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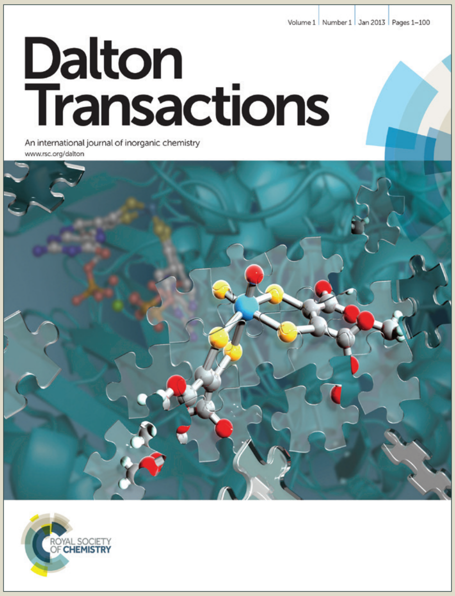

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Phosphotungstic acid encapsulated in the mesocages of amine-functionalized metal-organic framework for catalytic oxidative desulfurization

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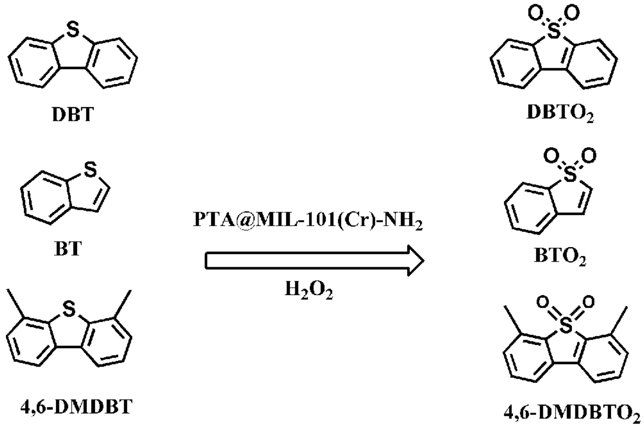
Highly dispersed Keggin-type phosphotungstic acid ($H_3PW_{12}O_{40}$, PTA) encapsulated in the mesocages of amine-functionalized metal-organic framework MIL-101(Cr)-NH_2 has been prepared by using anion-exchange method. PTA anions ($PW_{12}O_{40}^{3-}$) are stabilized in the mesocages via the electrostatic interaction with amino groups of the MIL-101(Cr)-NH_2. The obtained catalyst (denoted as PTA@MIL-101(Cr)-NH_2) exhibits high catalytic activity in the extractive and catalytic oxidative desulfurization (ECODS) system under mild conditions. Moreover, it can be easily recovered and recycled for several times without leaching and loss of activity.

Introduction

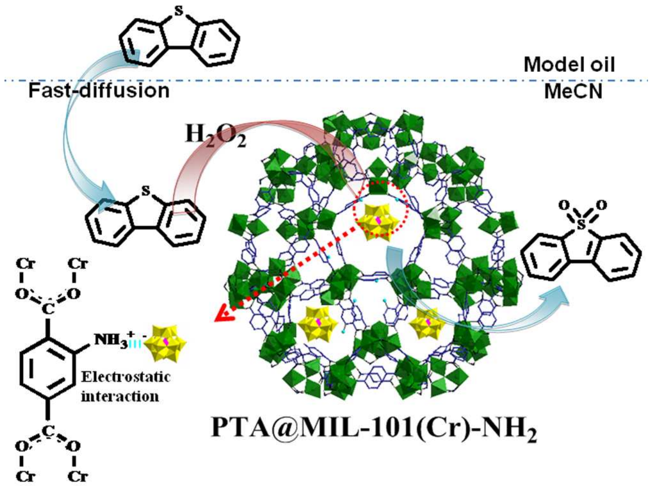
Recently, the demand for transportation fuel has been increasing in the world over the past two decades.[1,2] However, to reduce the sulfur content of transportation fuel to ultra low levels with the aim of lowering harmful vehicle exhaust and improving air quality, environmental legislations have been introduced in many countries.[1-5] Several processes had been proposed in the past to remove these compounds from transportation fuel,[6-13] and the most common industrial process is hydrodesulfurization. However, some refractory sulfur compounds, such as dibenzothiophene (DBT) and its derivatives are difficult to be removed via conventional hydrodesulfurization, due to their aromaticity and steric hindrance.[1,3] To avoid the drawbacks of hydrodesulfurization, efforts have been made to develop supplementary approaches to achieve ultra-deep desulfurization, such as selective adsorption desulfurization,[6-14] oxidative desulfurization,[15-17] biodesulfurization,[3,18,19] and sulfur-extraction using solvents.[20] Among these methods, oxidative desulfurization has attracted wide interest owing to its advantages such as mild conditions, high efficiency and selectivity.[3] The oxidative desulfurization is usually achieved through two steps. Firstly, organic sulfurs are selectively oxidized to sulfones, which further need to be removed by appropriate extractants or adsorbents.[15-17] Recently, extractive and catalytic oxidative desulfurization (ECODS) system composed of catalyst, H_2O_2, model oil and polar solvent (such as DMF, MeCN) has been found to suitable for the deep removal of refractory sulfur compound.[21,22]

In recent years, Keggin-type $[XM_{12}O_{40}]^{m-}$ (X : Si^{4+}, P^{5+}, etc, M : Mo^{6+} or W^{6+}) have shown highly catalytic performance in oxidative desulfurization and other catalytic reactions.[16,21-37] However, most of the homogenous catalysts are difficult to be separated from the products. In contrast, heterogeneous catalysts have been proven to be promising alternatives to avoid these problems. Various materials, such as SiO_2,[26-28] CeO_2,[29] activated carbon,[30,31] cucurbit[n]uril,[32] and mesoporous sieves[33-35] have been employed as supports for Keggin-type catalysts. However, most of these supports have some limitations, such as low loading of PTA, high leaching of PTA and/or active sites that are unevenly dispersed. Therefore, finding a suitable solid matrix as support to overcome the drawbacks is important.

