosphomolybdic acid and the presence of silicomolybdic acid acted synergistically as active sites for the partial oxidation of methane.

In this study, the dibenzothiophene (DBT) in the *n*-octane solution was used as simulated diesel oil. The "ship-in-the-bottle" type heteropoly acids encaged Y-type zeolites were evaluated as catalyst with hydrogen peroxide as oxidant, in *n*-octane/acetonitrile biphasic system. To the best of our knowledge, the results derived from performance evaluation of this new catalyst have not been reported in previous studies. The main factors affecting the process were evaluated to determine the optimum reaction condition. Furthermore the reusability of catalyst proved to be satisfactory in veritable diesel oil under favourable conditions.

EXPERIMENTAL

Materials and Instruments

Materials. Dibenzothiophene ($C_{12}H_8S$) was purchased from Sigma–Aldrich and used without further purification. NaY zeolite (Si/Al = 5) were supplied by the Qilu Petrochemical Zhoucun catalyst factory. AR-grade phosphomolybdic acid ($H_3PMo_{12}O_{40}\cdot 12H_2O$) was purchased from the National Drug and Chemical Group Co., Ltd. Hydrogen peroxide (H_2O_2, AR) was supplied by Laiyang Kangde Chemicals Co., Ltd. Tungsten trioxide (WO_3, AR) and molybdenum trioxide (MoO_3, AR) were purchased from Tianjin Reagent Chemicals Co., Ltd. Normal octane (C_8H_{18}, AR) and acetonitrile (CH_3CN, AR) were purchased from Tianjin kermel Chemicals Reagent Co., Ltd.

Instruments. The gas chromatograph equipped with a flame ionisation detector (GC-FID, SP-6890) was from Shandong Lunan Ruihong Chemical Instruments Co., Ltd. The existence of PMo12 in the catalyst was confirmed using a Fourier transform infrared spectrometer (FT-IR; Avatar370) and an X-ray diffraction analyzer (XRD; Germany Bruker, Advance D8). The specific surface areas of the catalysts were determined by a Quadrasorb SI specific surface area analyzer.

Preparation of HPAs Encaged Y-Type Zeolite Catalyst

The catalysts were prepared according to literature[9]. Y-type zeolite was used as the catalyst support and converted to H^+ type first. Then, prior to catalyst preparation, H^+ was exchanged with NH_4^+ using an aqueous NH_4Cl solution. Because the presence of aluminium atoms in the zeolite framework disturbs the formation of HPAs, the zeolite was dealuminated in a steam atmosphere for 10 h.

Encaged catalysts were obtained using H_3PO_4 as the P source and water soluble MoO_3 as the Mo source. First, in accordance with a certain mass fraction, MoO_3 powder (10, 20, and 30 wt.%) and prepared NH_4-Y zeolite support were quantified. Next, the mixed sample was ground uniformly to fine powder in agate mortar by manual handling. The mixed powder was calcined at 500 °C for 4 h and MoO_3 could spontaneously disperse onto the Y-type zeolite surface to form an amorphous layer[11]. Subsequently, the cooled mixed powder was immersed into deionised water, and then the slurry was agitated at room temperature for 24 h. Finally, 85 wt.% H_3PO_4 with the amount of 0.9 g g^{-1} MoO_3 was added to the slurry, after which the slurry was heated to 95 °C and kept at this temperature for 3 h. The slurry was filtered and washed three times with hot water to wash away the HPAs loaded on the zeolite surface, and dried at 95 °C. PMo encaged Y-type zeolite catalyst (PMo-Y) was then obtained. The same procedures were used to obtain 10% PW-Y.

Measurement of Catalyst in Simulated Diesel Oil

The "ship-in-the-bottle" type catalysts were used as catalyst in this work. The catalytic activity was measured according to the method described in our previous report[12]. The solution of DBT in *n*-octane was used as simulated diesel oil, in which initial sulfur content of 500 ppm was set by fixing the dosage of DBT. The catalyst was pre-immersed with needed amount of H_2O_2 solution for a fixed contact time, and then added in the *n*-octane/acetonitrile mixture liquid. The oxidation reactions were carried out in the acetonitrile phase and the temperature of thermostat water bath was set as 60 °C. After fixed time reactions, tested samples were withdrawn from the *n*-octane phase and the sulfur contents were analyzed 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 detector, and 270 °C for the oven. The concentration of DBT was quantified by external standard method.

