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Performance evaluation of the carbon nanotubes supported $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as efficient and recoverable catalyst for the oxidative removal of dibenzothiophene

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ABSTRACT

With the issues of increasingly stringent legislations on sulfur level in transportation fuels, clean fuels research including desulfurization has become a more important subject of environmental catalysis studies. Oxidative desulfurization (ODS) combined with extraction is one of the most promising desulfurization processes. With the loading of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, a new multi-walled carbon nanotube (MWNT) supported catalyst ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT) has been developed in this study. Through experimental evaluations, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT was found to be very effective for the oxidative removal of DBT, with a desulfurization efficiency of up to 100%. Factors affecting the process, including reaction temperature, O/S molar ratio, initial sulfur content, catalyst dosage, and pre-immersion time of the catalyst in H_2O_2 solution, were evaluated, and the favourable operating conditions were determined. Sulfone species was confirmed by GC–MS analysis to be the only product from DBT oxidation by H_2O_2 in the presence of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT after 160 min. Moreover, the new catalyst developed is recoverable. The recovered $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT demonstrates quite close catalytic activity to that of the fresh. As a whole, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT has a high potential for using as an effective catalyst for deep desulfurization of diesel.

1. Introduction

The presence of sulfur compounds in transportation fuels has been recognized as a major source of SO_x which contributes to air pollution, acid rain and damage of 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 been updated dramatically 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]. Actually, diesel fuel and gasoline with less than 10 ppmw of sulfur content were available commercially by the end of 2005 in Japan. 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]; the level of 300 ppmw in automotive gasoline starting in 2004 was reduced to 15 ppmw in 2006 [1]. 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 and gasoline 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 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 ultra-low 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 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 easily oxidized to their corresponding sulfoxides and sulfones, which can be removed by extraction or adsorption. The commonly used oxidant in ODS is H_2O_2, owing to its low cost, environmental compatibility, and commercial availability. In very recent years, polyoxometalates (POMs), renowned as green catalysts in many processes, have won particular attention for their effectiveness in ODS with H_2O_2

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[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. Heteropoly compounds, affiliated to POMs as a branch, are remarkably important due to the significant opportunities they offered in fundamental and applied catalysis. However, reported ODS processes catalyzed by POMs are quite limited to date, and heteropoly compounds were used in almost all these reports. Although single heteropoly compound catalyst showed good activity in the ODS process coupled with extraction, however, the used catalyst was very difficult to recover. In view of this drawback, a superior and recoverable ODS catalyst, i.e., multi-walled carbon nanotube (MWNT) supported $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT), has been developed in this study. Since the discovery of carbon nanotubes (CNTs), they have triggered intensive research due to the wide applications they demonstrated. As a good adsorbent for many species, MWNT may promote the ODS activity of the heteropoly compound catalyst supported, hence it was chosen as support. Bulk $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, because of its high surface area, has been found to catalyze many organic reactions more effectively than the bulk parent acid $H_3PW_{12}O_{40}$. Moreover, owing to its insolubility in water, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is superior to $H_3PW_{12}O_{40}$ in that it can be reclaimed after use. However, used for ODS process, single $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is not active enough to reach the goal of deep desulfurization. The composite material of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT would be of interest as catalyst to researchers in the field of fuel oil deep desulfurization once its performance is found to be high. Through experimental evaluations, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT was found to be very effective for the oxidative removal of DBT, with a desulfurization efficiency of up to 100%. Moreover, the catalyst is recoverable. The recovered catalyst demonstrates quite close catalytic activity to that of the fresh.

Of all factors governing the activity of the above catalyst, we found that pre-immersion of the catalyst in H_2O_2 is a key step to get high activity. This is due to the formation of the so-called peroxo-heteropoly compound which has been reported to possess high activity for the oxidation of many organic compounds in the presence of H_2O_2 [22].

As to the knowledge of the authors, the results derived from performance evaluation of this new catalyst were reported herein with no literature precedent.