Metal-organic frameworks (MOFs) have been emerging as very promising heterogeneous catalytic materials due to their high surface area, porosity, and chemical tunability.[36-44] MIL-101(Cr) is an excellent MOF material due to its high specific surface area, pore volume, thermal (up to 300°C) and chemical stability to water and common organic solvents.[45] It has two



Scheme 1 Simplified names and reactions of sulfur compounds following the ECODS system.



Scheme 2 Schematic description of the ECODS using PTA@MIL-101(Cr)-NH_2 as catalyst. Electrostatic interaction: between $–NH_3^+$ and $[PW_{12}O_{40}]^{3-}$ anions (PTA).

types of mesoporous cages (2.9 and 3.4 nm) accessible through microporous windows (1.2 and 1.6 nm).[17,45-49] Recently, Hu et al. have utilized "bottle around ship" method to encapsulate PTA in MIL-101(Cr), and the obtained composite material was used as catalyst for oxidative desulfurization performance.[17] Soon afterwards, Ribeiro et al reported the application of a PTA-based catalyst immobilized in MIL-101(Cr) as a efficient heterogeneous catalyst in oxidative desulfurization system, with ion liquid as extraction and reaction medium.[50] However, the PTA anions (1.3-1.4 nm diameters) may leach out from mesocages of the composite catalyst because their size is smaller than the larger windows (1.6 nm diameter) of MIL-101.[17] As we know, two components with opposite charge can associate with each other through electrostatic interaction.[47,51-55] Following this idea, Pd particles encapsulated in the amine functionalized MIL-101(Cr)-NH_2 has been prepared via anion-exchange method and shows excellent catalytic activity for dehalogenation of aryl chlorides and Suzuki-Miyaura reaction.[47,54] To the best of our knowledge, PTA encapsulated in the mesocages of amine-functionalized MOF as composite catalyst for ECODS system has not been studied up to now.

Here, anion-exchange strategy has been used to introduce Keggin PTA into the mesocages of amine-functionalized MIL-101(Cr)-NH_2 (denoted as PTA@MIL-101(Cr)-NH_2) for highly oxidative desulfurization.

Experimental

Reagents and Chemicals

The reagents, namely phosphotungstic acid (Sinopharm, AR), $CrCl_3{\cdot}6H_2O$ (Adamas, 99%), 2-nitroterephthalic acid (Aladdin, 99%), dibenzothiophene (DBT, Adamas, 99%), benzothiophene (BT, Adamas, 99%), 4,6-dimethyldibenzothiophene (4,6-DMDBT, Adamas, 98%), acetonitrile (MeCN, Sinopharm, 99%), n-heptane (Ourchem, 97%), N,N-dimethylformamide (DMF, Sinopharm, AR), 30% H_2O_2 (Xilong, AR), $SnCl_2{\cdot}2H_2O$ (Sinopharm, 99%), n-dodecane (Aladdin, 99%) were used as received without further purification.

Composite material PTA@ MIL-101(Cr)-NH_2

The porous material MIL-101(Cr)-NH_2 was prepared according to the method described by Stock et al.[48,49] Firstly, MIL-101(Cr)-NO_2 was synthesized under hydrothermal condition, and then reduced to MIL-101(Cr)-NH_2 by $SnCl_2{\cdot}2H_2O$ (see the Supporting Information).

The composite material PTA@MIL-101(Cr)-NH_2 was prepared by immobilization of PTA in the mesocages of MIL-101(Cr)-NH_2. PTA was dissolved in 0.1 M HCl aqueous solution, then added MIL-101(Cr)-NH_2, and stirred for 10 h at room temperature. After that, the impregnated MIL-101(Cr)-NH_2 catalyst was centrifuged and washed with distilled water, then dried at 70 °C for 10 h.

Preparation of model oil

20 mmol DBT (Scheme 1) and 2 mL dodecane (internal standard) were dissolved in n-heptane to form 1000 mL model oil, the sulfur content of which was about 950 ppmw. Other kinds of model oil were prepared with the same method by dissolving BT and 4,6-DMDBT in n-heptane with sulfur contents of 950 ppmw and 950 ppmw, respectively.

