Ultrasonics Sonochemistry 34 (2017) 713–720

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

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

Ultrasound-assisted oxidative desulfurization process of liquid fuel by phosphotungstic acid encapsulated in a interpenetrating amine-functionalized Zn(II)-based MOF as catalyst

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ARTICLE INFO

Article history:
Received 11 February 2016
Received in revised form 13 July 2016
Accepted 14 July 2016
Available online 15 July 2016

Keywords:
Oxidative desulfurization
MOFs
Encapsulation
Phosphotungstic acid
Ultrasound waves
Fuel

ABSTRACT

In this work, ultrasound-assisted oxidative desulfurization (UAOD) of liquid fuels performed with a novel heterogeneous highly dispersed Keggin-type phosphotungstic acid ($H_3PW_{12}O_{40}$, PTA) catalyst that encapsulated into an amino-functionalized MOF (TMU-17-NH_2). The prepared composite exhibits high catalytic activity and reusability in oxidative desulfurization of model fuel. Ultrasound-assisted oxidative desulfurization (UAOD) is a new way to performed oxidation reaction of sulfur-contain compounds rapidly, economically, environment-friendly and safely, under mild conditions. Ultrasound waves can be apply as an efficient tool to decrease the reaction time and improves oxidative desulfurization system performance. PTA@TMU-17-NH_2 could be completely performed desulfurization of the model oil by 20 mg of catalyst, O/S molar ratio of 1:1 in presence of MeCN as extraction solvent. The obtained results indicated that the conversions of DBT to $DBTO_2$ achieve 98% after 15 min in ambient temperature. In this work, we prepared TMU-17-NH_2 and PTA/TMU-17-NH_2 composite by ultrasound irradiation for first time and employed in UAOD process. Prepared catalyst exhibit an excellent reusability without PTA leaching and loss of activity.

1. Introduction

Air pollution with various pollutants is one of the serious dangers that link to health issues in humans, animals and plants. Sulfur compounds naturally exist in crude oil in the form of sulfides, thiols, thiophenes, substituted benzo- and dibenzothiophenes, etc. The sulfur oxides (SO_x) which are responsible for smog, acid rain, and respiratory disorders in humans originated from the ignition of fusil fuels and polluted air [1–3]. Many countries are tightening limits on the sulfur content of fuel products. Therefore, removing processes of sulfide compound from fuels has become an increasingly essential research subject [4]. Generally, the conventional hydrodesulfurization (HDS) technique was industrially employed to removal of sulfur compounds from fusil fuels. However, this technique can hardly reduce harmful and refractory heterocyclic sulfur-containing compounds such as dibenzothiophene (DBT) and its derivatives, so does not seem very useful way for removing this compounds from fuels. Additionally, HDC needed high temperatures, high pressures and high hydrogen consumption that limit its applications on a large scale [5–7]. In recent years, oxidative desulfurization (ODS) has generated a rapid development due to operate under mild conditions. ODS is an economical and efficient process to remove the refractory aromatic sulfur compounds from liquid fuels. Although ODS is a favorable process, there are still economic and environmental issues that need to be considered [8–10]. Ultrasound-assisted oxidative desulfurization (UAOD) is a new green technique to perform the oxidation reaction of sulfur-contain compounds rapidly, economically, environment-friendly and safely, under mild conditions. The ultrasound approach as an attractive and efficient method employed for acceleration of the chemical processes [11,12]. When the liquids contact with high-intensity ultrasonic irradiation, shock waves lead to acoustic cavitation in medium. The formation and subsequent violent collapse of bubbles can create high temperature (up to 5000 K) and pressure (up to 1000 atm) localized spots in liquid [13]. The oxidative desulfurization performed in the biphasic system including extraction solvent and oil that ultrasound waves can be disperse emulsion-like of biphasic system.

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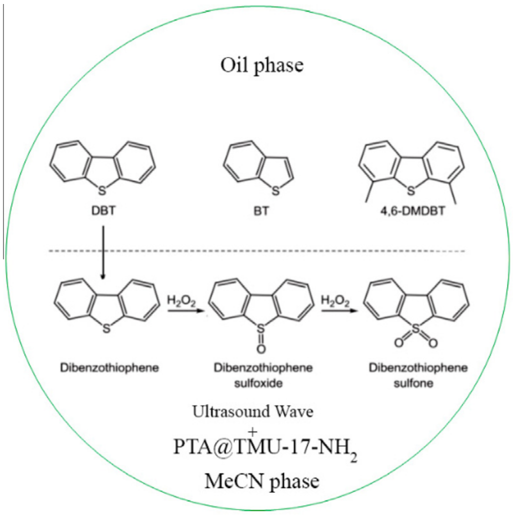
http://dx.doi.org/10.1016/j.ultsonch.2016.07.006
1350-4177/

Heteropoly acids as known a unique class of metal-oxide clusters, have many properties that make them candidates for environmentally catalyst in green chemistry filed. Keggin-type heteropoly acids have been extensively employed as the oxidative desulfurization catalysts because of their high active and selective indicated in ODS but these materials have low surface area (1–10 m^2/g) and high solubility in presence of solvents [14,15]. In order to overcoming these disadvantages, heteropoly acids immobilized or encapsulated in various porous materials such as silica, activated carbon, and metal organic frameworks (MOFs) [16–18].