2. Experimental

2.1. Chemicals

MWNT with outside diameters of 30–50 nm, inside diameters of 5–12 nm, lengths of 10–20 μm, and specific surface area of 134.8 m^2/g was purchased from Chengdu Organic Chemicals Co. Ltd. AC with diameters of 550–600 μm and specific surface area of 360.3 m^2/g, and phosphotungstic acid ($H_3PW_{12}O_{40}\cdot 12H_2O$) of analytical reagent grade, were purchased from National Drug & Chemical Group Co. Ltd. Hydrochloric acid (HCl, 37 wt%), hydrogen peroxide (H_2O_2, 37 wt%), normal octane (C_8H_{18}, AR), acetonitrile (CH_3CN, AR), and dibenzothiophene ($C_{12}H_8S$, AR), were all purchased from suppliers and used without further purification.

2.2. Catalysts preparation

The catalysts used in this study comprise $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/AC, and were prepared by impregnation according to literature method [23]. The pristine MWNT or AC was immersed in 20 wt% hydrochloric acid for 12 h, and washed with deionized water and separated by centrifuging/washing till a neutral pH value was attained. The resultant solid was dried in vacuum at 80 °C and added into an aqueous solution containing desired amount of Cs_2CO_3. The mixture was stirred at room temperature for 3 h, dried in vacuum at 120 °C for 12 h, and calcinated at 300 °C in N_2 atmosphere for 3 h. The solid was impregnated stoichiometrically with $H_3PW_{12}O_{40}$ solution under agitation for 2 h and kept overnight. After the same procedures of drying and calcination, the target catalyst was gained.

2.3. Experimental method

The solution of DBT in normal octane was used as simulated diesel, 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 catalyst was pre-immersed with needed amount of H_2O_2 solution for a fixed time, then mixed with 60 mL of acetonitrile. The oxidation reaction was started by further addition of the above mixture into 60 mL of the simulated diesel. During the reactions, test samples were withdrawn from the *n*-octane phase of the reaction mixture and the sulfur content 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 sulfur content was quantified by external standard method. The product derived from DBT oxidation by H_2O_2 was identified using Agilent HP-6890N/MS-5793 GC–MS analyzer.

TEM observation of the catalysts was conducted using a JEM-100CXII transmission electron microscope at an acceleration voltage of 200 kV. The specific surface areas of the catalysts were determined by a Quadrasorb SI specific surface area analyzer.

3. Results and discussion

3.1. Dispersion of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ on MWNT

TEM observation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ supported on MWNT was carried out at a magnification of 36,000. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was found to be in the form of irregular aggregates immobilized on MWNT and dispersed heterogeneously all around MWNT. The fact that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ aggregates are not well dispersed could depend on the impregnating process itself but could also be the result of a mobility of the species under the TEM beam and the resulting increase of temperature.

3.2. Main factors affecting the process

First of all, a comparison of the effects of MWNT and AC as alternative supports for $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was made, concerning the oxidative removal of DBT. The experiments were carried out at 60 °C for 120 min, using the foregoing biphasic system with an initial sulfur content of 500 ppmw and an O/S molar ratio (equivalent to $2[H_2O_2]/[S]$) of 20. For all the experiments, unless otherwise specified, the amount of catalyst used was 1 wt% of normal octane, and the catalysts were pre-immersed in H_2O_2 solution (containing needed amount of H_2O_2 with minimum water) for 30 min before fed into the reaction mixture. As a result, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT was found to be superior to $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/AC, although the specific surface areas of them correspond to 91.6 m^2/g and 349.6 m^2/g respectively. Apparently, the adsorption effect due to high surface area is not a predominant factor. The desulfurization efficiency of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT (30 wt% loading) is 100%, evidently higher than that of

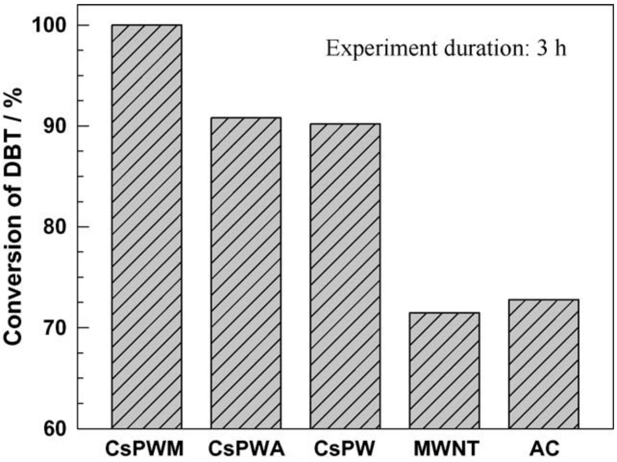


Fig. 1. Comparison of the effects of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT (CsPWM), $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/AC (CsPWA), $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW), MWNT and AC.