The desulfurization efficiency which expresses the activity of the catalysts for sulfur removal can be calculated as

$$\text{desulfurization efficiency} = [(C_\mathrm{i} - C_t)/C_\mathrm{i}] \times 100\%$$

where C_i is the initial sulfur concentration in the *n*-octane solution, C_t is the sulfur concentration in the *n*-octane solution after *t* min oxidative reaction combined with an extraction. The term "desulfurization efficiency" in this study refers to the percentage ratio of sulfur concentration decrease in the *n*-octane phase to its initial sulfur concentration.

Measurement of Catalyst in Veritable Diesel Oil

Two samples of veritable diesel oil were tested using the same procedure as simulated diesel oil. Acetonitrile liquids of 120 and 60 ml were mixed with diesel samples A and B correspondingly, before ODS reaction. Extraction with 60 ml acetonitrile was performed on diesel sample B, which had undergone ODS treatment. The diesel and acetonitrile solutions were separated by a funnel.

RESULTS AND DISCUSSION

Catalyst Confirmation

The FT-IR spectrum of PMo encaged Y-type zeolite is shown in Fig. 1. The spectra of Y-type zeolite and PMo are also shown in the figure for comparison. The typical Keggin structure absorption band P–O (1062–1068 cm^{-1}) in

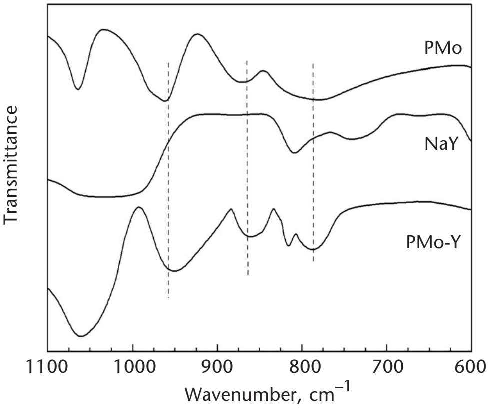

FIG. 1
FT-IR spectra of Y-type zeolite, PMo and PMo encaged zeolites

PMo is not observed in PMo-Y because of the overlap with the absorption band of NaY zeolite. The remaining typical absorption bands in PMo, corresponding to Mo=O_t (954–975 cm^{-1}), Mo–O_c–Mo (869–880 cm^{-1}), and Mo–O_e–Mo (778–795 cm^{-1}), can be clearly observed in PMo-Y, a result consistent with previous report[7]. The presence of Keggin structure PMo in obtained encaged catalyst was confirmed by FT-IR analysis.

The XRD patterns of Y-type zeolite, PMo and PMo encaged Y-type zeolite catalysts were shown in Fig. 2. It can be noticed that XRD spectra of PMo-Y agrees with that of Y-type zeolite. The peaks corresponding to PMo have disappeared in the XRD spectra of PMo-Y catalysts, which indicate the PMo loaded on the zeolite surface have been removed in obtained encaged catalysts.

Based on FT-IR and XRD analysis, it was confirmed that PMo was encaged in the zeolite cavities not on the surface in encaged type catalysts.

Comparison of the Heteropoly Acid Encaged Y-Type Zeolites as Catalysts

The activity of the prepared catalysts on the oxidation of DBT was evaluated in *n*-octane/acetonitrile biphasic system at the reaction temperature of 60 °C with an initial sulfur concentration of 500 ppm. The identical conditions have a contacting time between catalyst and oxidant of 30 min in pre-immersion, a catalyst amount of 1 wt.% of *n*-octane and an O/S molar ratio of 20. The results were shown in Table I.