MOFs are new class of nanoporous inorganic–organic hybrid materials that as well as extensively potential applications such as catalysis, separation, gas storage, carbon dioxide capture. Large surface area, high porosity, and flexible pore size properties lead to introduce new class of materials as a heterogeneous catalyst or a catalyst carrier for chemical reactions [19]. When MOFs apply as a carrier some functional groups such as amine on framework surfaces can be help to immobilization the catalyst in pores. Recently, Wang et al. employed the phosphotungstic acid that encapsulated in the mesocages of amine-functionalized metal–organic frameworks (MIL-101(Cr)-NH_2) as a catalyst for oxidative desulfurization performance [20]. In 2013, Ribeiro et al. reported an efficient heterogeneous catalyst for oxidative desulfurization of model fuel [21]. Wan et al. reported application of a transition metal complex and quaternary ammonium salts (QAS) phase transfer agents with aqueous hydrogen peroxide as oxidant in the UAOD process [22].

In this work for first time, TMU-17-NH_2 that is a mixed-ligand twofold interpenetrated metal-organic framework was prepared with ultrasound irradiation. MOFs were traditionally prepared by solvothermal processes which this method suffer from drawbacks such high temperature using conventional electric heating. The ultrasound technologies are quicker, more efficient and greener alternatives to traditional synthesis methods. We were also reported the encapsulation of phosphotungstic acid (PTA) in TMU-17-NH_2 that is an efficient heterogeneous catalyst for successful ultrasound-assisted oxidative desulfurization of three refractory sulfur-containing compounds (benzothiophene, BT; dibenzothiophene, DBT; and 4,6-dimethyldibenzothiophene, 4,6-DMDBT) using H_2O_2 as the oxidant. Schematic representation of the UAOD system is shown in Scheme 1.



Scheme 1. Schematic representation of the UAOD system.

2. Experimental

2.1. Materials and method

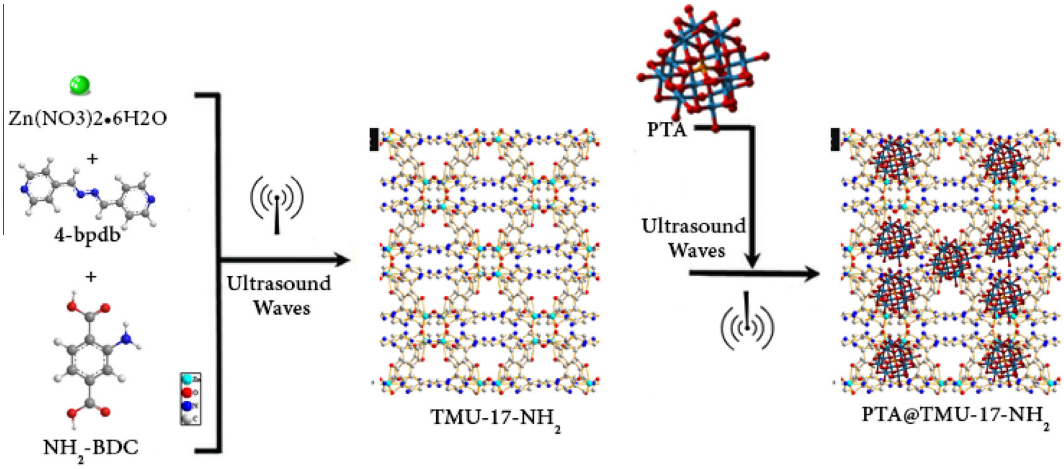
In this study, all of the reagents used were analytical grade and no further purification required. Elemental analyses (carbon, hydrogen, and nitrogen) were carried out using an ECS4010 CHNSO made in Costech. Italy. The powder X-ray diffraction patterns (PXRD) were obtained by using a Philips X'pert diffractometer with monochromated Cu-k_α radiation ($\lambda = 1.54056$ Å). The Fourier transform infrared spectra (FT-IR) were recorded by a Perkin-Elmer system 2000 FT-IR spectrometer using the KBr disk technique at room temperature. Thermogravimetric analyses (TGA) of the materials catalyst was obtained by a TGA-50 Shimadzu thermo-balance. The gas chromatography-mass spectrometer (GC–MS) (Agilent 7890/5975C-GC/MSD; HP-5 137 MS column, 30 m × 250 μm i.d × 0.25 μm) used to characterize the oxidized sulfur-containing compounds. An Optima 8000 ICP-OES spectrometer was used to determination of heteropoly acid amount encapsulated in MOF. Ultrasound waves generated by an ultrasound bath (Sonic 6mx, 37 kHz with a maximum power output of 240 W, Polsonic, Warsaw, Poland. S-4800 field-emission scanning electron microscope (Hitachi, Japan) was employed to SEM images. Nitrogen adsorption isotherms that performed with a Micromeritics ASAP 2000 over $P/P_0 = 0.0–1.0$ .In order to monitoring the product of desulfurization process, gas chromatography-flame photometric detector (GC-FPD) was used. (Agilent 6890N equipped with a capillary column (PONA, 50 m × 0.2 mm, id × 0.5 mm) and flame photometric detector (FPD): Agilent H9261).