ECODS experiments

The refractory sulfur-compounds can be extracted by polar solvent and be readily oxidized to their corresponding sulfones in the ECODS process (Scheme 2). In most cases, the polar solvents (as polar phase) lie in the lower layer. The ECODS system was carried out under air (atmospheric pressure) in a round-bottom flask equipped with a magnetic stirrer in a thermostated oil bath. The catalytic performance of the composite PTA@MIL-101(Cr)-NH_2 was investigated by oxidation of sulfur-containing compounds (DBT, BT or 4,6-DMDBT) via using H_2O_2 as oxidant. The ratio of model oil to polar solvent was 1 : 1. In a typical experiment, PTA@MIL-

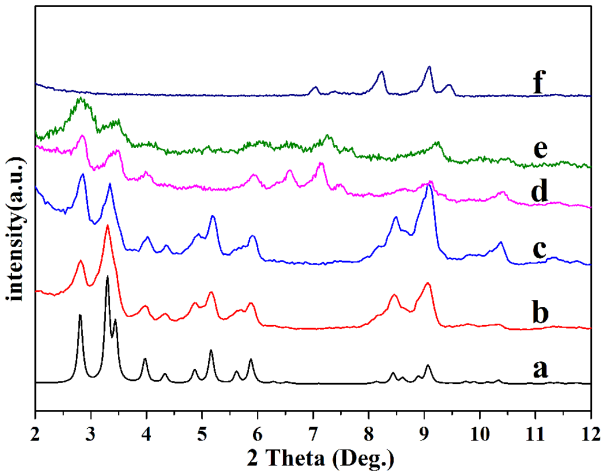


Fig. 1 PXRD patterns of samples (a) simulated MIL-101(Cr), (b) as prepared MIL-101(Cr)-NO_2, (c) as prepared MIL-101(Cr)-NH_2, (d) as prepared PTA@ MIL-101(Cr)-NH_2, (e) PTA@ MIL-101(Cr)-NH_2 after six catalysis cycles, (f) pure PTA.

Table 1 Surface area measurements for MIL-101(Cr)-NO_2, MIL-101(Cr)-NH_2 and PTA@MIL-101(Cr)-NH_2 (0.121 mmol g^{-1}).

Sample	BET surface area (m^2 g^{-1})	Langmuir surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
MIL-101(Cr)-NO_2	2088	3275	1.09
MIL-101(Cr)-NH_2	2700	4301	1.34
PTA@MIL-101(Cr)-NH_2	832	1259	0.45

Table 2 PSD of MIL-101(Cr)-NO_2, MIL-101(Cr)-NH_2 and PTA@MIL-101(Cr)-NH_2 (0.121 mmol g^{-1}).

Sample	Size of larger mesocage (nm)	Size of smaller mesocage (nm)	Size of larger window (nm)	Size of smaller window (nm)
MIL-101(Cr)-NO_2	2.51	1.99	1.50	1.17
MIL-101(Cr)-NH_2	2.74	2.16	1.51	1.27
PTA@MIL-101(Cr)-NH_2	2.34	2.16	1.51	1.26

101(Cr)-NH_2 (50 mg), H_2O_2 (40 µL), and DMF or MeCN (5 mL) were placed in a round-bottom flask (25 mL) and stirred. Then, the reaction started after the addition of model oil (5 mL) at temperature of 50 °C. Finally, the flask was put into an ice bath to stop the reaction. With respect to the recycling experiment, model oil in upper layer was cast out, then the catalyst in lower layer was collected by centrifugation and washed with MeCN for three times after the reaction. To evaluate the possible loss of PTA from the supported catalyst to solution, The W content of the composite catalyst was detected by ICP-AES after six consecutive reaction cycles.

Analysis of treated model oil

The qualitative analysis of various sulfur compounds in the model oil and the polar solvent were carried out by a gas chromatograph (Angilent G7890A) equipped with a FID detector. The compounds were separated by a HP-5 capillary column (30 m × 0.32 mm × 0.25 µm film thickness). The GC parameters were as follows: split ratio, 20 : 1; injector port temperature, 340 °C; detector temperature, 300 °C; injection volume, 1.0 µL. The oven temperature was initially set at 50 °C and held at this temperature for 4 min, then increased to 110 °C at a ramp of 5 °C min^{-1}, immediately increased to 300 °C at a ramp of 20 °C min^{-1}, and held at this temperature for 20 min. High purity nitrogen gas was used as a carrier gas at a flow rate of 20 mL min^{-1}. In this analysis, n-dodecane was used as an internal standard.

Results and discussion

Catalyst preparation and characterization

MIL-101(Cr)-NH_2 material was prepared using postsynthetic modification of MIL-101(Cr)-NO_2 with $SnCl_2·2H_2O$ as reducing agent reported by Stock et al[48,49]. The nitro functionalized MIL-101(Cr)-NO_2 was synthesized under hydrothermal condition. Subsequently, the nitro groups were reduced to amino groups using $SnCl_2·2H_2O$ as reducing agent to give green MIL-101(Cr)-NH_2. The powder X-ray diffraction (PXRD) patterns of the resulting green solids are similar to those MIL-101(Cr) (Fig. 1).[47]

The successful linker modification (nitro groups to amino groups) can be characterized by FT-IR spectroscopy (Fig. S1). After the reduction, the stretching vibration signal (1542 cm^{-1}) of nitro is absent, and the -C-N stretching vibrations (1340 and 1259 cm^{-1}) of MIL-101(Cr)-NH_2 are clearly observed in the IR spectrum[48,49]. Nitrogen adsorption measurements show higher specific surface area of the amine-functionalized porous MIL-101(Cr)-NH_2 (S_{BET} = 2700 m^2 g^{-1}, Fig. 2A, Table 1) than the nitro-functionalized MIL-101(Cr)-NO_2 (S_{BET} =2088 m^2 g^{-1}, Fig. 2A, Table 1) because of the bigger size of the nitro occupied in the pores. Furthermore, TGA indicates that their structures exhibit high thermal stability up to 300 °C (Fig. S4). Meanwhile, the pore sizes distribution (PSD) calculated from density function theory (DFT) method (Fig. 2B and Table 2)[17,56,57] illustrates that the two mesocages (2.16 and 2.74 nm) corresponding to the two windows (1.27 nm and 1.51 nm) in MIL-101(Cr)-NH_2 are also exist after reduction, which cannot preserve the PTA anions (1.3-1.4 nm diameters) enter into the larger mesocages.[17]