Among the catalysts NH_4-Y zeolite, 10 wt.% PW-Y, and 10 wt.% PMo-Y, the catalytic activities followed the order NH_4-Y zeolite < 10 wt.% PW-Y < 10 wt.% PMo-Y. Compared with encaged catalysts, the porous NH_4-Y zeolite showed lower sulfur elimination in the oxidative reaction. Encaging the heteropoly compounds in Y-type zeolite enhanced catalytic activity. The catalytic activity of 10 wt.% PMo-Y, which has higher oxidation capacity, was superior to that of 10 wt.% PW-Y.

Among the catalysts 10, 20, and 30 wt.% PMo-Y, the first exhibited higher activity than the others. During calcining, the interaction between dispersed MoO_3 and zeolite framwork resulted in the destruction of the zeolite crystalline structure. The increase in dispersed MoO_3 amount reduced the specific surface area (Table I) and crystallinity of Y-type zeolite (Fig. 2), and thereby decreasing sulfur removal[11].

The catalytic activity of 10 wt.% PMo-Y (TOF = 27.9 h^{-1}) was not as good as that of PMo (TOF = 153.6 h^{-1}), possibly owing to the limited amount of PMo introduced in the Y-type support. The investigation was made to determine that the amount of PMo encaged in the zeolite was approximately

0.09 g g^{-1} support in previous study[7]. Further research on the influence of properties of the zeolite support is required to increase the amount of encapsulation. Meanwhile we can consider this comparison from another viewpoint that 10 wt.% PMo-Y have an advantage of reusability. The encaged type catalyst can be recovered in convenient recovery process and the recovered catalyst exhibited excellence catalytic performance close to that of the fresh.

On the basis of the results, 10 wt.% PMo-Y was chosen for additional experiments on the effects of several operational factors.

TABLE I
Desulfurization effects and specific surface area of obtained catalysts

Catalyst	Efficiency %	$r_i^a \times 10^{-2}$ g h^{-1}	$TOF^b \times 10^{-2}$ h^{-1}	Specific surface m^2 g^{-1}
NH_4-Y zeolite	73.9	3.1	7.5	623.2
10 wt.% PW-Y	79.3	6.2	14.7	455.4
10 wt.% PMo-Y	83.2	11.7	27.9	468.8
20 wt.% PMo-Y	77.6	7.8	18.5	371.6
30 wt.% PMo-Y	77.0	6.3	14.9	285.5
PMo	98.8	64.5	153.6	–

[a] Intital rate $r_i = dm_{DBT}/dt$ (t = 0). [b] Turnover frequency TOF = $m_{DBT}/tm_{cat} = r_i/m_{cat}$.

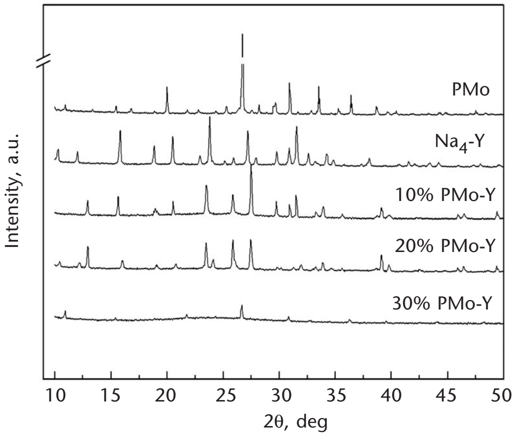

FIG. 2
XRD patterns of Y-type zeolite, PMo and PMo encaged zeolite catalysts

Role of Main Factors Affecting the Process

Effect of the contact time between oxidant and catalyst. Using the same experimental system, contact time between oxidant and catalyst was investigated under identical conditions to the above mentioned. The result was shown in Fig. 3. It can be seen that, with an increase in the contact time of H_2O_2 reaction with the catalysts from 10 to 20 min, the final DBT elimination increased from 78.4 to 84.8%. As the contact time reached 30 and 40 min respectively, desulfurization efficiencies of 83.2 and 76.1% were obtained accordingly. The maximum sulfur removal was achieved at a contact time of 20 min.