2.2. Preparation of PTA@TMU-17-NH_2

Safarifard et al. solvothermally synthesized The TMU-17-NH_2 that reported in the previous paper [23]. TMU-17-NH_2 is an amino-functionalized Zn-based MOF that has been synthesized by using 1,4-bis(4-pyridyl)-2,3-diaza-2,3-butadiene (4-bpdb), and linear 2-aminoterephthalic acid (NH_2-BDC) as organic linker. 4-bpdb was prepared with same procedure that reported by Ciurtin et al. [24]. In this work we prepared TMU-17-NH_2 and PTA/TMU-17-NH_2 composite by ultrasound irradiation for first time. In a typical process, 0.297 g (1 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$, 0.210 g (1 mmol) of 4-bpdb, 0.181 g (1 mmol) of NH_2-BDC were dissolved in 15 ml of dimethylformamide (DMF). Then the reaction flask transferred into ultrasonic bath in ambient temperature. The mixture was exposed to ultrasound waves with 37 kHz frequency and 240 W output power a predetermined time (i.e. 5 min, 10 or 15 min). The obtained material was filtered and washed with DMF and then dried overnight at 60 °C under vacuum. The PTA@TMU-17-NH_2 was performed with same method in presence of various amount of PTA (0.30, 0.60, 0.90 and 1.25 g). The proposed strategy for synthesis of TMU-17-NH_2 and PTA@TMU-17-NH_2 was indicated in Scheme 2.

2.3. Ultrasound-assisted oxidative desulfurization process (UAOD)

The UAOD generally carry out in biphasic system that consists of a polar solvent and model fuel. The UAOD studies were performed with model oil, with refractory sulfur compounds commonly found in fuels (BT, DBT or 4,6-DMDBT), was prepared by dissolving in n-octane (500 $mg.L^{-1}$ for each compound). The UAOD reactions were carried out in a biphasic medium that formed by the model fuel and different polar solvent such as water, acetonitrile (MeCN), isopropanol and dimethylformamide (DMF). In a generic experiment, 15 mg of PTA@TMU-17-NH_2 (containing 20 wt% of PTA) was placed in the vessel then a mixture of MeCN



Scheme 2. Synthesis of TMU-17-NH_2 and PTA@TMU-17-NH_2.

(5 mL) and model fuel (5 mL, 2.5 mgr of DBT) was added to it and the catalytic process was started with addition of H_2O_2 30% (1:1 oxidant/S-contain compound molar ratio (O/S)) as oxidant in reaction medium. In next step, the resulting mixture was exposed ultrasound waves for 5 min in an ultrasonic bath at ambient temperature (100 W and 37 kHz). In order to stop the reaction, the flask was put into an ice bath. Supernatant layer that is model oil was decanted, then catalyst was separated from the lower layer with centrifuge. The reaction progress was quantified periodically by GC and tetradecane as a standard. PTA@TMU-17-NH_2 could be recycled by centrifuge the catalyst after each UAOD cycle, then, soaking MeCN at room temperature. The UAOD system was optimized using PTA@TMU-17-NH_2 as catalyst (5–30 mg), different extraction solvent and various O/S molar ratio (1:1, 2:1, 3:1) in different time (5–20 min) under various powers of ultrasonic irradiation (50–150 W, 37 kHz) at ambient temperature.

3. Results and discussion

3.1. Characterization of the materials

The elemental analysis data indicated that the formula of as-synthesized TMU-17-NH_2 was determined to be [Zn(NH_2-BDC)(4-bpdb)].2DMF (calculated (%): C, 51.46; H, 4.82; N, 16.16. Found (%): C, 52.47; H, 4.74; N, 15.50.) that is in good agreement with the reported results by solvothermal method.

The PXRD patterns of the synthesized materials are shown in Fig. 1. As shown in Fig. 1(a), comparison between PXRD of TMU-17-NH_2 and as-synthesized MOF was indicated that TMU-17-NH_2 prepared with ultrasound irradiation. In Fig. 1(b), the Peaks of TMU-17-NH_2 are in agreement with the data reported in the previous paper. Obtained results approximately show no difference between the TMU-17-NH_2 and the samples of the TMU-17-NH_2 encapsulated heteropoly acid. Some picks disappeared in 3–10° which demonstrated that the encapsulation of PTA in pores of MOF. Obtained results of PXRD patterns were indicated that the structure of the ePTA@TMU-17-NH_2 remained unchanged after sequential UAOD cycle.