The linker modification with amino group is obvious essential, because it provides electrostatic interaction with PTA anions, which make MIL-101(Cr)-NH_2 increase the loading of PTA. The PTA@MIL-101(Cr)-NH_2 with PTA loading of 0.126 mmol g^{-1} (ICP-AES) was prepared by anion-exchange method. A comparison of the PXRD patterns of MIL-101(Cr)-NH_2 and PTA@MIL-101(Cr)-NH_2 (2θ ranges 2-6 ° and 8-12 °) shows that the Bragg reflections characteristic of MIL-101(Cr)-NH_2 are retained at the same positions (Fig. 1). However, several

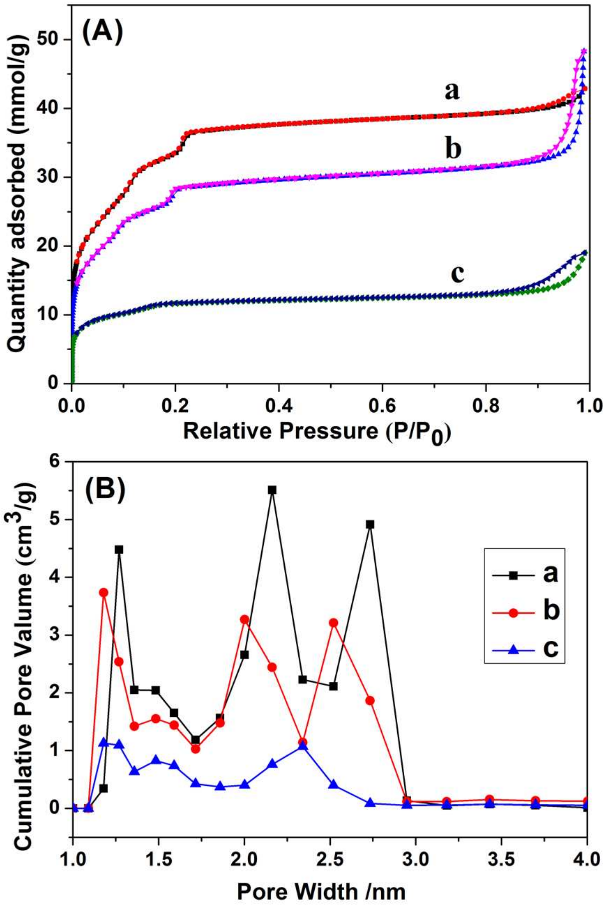


Fig. 2 **(A)** Nitrogen sorption isotherms and **(B)** Density functional theory pore size distribution (PSD) profiles of (a) MIL-101(Cr)-NH$_2$, (b) MIL-101(Cr)-NO$_2$, (c) PTA@MIL-101(Cr)-NH$_2$.

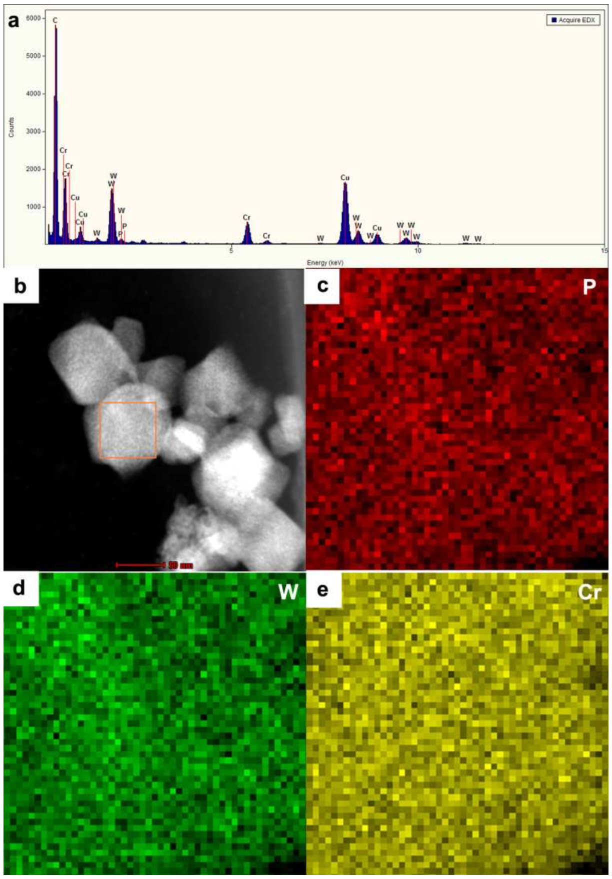


Fig. 3 (a) EDS analysis of PTA@MIL-101(Cr)-NH$_2$, (b) HAADF-STEM image, and (c-e) the corresponding EDS mapping of P, W, and Cr elements.