$Cs_{2.5}H_{0.5}PW_{12}O_{40}$/AC (30 wt% loading) being 90.8% (Fig. 1). Since both MWNT and AC can adsorb DBT in the above experiments and hence contribute positively to the results, further experiments on the net effects of them were conducted, yielding close desulfurization efficiencies of 71.5% and 72.8% for MWNT and AC respectively (Fig. 1). Whereas, using single $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, a desulfurization efficiency of 90.2% was gained (Fig. 1). Hence, loading of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ onto MWNT is essential to deep desulfurization of the simulated diesel. Moreover, using MWNT as support, 30 wt% of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was confirmed to be the optimum loading for deep desulfurization and therefore used for the following evaluations.

3.2.1. Temperature

Temperature plays an important role in the oxidation of DBT with H_2O_2. From the results shown in Fig. 2, it is evident that the desulfurization efficiency after 160 min' reaction increases with the increase of temperature till reaching a maximum of 100% at 60 °C and more quickly at 70 °C. Below 60 °C, corresponding to 40 and 50 °C, efficiencies of 96.6% and 98.2% can be obtained respectively. From the viewpoint of chemical kinetics, increasing temperature leads to the improvement of the reaction rate. This accounts for the effect of temperature. As a whole, an optimal temperature of 60 °C can be recommended.

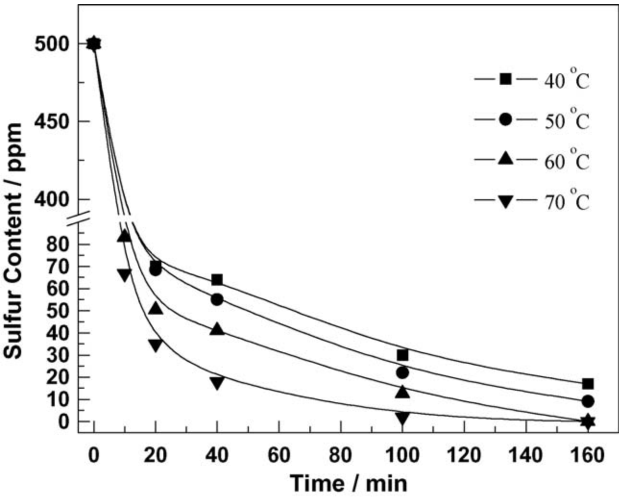


Fig. 2. Temperature dependence of the process. *Conditions*: initial sulfur content, 500 ppmw; O/S molar ratio, 20; catalyst dosage, 1 wt% of *n*-octane.

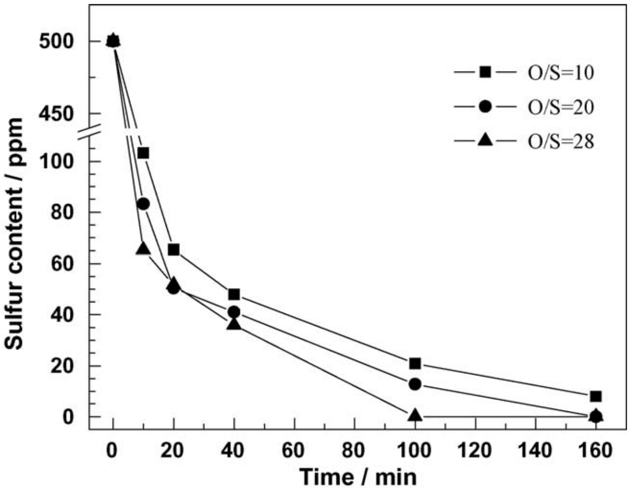


Fig. 3. The effect of O/S molar ratio. *Conditions*: temperature, 60 °C; initial sulfur content, 500 ppmw; catalyst dosage, 1 wt% of *n*-octane.