The FT-IR spectra of the catalyst are shown in Fig. 2. The obtained FT-IR Spectra of the as-synthesized TMU-17-NH_2 demonstrated the band in 3462.05 (s), 3364.90 (s), 1676.84 (vs), 1609.95 (vs), 1574.38 (vs), 1425.94 (vs), 1380.69 (vs), 1253.26 (s), 1094.03 (m), 1014.26 (m), 830.72 (s), 772.04 (s), 688.79 (s), 519.39 (s) (cm^{-1}). By comparing the FT-IR spectra of the as-synthesized MOF and TMU-17-NH_2, it was observed that both the materiel have the similar structure. TMU-17-NH_2 was prepared under 5 min ultrasound irradiation. Obtained result of PTA@TMU-17-NH_2 contain typical infrared bands belonging to phosphotungstic acid at 1066, 964, 891, and 820 cm^{-1}. These were attributed to ν_{as} (P-O_a), ν_{as} (W-O_d), ν_{as} (W-O_b-W), and ν_{as} (W-Oc-W) vibrations in PTA structure.

The amount of PTA that encapsulated into MOF was analyzed by inductively coupled plasma (ICP). Obtained results demonstrated that the $H_3PW_{12}O_{40}$ units are encapsulated in the channels and cavities of TMU-17-NH_2 (10–40 wt.% based on TMU-17-NH_2). The network of TMU-17-NH_2 is rich in amino groups which can be used for supporting of PTA. Electrostatic interaction between PTA and amine group increase the loading of PTA.

The thermogravimetric analysis (TGA) curves for the composite and TMU-17-NH_2 were show in Fig. 3. The weight loss of PTA@TMU-17-NH_2 is lower than that for the bare TMU-17-NH_2, as would be anticipated from the presence of the PTA in the composite.

Scanning electron microscope (SEM) that is shown in Fig. 4. After encapsulation process under ultrasound irradiation and the grafting of the PTA, the surface of TMU-17-NH_2 becomes uneven and the prepared material still remain the original structure. The characterization results confirmed that a large number of PTA grown onto the surface of TMU-17-NH_2.

The porosity and the specific surface area of prepared composite were studied with N_2 adsorption-desorption isotherms that are shown in Fig. 5. According to the obtained results of BET (Brunauer-Emmett-Teller) surface area analyze, the PTA@TMU-17-NH_2 has lower surface area and pore volume as compared to the TMU-17-NH_2. This observation may be explained with filling the pores of the MOF by PTA particles. (Pore volume and surface area were decreased from 239 to 137 $cm^3.g^{-1}$ and 1050 to 814 $m^2.g^{-1}$, respectively).

3.2. Preparation of TMU-17-NH_2 and PTA@TMU-17-NH_2

TMU-17-NH_2 and PTA-TMU-17-NH_2 composite synthesized by means of ultrasound irradiation at room temperature. The PXRD patterns, FT-IR spectra and elemental analysis data of the as-synthesized samples match well with those reported earlier that solvothermally prepared. TMU-17-NH_2 were synthesized in as quickly as 5 min from ultrasonic synthesis. In solvothermal method, TMU-17-NH_2 synthesized after 4320 min from heating in electric oven. The acoustic cavitation can generated great amount energy in liquid with formation, growth, and implosive