"new" peaks emerged (2θ ranges 6-8 °), which do not match with those of pure PTA. Such similar phenomenon has been found in those PTA@MIL-101 reported previously by Bromberg[58] and Jia.[57] In fact, according to Bromberg, the new peaks are consistent with the unit cell of MIL-101(Cr)-NH$_2$ (the corresponding peaks of unloaded MIL-101(Cr)-NH$_2$ have null intensity.) It is proposed that the electron density of the crystal structure of MIL-101(Cr)-NH$_2$ increases after incorporation of PTA, thus creating the observed diffracted intensity at these peak positions. This hypothesis is supported by the comparison of the experimental PXRD with a calculated pattern for a structural model comprising PTA molecules located in mesocages of MIL-101(Cr). The absence of reflections characteristic of bulk PTA in the diffraction pattern of PTA@MIL-101(Cr)-NH$_2$ indicates that the PTA have been well-dispersed in the mesocages of solid support.

The FT-IR also confirmed that the PTA anions were retained in the composite PTA@MIL-101(Cr)-NH$_2$, because the vibrational spectra of the catalyst exhibit the characteristic bands of both the MIL-101(Cr)-NH$_2$ and the Keggin structure of the PTA anion (Fig. S1). The peaks of pure PTA at 1083 cm^{-1} is attributed to the asymmetric vibrations of the P-O in tetrahedral PO$_4$, whereas the bands at 986, 891, and 805 cm^{-1} are assigned to the stretching modes of the terminal W=O, edge sharing of W-O$_b$-W, and corner sharing of W-O$_c$-W units, respectively. These bands are characteristics of a Keggin structure.[50] The characteristic bands of $[PW_{12}O_{40}]^{3-}$ in the PTA@MIL-101(Cr)-NH$_2$ was a little different from those of the unsupported one, indicating a strong electrostatic interaction between $[PW_{12}O_{40}]^{3-}$ and MIL-101(Cr)-NH$_2$.[55] As expected, the BET specific surface area of MIL-101(Cr)-NH$_2$ decreased (from 2700 to 832 m^2 g^{-1}) with PTA supported (Fig. 2A, Table 1). The result indicates that PTA anions have been encapsulated by the mesocages of MIL-101(Cr)-NH$_2$. What's more, the good distribution of Cr, P, and W elements of PTA@MIL-101(Cr)-NH$_2$ also indicates that PTA anions were well distributed in the mesocages of MIL-101(Cr)-NH$_2$, shown by the EDS mapping of different elements (Fig. 3). The PSD profile of MIL-101(Cr)-NH$_2$ demonstrates that the two windows of mesocages retained with PTA supported, which ensures that substrates enter into the mesocages and react with PTA (Fig. 2B and Table 2).[46-48] It should be noted that the size of octahedral PTA@MIL-101(Cr)-NH$_2$ is about 100 nm (Fig. S2， Fig. S3), which enhanced the contact chance of the substrates and catalyst.[59]

Investigation of catalytic performance

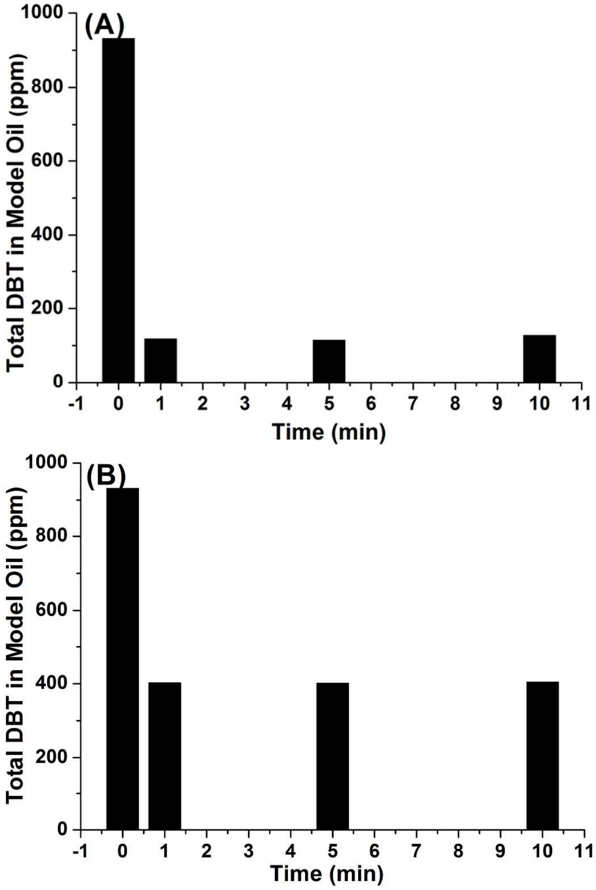


Fig. 4 **(A)** Total DBT in model oil after extractive by DMF (0, 1, 5, 10 min) Condition: room temperature, **(B)** Total DBT in model oil after extractive by MeCN (0, 1, 5, 10 min). Condition: room temperature.

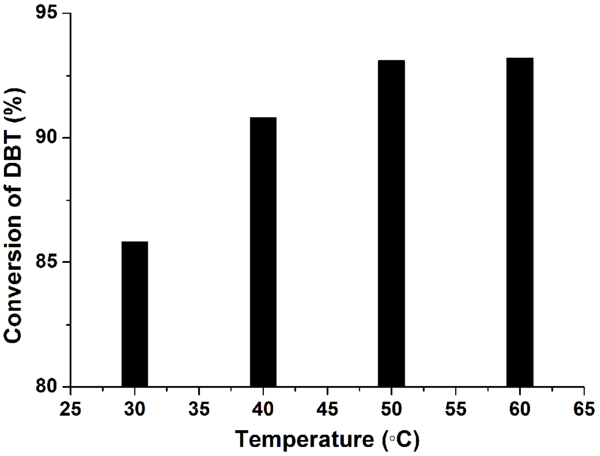


Fig. 5 Oxidation activity of DBT under different temperature with DMF as extraction and reaction medium. Condition: time, 4 h, O/S = 50.