3.2.2. O/S molar ratio

As a common principle, to a given chemical reaction with multiple reactants, the increase in concentration of any reactant will lead to the increase of the conversion of the rest reactants as well as increasing the reaction rate. This is the case as observed in Fig. 3 when the O/S molar ratio (equivalent to $2[H_2O_2]/[S]$) was increased from 10 to 28. Same desulfurization efficiency of 100% was achieved in 160 min under O/S molar ratios of 20 and 28, except that a quicker reaction speed can be observed in the latter case. From the results, the favourable O/S can be chosen as 20.

3.2.3. Initial sulfur content

To a given sulfur containing diesel to be desulfurized, initial sulfur content embodies the task to be undertaken. In order to understand the desulfurization efficiencies at different sulfur levels, the effect of initial sulfur content was investigated. From the results in Fig. 4, it can be seen that, within the initial sulfur content range from 100 to 500 ppmw, the same final desulfurization efficiency of 100% was achieved in 160 min. As the initial sulfur contents increase to 800 and 1100 ppmw respectively, the final desulfurization efficiencies were found to be 98.5% and 97.5% accordingly.

The increase in initial sulfur content can speed up the oxidation of DBT by H_2O_2 and meanwhile deepens the consumption of both

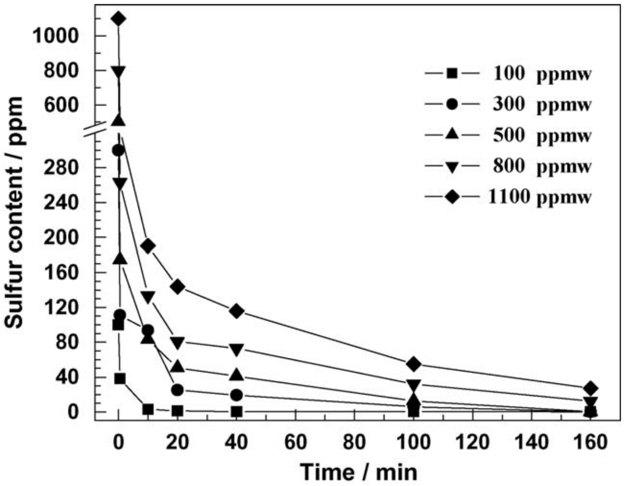


Fig. 4. The effect of initial sulfur content. *Conditions*: temperature, 60 °C; O/S molar ratio, 20; catalyst dosage, 1 wt% of *n*-octane.

species. Accordingly, the desulfurization efficiency will rise when the initial sulfur content is not too high. However, after a certain high content of initial sulfur, owing to the large amount of excessive DBT in the reaction mixture, the conversion of DBT will definitely decline. From the results demonstrated, agreeable effect of deep desulfurization has been achieved within the initial sulfur content below 1100 ppmw.

3.2.4. Catalyst dosage

Another factor that should be concerned is the catalyst dosage. It was found that the catalyst dosage does have a marked influence on the process efficiency (Fig. 5). Under otherwise identical conditions, without catalyst, 66% of the DBT is removed from the *n*-octane phase in 160 min by the joint action of extraction and direct oxidation; the efficiencies of DBT removal in the presence of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT were found to be 83%, 97.5% and 100%, corresponding to catalyst dosages of 0.25, 0.5 and 1.0 wt% respectively. Compared to the direct oxidation of DBT with H_2O_2, the presence of catalyst provides an efficient reaction pathway. Since $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ can react with H_2O_2, producing active intermediates known as peroxo-heteropoly compound [22,24,25] which can oxidize DBT more easily. In light of literatures reports [22,24,25] and phenomena observed from the immersion of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ in 30% H_2O_2 solution, the active intermediate can be the insoluble $Cs_{2.5}H_{0.5}\{PO_4[WO(O_2)_2]_4\}$ immobilized on MWNT. Since, on one hand, $\{PO_4[WO(O_2)_2]_4\}^{3-}$ has been confirmed to be the active intermediate in oxidation with H_2O_2 in the presence of $H_3PW_{12}O_{40}$ [22,24,25]; on the other hand, we found $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is insoluble in 30% H_2O_2 solution. Although the emphasis has been focused on the performance evaluation of the catalyst, as a further study, confirmation of the exact composition of the active intermediate is still need.