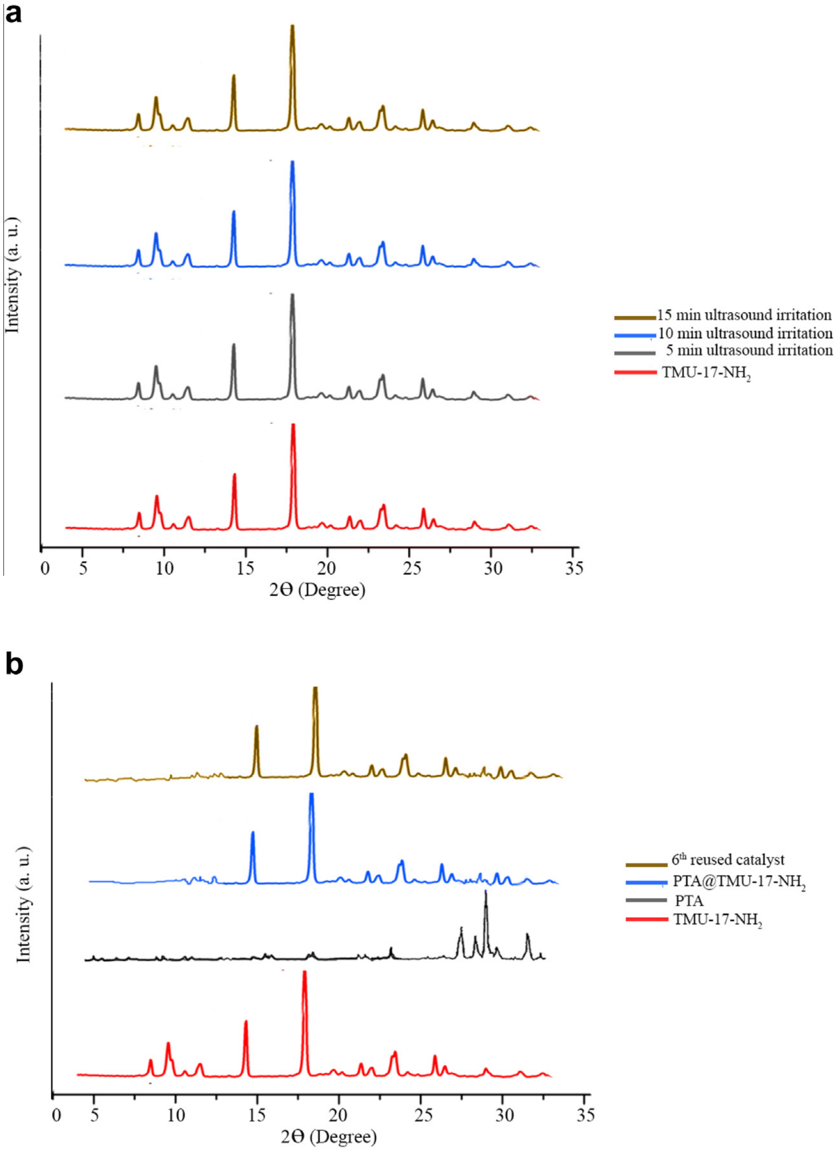


Fig. 1. PXRD patterns of a) TMU-17-NH$_2$, b) PTA@TMU-17-NH$_2$ and recovered PTA@TMU-17-NH$_2$ for 6 runs.

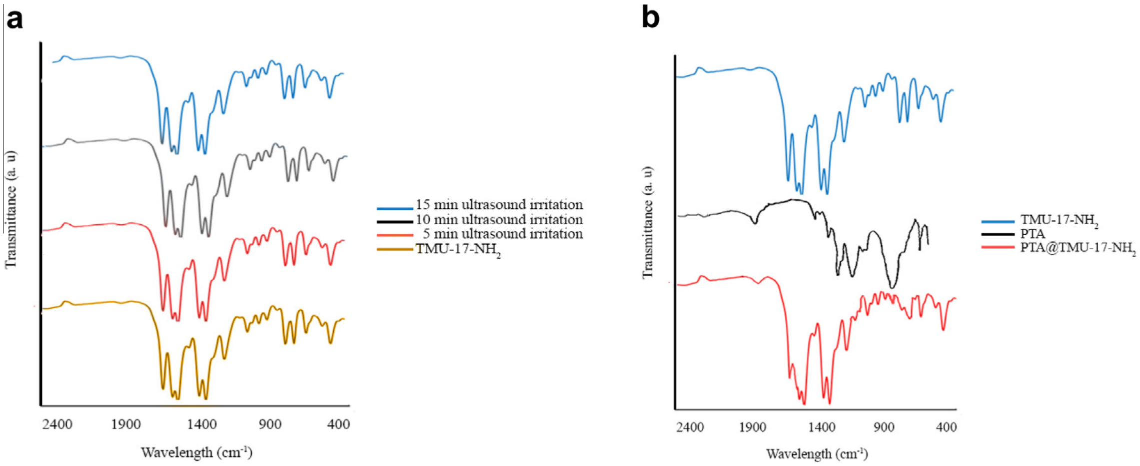


Fig. 2. FT-IR spectra of a) TMU-17-NH$_2$, b) PTA@TMU-17-NH$_2$.

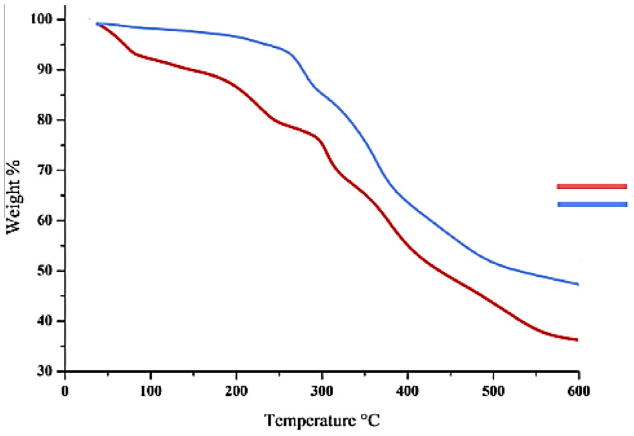


Fig. 3. TGA curves of a) TMU-17-NH_2 and b) PTA@TMU-17-NH_2.

collapse of bubbles. Ultrasound irradiation expend far less energy than electric heating with oven in solvothermal method, which confirms that ultrasound technologies are quicker, more efficient and greener alternatives to conventional synthesis methods.