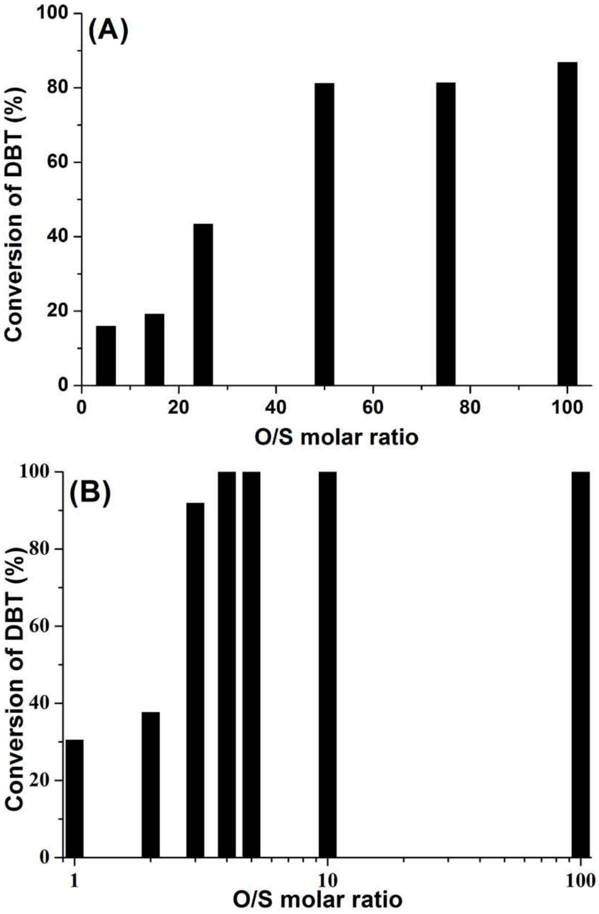


Fig. 6 Oxidation activity of DBT with (A) DMF, (B) MeCN as extraction and reaction medium under various O/S molar ratio. Condition: temperature, 50 °C, time, 1 h.

Dibenzothiophene (DBT, Scheme 1) is one of the most refractory sulfur compounds to be removed from diesel by conventional desulfurization process. Therefore DBT was firstly chosen to study the ECODS using the composite material PTA@MIL-101(Cr)-NH_2 as catalyst. The ECODS system consists of two main steps: an extraction of the DBT from the model oil (apolar phase) followed by the catalytic oxidation of DBT in polar phase (DMF or MeCN phase, Scheme 2) simultaneously.

To prove the significant of ECODS, we have investigated the distribution of DBT and its corresponding sulfone $DBTO_2$ in the model oil and polar solvents (detailed procedure see supporting information). Two solvents have been used as polar phase. Take MeCN as example, only 57% DBT distributed in polar phase. Interestingly, if we conversed all DBT to its corresponding sulfone, more than 99 % $DBTO_2$ distributed in polar phase. It can be illustrated that the higher conversion rate of DBT to sulfone, the lower residual sulfur in model oil, due to their increased polarity. So, the conversion rate of sulfur-containing compound in the sample is used as a measure of the catalysis performance. Furthermore, the extraction of DBT from model oil to the polar solvent phase with very short time (Fig. 4, Scheme 2). In all studies, H_2O_2 was used as oxidant and reactions were performed with 50 mg catalysts. Control experiments using PTA only, or, separately, MIL-101(Cr)-NH_2 only have been done.

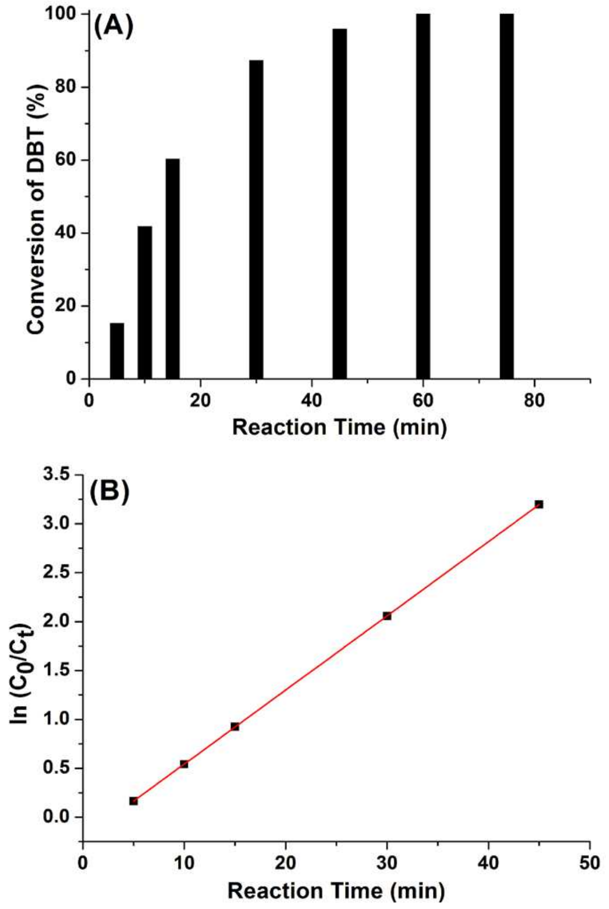


Fig. 7 **(A)** Oxidative activity of DBT with MeCN as extraction and reaction medium under different reaction time, **(B)** Kinetic profile for the oxidation of DBT. Condition: temperature, 50 °C, O/S = 4.