The above results can be explained in terms of the mechanism for oxidation reactions in the previous work[13] that the tungsten and molybdenum HPAs with a Keggin structure converted to polyoxoperoxo species in the presence of hydrogen peroxide. The phosphotungstic and phosphomolybdic compounds are catalyst precursors and the actual active species are polyoxoperoxo complexes, such as, $PO_4[MO(\mu\text{-}O_2)(O_2)]_4{}^{3-}$ or $PO_4[MO(\mu\text{-}O_2)(O_2)]_2{}^{3-}$. In the pre-immersion step, the solid encaged catalyst can react with H_2O_2 solution, producing active peroxo species (APS) which possess high activity for the DBT oxidation. Compared to longer contact time, a contact time of 10 min for the solid-liquid reaction was insufficient to completely produce APS, and therefore, lower DBT removal was achieved. On the other hand, with excessive contact time of 30 and 40 min, the DBT removal was also de-

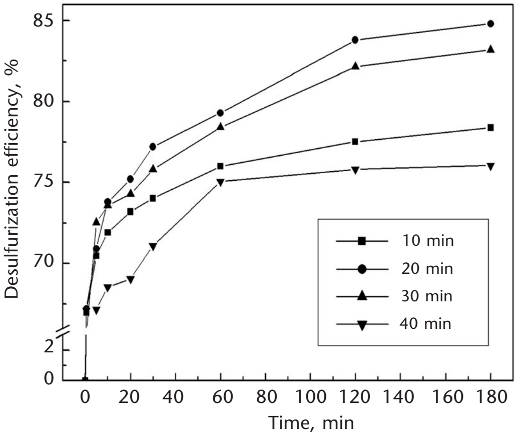

FIG. 3
The effect of contacting time on desulfurization efficiency. Experimental conditions: temperature, 60 °C; O/S molar ratio, 20; catalyst dosage, 1% of the mass of *n*-octane and DBT

clined, possibly due to the competing reactions in the pre-immersion step. It is possible to produce other peroxo species (OPS), unlike APS, which are inefficient for the DBT oxidation. A longer contact time may be in favour of the formation of OPS rather than APS which decreased desulfurization efficiency. Besides, we suppose that excessive contact time promoted H_2O_2 decomposition reactions which reduced the amount of the H_2O_2 and had a negative effect on the oxidation process. These results suggested that the suitable contact time can be chosen as 20 min.

Effect of the amount of catalyst. Catalyst amount also plays a significant role in the oxidation of DBT. With the catalyst dosage ranging from 0.5 to 2 wt.% of *n*-octane, the desulfurization efficiencies increased from 79.2 to 84.8% and then to 84.4% at a reaction time of 180 min (Fig. 4).

On the whole, the desulfurization efficiency was proportional to the mass of the catalyst at low amounts. Conversely, the desulfurization efficiency was independent of the mass of the catalyst at high amounts. The favourable catalyst amount can therefore be recommended as 1 wt.% of *n*-octane.

Effect of the O/S molar ratio. As a predominant factor, the O/S molar ratio was investigated under identical conditions. The results were shown in Fig. 5. As the O/S molar ratio varied from 10 to 20, the desulfurization efficiency increased from 78.2 to 84.8% at a reaction time of 180 min. Increasing the O/S molar ratio to 25 results in failure to significantly improve the desul-

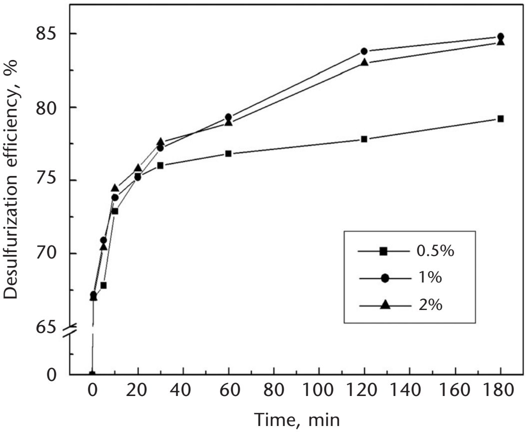

FIG. 4
The effect of the amount of catalyst on desulfurization efficiency. Experimental conditions: temperature, 60 °C; O/S molar ratio, 20; contacting time, 20 min