3.3. Catalytic results

The catalytic activity of the prepared catalyst was evaluated in ultrasound-assisted oxidative desulfurization of DBT. The results of the optimization of reaction conditions are summarized in Table 1. Obtained result indicated that UAOD process performed in MeCN gives the best result and selected as the optimum extraction solvent. When reaction was performed in MeCN, the desulfurization achieve with high yield and all DBT completely converted to sulfone. The sulfur-specific GC-FPD chromatograms of the oxidation of DBT in Fig. 6.

The poor conversion were observed in the water medium, no conversion of DBT was observed after 20 min and no any molecule of DBT removed from the oil phase. The polarity of the different solvents that employed in this work as follows: isopropanol < MeCN < DMF < water. We expect that DMF can remove a greater amount of DBT from model fuel but MeCN demonstrated the higher the conversion rate of DBT to sulfone. This result possible attributed to the different affinity of the solvents for the catalyst (Table 1) [25].

In order to understand the effect of catalyst amount on UAOD system, desulfurization of DBT was performed with various amount of PTA@TMU-17-NH_2. The experiment data demonstrated that increasing the amount of PTA/MOF composite, resulted in an increase of sulfur removal. However, the excess amount of catalyst lead to small improved in the progress of reaction. These result could be consider to cover the active sites with surplus catalyst and indicated that the best yield was obtained by 20 mg of catalyst (Table 1). Also, UAOD process was carried out the presence of PTA@TMU-17-NH_2 containing different PTA loading. The results were indicated that best conversion of DBT to its corresponding sulfone obtained with 20 wt% (based on DBT) of PTA. The overlapping of active sites and occupation of pores by excess amount of PTA lead to the decrease in the total surface area available to reactant.

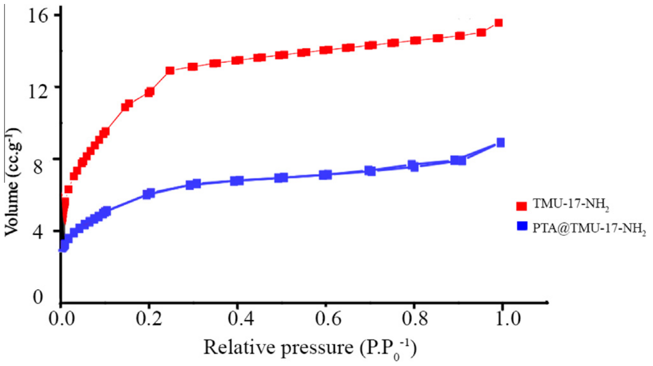


Fig. 5. Comparison of N_2 adsorption-desorption isotherms of TMU-17-NH_2 and PTA@TMU-17-NH_2.

Enhancement of the catalytic activity at a low oxidant/S-contain compound molar ratio is a serious challenge for ODS system and most catalytic systems have higher O/S molar ratios. This disadvantage limited ODS on large scale and raises the cost of operations. The influence of the oxidant amount also investigated using the various O/S molar ratio (Table 1). The worst catalytic performance was obtained when O/S molar ratio of 3:1 was used. According to the results, DBT oxidation was performed in 1:1 M ratio gives the best result. These result may be explained by this fact that oxidant placed in between the two phases (MeCN and oil), therefore, high amount of oxidant may be barricade the effective contiguity between oil phase and extraction solvent. High temperature and high pressure condition that generated by the acoustic cavitation may be provide appropriate conditions for contribution of molecular oxygen in reaction.

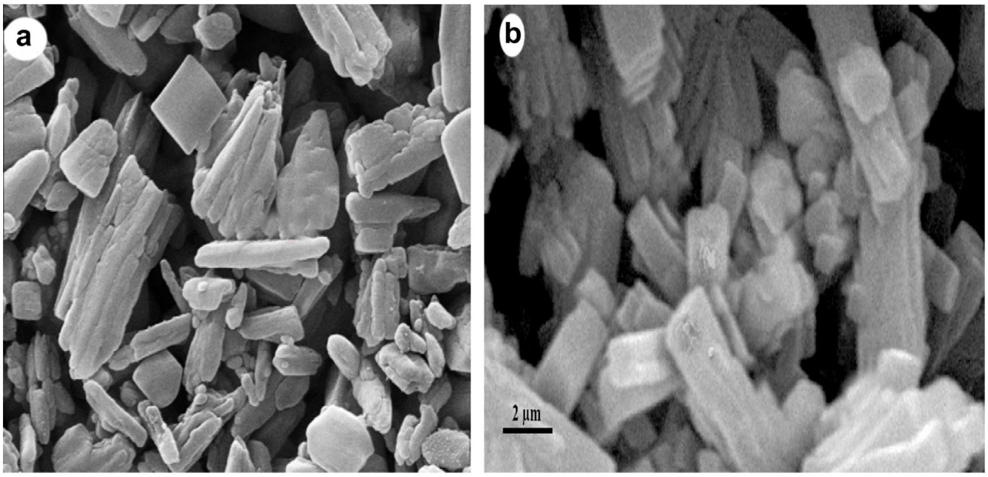


Fig. 4. SEM image of a) TMU-17-NH_2 and b) PTA@TMU-17- NH_2.