In principle, increasing reaction temperature accelerates the oxidation of DBT. The influence of the temperature was examined firstly, using DMF as extraction and reaction solvent (Fig. 5). The results obtained from the oxidation studies of DBT indicated that only sulfone was observed by GC-MS after the reaction (Scheme 1). The conversion of DBT increased with elevating the temperature, which might be attributed to increasing the formation of metallic peroxide with higher reaction temperatures and its oxidative ability towards sulfone.[17] Interestingly, the conversion of DBT after 4 h reached 93.1% at 50 °C and didn't increase much at higher temperature. For the economical point, 50 °C was chosen as the optimal temperature.

Polar solvent is another key factor for ECODS. It has much effect not only on extraction but also on the conversion rate of DBT to corresponding sulfone. Influence of polar solvents on extraction have been studied by simple stirring of two phases at room temperature (Fig. 4). Two organic solvents were tested using model oil of DBT in n-heptane and the PTA@MIL-101(Cr)-NH_2. The polarity of DMF is higher than MeCN. The DBT removal from the oil to the extracting solvent follows the order: MeCN (57%) < DMF (87%). The extraction of DBT from the oil must be related with its solubility in the extraction phase. Thus, the DBT must be more soluble in higher polar organic solvents.[60] Influence of polar solvents on catalytic performance have been investigated at 50 °C (Fig. 6). The DBT can be completely conversed to sulfone using MeCN as polar phase, and the residual DBT in model oil was negligible (Condition: O/S = 5, temperature 50 °C, Fig. 6B). However, the conversion of DBT was only 15.9% using DMF as polar phase, and the residual DBT in model oil was 116 ppmw (about 12.5% DBT residual in model oil) under the similar condition (Condition: O/S = 5, temperature 50 °C, Fig. 6A). The results indicate that the catalyst has better performance using MeCN as polar phase. It may be ascribed to the different affinity of the solvents with the catalyst.[60] In addition, due to the low boiling point of MeCN, it can be easily recovered by distillation for next cycle. Base on the above discussion, MeCN was chosen as the optimal polar reaction solvent in this ECODS system.

Improvement of catalytic activity at low H_2O_2/S (O/S) molar ratio is a challenge for ECODS.[3] In previous reports, many catalytic systems are very active in the oxidation of sulfur compounds.[17,21,50,60,61] However, most catalytic systems have higher O/S molar ratio (about 100 : 1). To study the influence of the amount of oxidizing agent on the catalytic activity of this system, the oxidation of DBT in the model oil under various H_2O_2/DBT (O/S) molar ratios was carried out at 50 °C (Fig. 6B). Interestingly, the rate of conversing DBT to $DBTO_2$ reached 100% with O/S molar ratio increasing to 4 : 1. Compared with previous report,[17,50,60,61] the PTA@MIL-101(Cr)-NH_2 catalyst needs less H_2O_2. Therefore, O/S molar ratio of 4 : 1 was chosen as the optimal condition.

The conversions rate of DBT versus reaction time at 50 °C are given in Fig. 7A. It is obvious that the conversions reach 95.91% after 45 minutes, and complete within one hour. The oxidation kinetics of DBT was also investigated under the optimal condition[15,29].[15,26] The rate constant k (0.076 min^{-1}) for the apparent consumption of DBT was obtained from the pseudo-first-order equation.

$$-dC/dt = kC \qquad (1)$$

$$\ln(C_0/C_t) = kt \qquad (2)$$

In the above equations, C was the concentration of DBT in MeCN, C_0 and C_t were the concentrations of DBT at time zero and t (min) respectively. The plot of $\ln(C_0/C_t)$ versus time is linear, with correlation coefficient R equal 1 (Fig. 7B), which indicated that the PTA@MIL-101(Cr)-NH_2 catalyzed oxidation of DBT by H_2O_2 is pseudo-first-order reaction.

Recyclability is one of the most significant factors for industrial application. The catalyst in reaction solvent was collected by centrifugation and washed with MeCN for three times after the reaction. The results demonstrate that the DBT conversion could remain 99% even after six consecutive cycles (Fig. 8). To evaluate the possible loss of PTA from the original composite catalyst (0.126 mmol g^{-1}, ICP-AES), the W content

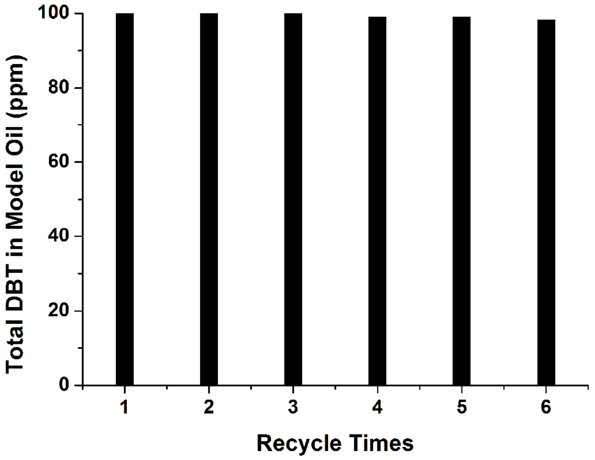


Fig. 8 Conversion data obtained for the oxidation of DBT after 1 h when PTA@MIL-101(Cr)-NH_2 was used for six consecutive ECODS cycles. Condition: temperature, 50 °C, O/S = 4, extraction and reaction solvent, MeCN.