According to literature [22], the presence of the peroxo complex can be confirmed by isolation of the peroxo species by the addition of methyltrioctylammonium chloride in dichloromethane. Separating out the formed $[(C_8H_{17})_3NCH_3]_3\{PO_4[WO(O_2)_2]_4\}$ for IR test, the IR data as the proof of the presence of the peroxo complex are: 1088, 1058 and 1035 (P–O), 975 (W=O), 856 and 846 (O–O), 591 and 523 (W–O–O) cm^{-1}.

The role of MWNT in the ODS process is to enhance the transfer of DBT onto the catalyst surface by adsorption, and hence facilitates the oxidation of DBT by the peroxo-heteropoly compound on MWNT.

Increasing the dosage of catalyst, more peroxo-heteropoly compound species can be formed and therefore deepens the reaction. Since no further enhancement can be found when the catalyst dosage exceeds 1.0 wt%, the optimal catalyst dosage can be recommended as 1.0 wt%.

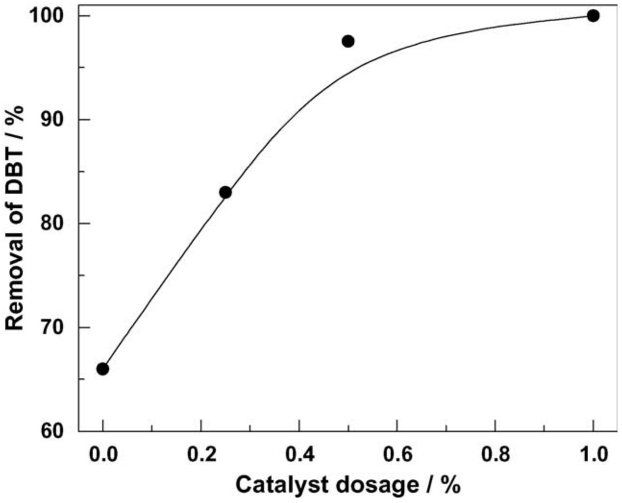


Fig. 5. The effect of catalyst dosage. *Conditions*: temperature, 60 °C; initial sulfur content, 500 ppmw; O/S molar ratio, 20; reaction time, 160 min.

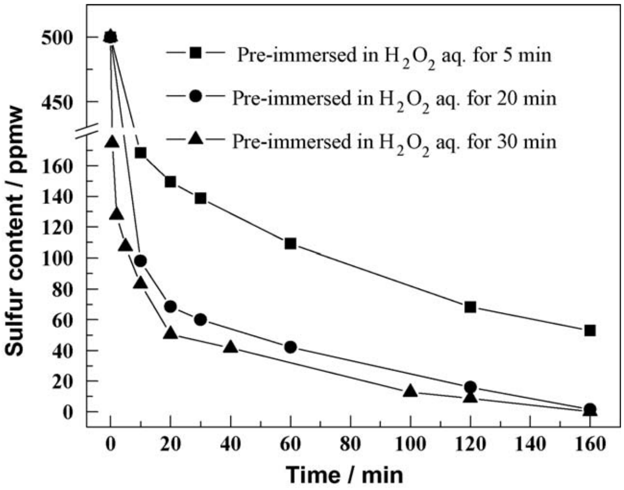


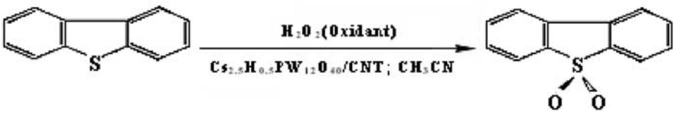
Fig. 6. Effect of pre-immersion of the catalyst in H_2O_2 solution. *Conditions*: temperature, 60 °C; initial sulfur content, 500 ppmw; O/S molar ratio, 20; catalyst dosage, 1 wt% of *n*-octane.