Table 1
Conditions applied to the UAOD process.

Entry	Solvent	Catalyst amount (mg)	O/S molar ratio	Reaction time (min)	Catalyst loading [b] (wt%)	Ultrasound irritation power [c] (W)	Yield [a] (%)
1	Isopropanol	15	2:1	5	20	100	71
2	DMF	15	2:1	5	20	100	83
3	Water	15	2:1	5	20	100	0
4	MeCN	15	2:1	5	20	100	90
5	MeCN	5	2:1	5	20	100	72
6	MeCN	10	2:1	5	20	100	84
7	MeCN	15	2:1	5	20	100	90
8	MeCN	20	2:1	5	20	100	95
9	MeCN	25	2:1	5	20	100	92
10	MeCN	30	2:1	5	20	100	92
11	MeCN	20	1:1	5	20	100	92
12	MeCN	20	3:1	5	20	100	91
13	MeCN	20	2:1	5	20	100	95
14	MeCN	20	2:1	10	20	100	96
15	MeCN	20	2:1	15	20	100	97
16	MeCN	20	2:1	20	20	100	97
17	MeCN	20	2:1	15	20	100	91
18	**MeCN**	**20**	**2:1**	**15**	**20**	**100**	**98**
19	MeCN	20	2:1	15	10	100	96
20	MeCN	20	2:1	15	30	100	96
21	MeCN	20	2:1	15	40	100	94
22	MeCN	20	2:1	15	20	50	95
23	MeCN	20	2:1	15	20	150	98
24	MeCN	20	2:1	15	0 [d]	100	19

[a] GC yield.
[b] Calculated for 2.5 mg of DBT.
[c] 37 kHz frequency.
[d] Bar MOF (without PTA).

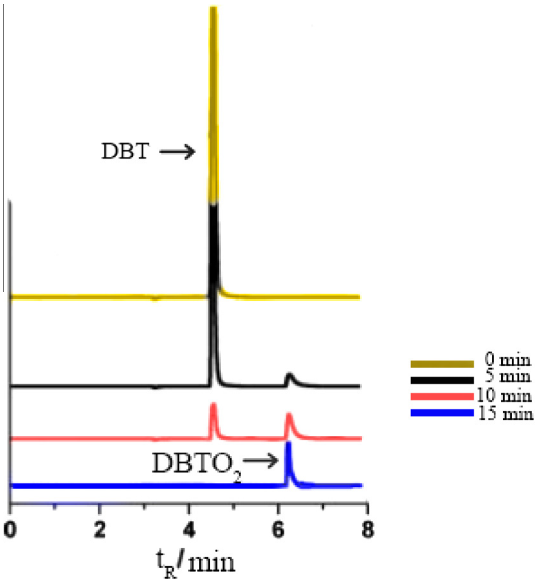


Fig. 6. Sulfur-specific GC-FPD chromatograms of the oxidation of DBT.

Table 2
UAOD process of various sulfur-contain compounds under optimal condition.

Entry	Yield[a] (%)
DBT	98
4,6-DMDBT	87
BT	71

[a] Reaction conditions: 5 mL of model oil, 5 mL of MeCN, 20 mg (20 wt%) of catalyst, O/S ratio of 2:1, 15 min reaction time and 100 W output power.

The influence of the time on conversion of sulfur-containing compounds was investigated and obtained results indicated that the conversions of DBT to DBTO$_2$ achieve 98% after 15 min. In principle, increasing the reaction time accelerates the oxidation of DBT (Table 1).

The ultrasound waves provide energy to the oxidation process. In this work, reaction was performed in various powers of ultrasonic irradiation and results indicated that power output significantly influenced on DBT conversion (Table 1). When the power output of ultrasonic bath was increased, subsequently, the number of active cavitation bubble increase and shock waves strongly expand in liquid. The strong movement that generated by the collapsing bubble leads to decreasing of particles size and breaking up the agglomerates. This changes could be improved the mass transfer at surface of the catalyst during the epoxidation reaction. Obtained results demonstrated that 100 W output power and 37 kHz frequency gave the best result. Therefore, UAOD need the least amount of energy for purification of diesel fuel. The ultrasound waves can provide better surface chemistry of catalysts by enhanced micro-mixing. Also, the acoustic cavitation causes good dispersion of the solvent and fuel phases. In previous articles, effects of ultrasonic frequency and power on UAOD process investigated and obtained results revealed that the best results are achieved with frequencies of 20–50 kHz and 50–100 W power [26,27].