furization efficiency. At a reaction time range of 0 to 3 h, the desulfurization rate exhibited its maximum level at the initial stage of the overall reaction time of 20 to 60 min (Fig. 5). The desulfurization rate decreased markedly at the reaction time from 20 to 120 min. At the final phase of the reaction, the desulfurization rate reached a level close to zero. The favourable O/S molar ratio is 20.

The results indicate that the favourable conditions are as follows: catalyst and oxidant contact times, 20 min; catalyst amount, 1 wt.% of *n*-octane; and O/S molar ratio, 20.

Catalyst Recovery

Under the foregoing conditions, reusability of 10 wt.% PMo-Y was investigated in the *n*-octane/acetonitrile biphasic system. After ODS reaction, the two-phase mixture was left to stand until the two layers of the *n*-octane phase and acetonitrile phase emerged. The acetonitrile phase was separated and the precipitate was filtered off. The precipitate contained the catalyst and the reaction product. The obtained mixture was washed three times with 60 ml pure acetonitrile. The catalyst was then recovered by drying the remaining precipitate at 120 °C. The sulfur elimination of the reused catalyst remained stable in three replications of the experiment (Table II). The reusability of the 10 wt.% PMo-Y catalyst is satisfactory.

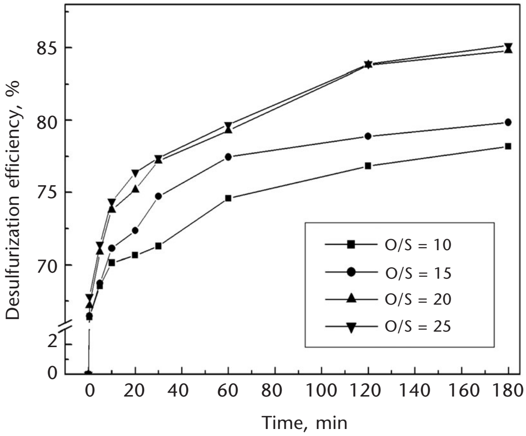

FIG. 5
The effect of O/S molar ratio on desulfurization efficiency. Experimental conditions: temperature, 60 °C; contacting time, 20 min; catalyst dosage, 1% of the mass of *n*-octane and DBT

TABLE II
Performance of reused catalyst and result on veritable diesel oil

Recovered catalyst/diesel sample	1st reused	2nd reused	3rd reused	Sample A	Sample B
Desulfurization efficiency (%)	83.8	83.4	83.1	73.2	78.3

Application to Diesel Oil

The 10 wt.% PMo-Y catalyst was applied to the veritable diesel oil with sulfur concentration of 300 ppm. In the same way, the experiments were carried out under above-mentioned favourable conditions. It can be observed in Table II that the residual sulfur content in the diesel sample B was much lower than that in sample A. The Keggin-type heteropoly acids encaged Y-type zeolite have good catalytic effect on the application of diesel oil in the ODS process.

CONCLUSION

In the *n*-octane/acetonitrile biphasic system with 500 ppm sulfur content, the new "ship-in-the-bottle" type heteropoly acid encaged Y-type zeolite catalysts were investigated with H_2O_2 as oxidant. The catalysts exhibited activity for the oxidation of dibenzothiophene with a desulfurization efficiency in the order NH_4-Y zeolite < 10 wt.% PW-Y < 10 wt.% PMo-Y. The efficiency of favourable 10 wt.% PMo-Y is 84.8%, achieved using a catalyst and oxidant contact time of 20 min, a catalyst amount of 1% of the mass of *n*-octane, and an O/S molar ratio of 20. Furthermore, the reusability of the catalyst was found satisfactory based on the replicated recovery experiments.

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