3.2.5. Pre-immersion of the catalyst in H_2O_2 solution

As an important factor, the pre-immersion time of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT in H_2O_2 solution was investigated. It can be found from Fig. 6 that, while the pre-immersion time of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT in H_2O_2 solution varies from 5 to 20 min and further to 30 min, the final desulfurization efficiency increases considerably from 89.4% to 99.7% and 100% accordingly. In light of the foregoing analyses, the reaction between H_2O_2 solution and solid $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ supported on MWNT for the formation of active intermediate is responsible for the above results. Since it takes time to reconstruct $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ into catalytically active species over MWNT through solid–liquid reaction, corresponding to a reaction time of 5 min, the amount of the produced active species is rather limited and hence demonstrates lower desulfurization efficiency compared to the case of longer reaction times. From the results, the optimal pre-immersion time can be determined as 30 min.

3.3. Reaction product

With the aid of GC–MS, the product from DBT oxidation by H_2O_2 in the presence of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT after 160 min was confirmed to contain the corresponding sulfone species only. Hence, the overall reaction equation can be expressed as follows.



3.4. Catalyst reuse

When the reaction was finished, the reaction mixture was kept still for 30 min. Two layers of *n*-octane phase and acetonitrile phase emerge. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT catalyst can be recovered from acetonitrile phase by filtration. After a further treatment of calcination at 350 °C and N_2 atmosphere (0.3 L/min) for 4 h, the catalyst can be reused. Evaluated through two recovery-reusing runs, the recovered catalyst was found to demonstrate an excellent catalytic performance, showing only a slight decline compared to

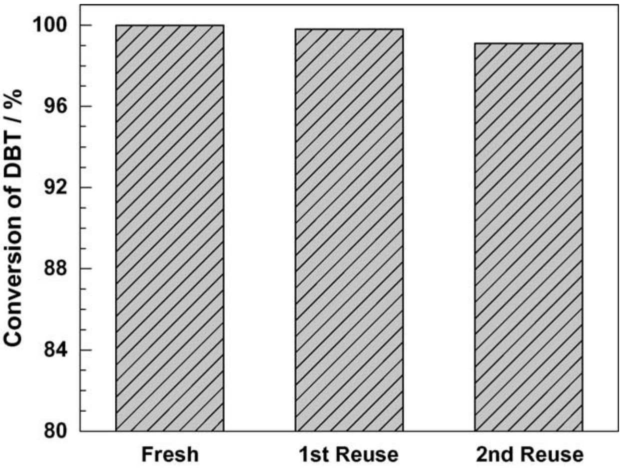


Fig. 7. Performance of the recovered catalyst. *Conditions*: temperature, 60 °C; initial sulfur content, 500 ppmw; O/S molar ratio, 20; catalyst dosage, 1 wt% of *n*-octane.

the fresh catalyst (Fig. 7). Hence, the new catalyst developed herein is promising for application in deep desulfurization of diesel.

4. Conclusions

MWNT is superior to AC as support of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ in that a more efficient catalyst for the oxidative removal of DBT can be obtained. The new catalyst, i.e., $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT, exhibits higher activity than that of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and MWNT. Factors affecting the ODS process, including reaction temperature, O/S molar ratio, initial sulfur content, catalyst dosage, and pre-immersion time of the catalyst in H_2O_2 solution, were evaluated. Resultantly, the favourable operating conditions were determined as: reaction temperature, 60 °C; O/S molar ratio, 20; initial sulfur content, below 1100 ppmw; pre-immersion time of the catalyst in H_2O_2 solution, 30 min; catalyst dosage, 1 wt% of *n*-octane. With the aid of GC-MS, sulfone species was confirmed to be the only product from DBT oxidation by H_2O_2 in the presence of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT after 160 min. Moreover, the recovered catalyst demonstrates quite close catalytic activity to that of the fresh. As a whole, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/MWNT has a high potential for using as an effective catalyst for deep desulfurization of diesel.

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