The heterogeneous catalyst was used to oxidation of other sulfur-compound in optimal condition that obtained results were summarized in Table 2. Result illustrated that conversion of 4,6-DMDBT and BT could achieve 87% and 71%, respectively. Electron density of S atom in this compounds is a key factor for explanation of oxidation activity [28,29]. In this case, the electron density on sulfur atom in BT is lower than other compounds. Therefore, BT indicted lowest reactivity. 4,6-DMDBT has the highest amount of electron density on sulfur atom, but steric

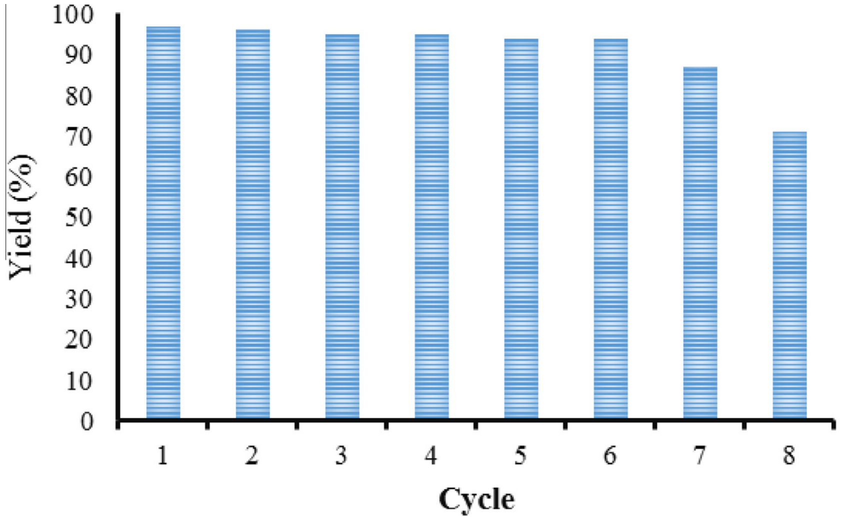


Fig. 7. Investigation of catalyst reusability in the UAOD cycle.

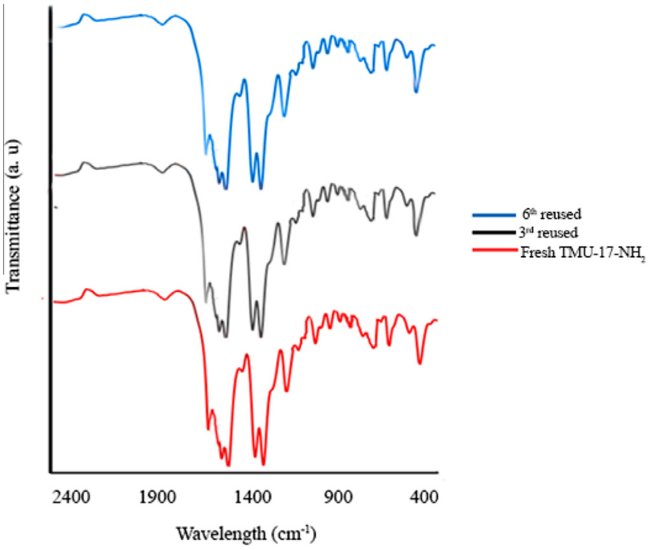


Fig. 8. FT-IR spectra of recovered PTA@TMU-17-NH_2.

hindrance of the methyl groups in its structure leads to difficult access to the active PTA anions.

3.4. Recyclability and reusability of PTA@TMU-17-NH_2

The regeneration of a catalyst is a very important factor for commercial practicality. The reusability of prepared PTA/MOF composite was also investigated and according to the results, catalyst could be recovered 6 times during DBT conversion (Fig. 7). The PXRD patterns indicated that structure of catalyst was stable during the UAOD cycles (Fig. 1). ICP analyses was demonstrated that approximately 5 wt% of PTA was leached during the recovery process. These results indicated that PTA anions clinging to the network of the MOF. Electrostatic interaction between PTA anions and network of TMU-17-NH_2 that is rich in amino groups can be play an important role to protection of composite in leaching process. Fig. 8 is demonstrated the stability of prepared composite after successive UAOD process.

4. Conclusions

In summary, we were rapidly prepared TMU-17-NH_2 and PTA-TMU-17-NH_2 composite by ultrasonic method. PTA@TMU-17-NH_2 was used as a novel catalyst for oxidative desulfurization of fuel under ultrasound irradiation. The prepared composite exhibits high catalytic activity and reusability in oxidative desulfurization of model fuel. The UAOD is a new way to performed ultra-deep desulfurization of liquid fuel rapidly, economically, environment-friendly and safely, under mild conditions. Ultrasound waves can be apply as an efficient tool to decrease the reaction time and improves oxidative desulfurization system performance. In order to optimize the efficient parameters such as solvent, reaction time, amount of oxidant, ultrasound power and amount of catalyst, batch experiment was performed. According to the recyclability and reusability experiments, catalyst could be recovered 6 times during DBT conversion. This work indicate that UAOD process with PTA-TMU-17-NH_2 composite is an efficient way for purification of diesel fuel.

Acknowledgement

The authors sincerely thank Payame Noor University of iran for financially supported this research.

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