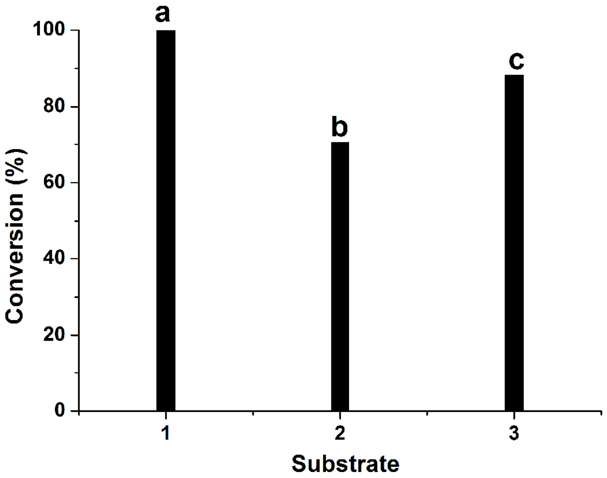


Fig. 9 Conversion data obtained for each sulfur-containing refractory compound (a DBT, b BT, c 4,6-DMDBT). Condition for DBT: temperature 50 °C, time, 1 h, O/S = 4, Condition for 4,6-DMDBT and BT: temperature 50 °C, time, 4 h, O/S = 10.

of composite catalyst was detected after six consecutive reaction cycles (0.121 mmol g^{-1}, ICP-AES), which indicated that only about 4% PTA was lost to solution. In contrast, without any protection, the catalyst PTA@MIL-101 prepared using impregnation method leached 45 % after only three recycle runs, although in the ionic liquids.[50] As for the Hu and co-workers reported PTA@MIL-101 catalyst (the PTA leached out is 9 % after four runs), they use “bottle around ship” method, which is different from our preparation approach. It can be attributed to that most of the PTAs are encapsulated in the small cages (2.9 nm), which are difficult to escape from the small windows (1.2 nm).[17] Thus it proves that the recycle ability of the PTA@MIL-101(Cr)-NH_2 is competitive and may be used as a highly active catalyst for further industrial application.

Combining both efficiency and stability into one catalytic species is very important. Apart from the recycling experiments, four lines of additional evidence indicate that PTA@MIL-101(Cr)-NH_2 stays intact during the catalytic oxidation: (1) the FT-IR of PTA@MIL-101(Cr)-NH_2 after reaction retains all the characteristic peaks of the polyanion, $[PW_{12}O_{40}]^{3-}$, and MIL-101(Cr)-NH_2, indicating that both structural components are stable (see Fig. S1). (2) the X-ray powder diffraction patterns of PTA@MIL-101(Cr)-NH_2 before and after used as catalyst are identical (see Fig. 1). (3) the size and shape of PTA@MIL-101(Cr)-NH_2 before and after used as catalyst are the same (see Fig. S3).(4) no essential difference in thermal stability between PTA@MIL-101(Cr)-NH_2 before and after used as catalyst (Fig. S4).

Control experiments in ECODS using pure PTA only or, separately, pure MIL-101(Cr)-NH_2 only have been done (Table S1). It can be indicated that dibenzothiophene sulfone ($DBTO_2$) didn’t produce much without catalyst (conversion rate, 4.79%), and the pure MIL-101(Cr)-NH_2 also shows low catalytic activity under the same condition (conversion rate, 2.84%). Compared with PTA@MIL-101(Cr)-NH_2 (conversion rate, 100%), the catalytic activity is negligible. In addition, though PTA has a high catalytic activity (conversion rate, 99.6%), it is hard to be recovered for next cycle. Notably, both PTA and PTA@MIL-101(Cr)-NH_2 have no catalytic activity without H_2O_2.

The nature of the substrates is a critical factor in influencing the sulfur removal in the desulfurization system. Here, other two inflexible substrates (4,6-DMDBT and BT) were studied in our desulfurization system (Fig. 9). Conversion of 4,6-DMDBT and BT could reach 88.2% and 70.5% respectively, which indicated that the oxidation reactivity decreased in the order of DBT > 4,6-DMDBT > BT. This is consistent with previous results reported by others.[28,29] The electron density on the sulfur atom of BT, DBT and 4,6-DMDBT are 5.739, 5.758 and 5.760, respectively[28,29]. The lowest electron density on the sulfur atom of BT leads to the lowest oxidative activity. The electron density of DBT on the sulfur atom is lower than that of 4,6-DMDBT, but with a higher conversion of DBT to corresponding sulfone. It may be ascribed to that the sulfur atoms are difficult to access the active PTA anions due to steric hindrance of methyl groups of 4,6-DMDBT. These results indicate that the oxidative activity is not only relate to the electron density but also to the steric hindrance on the sulfur atom.

Conclusion

In summary, PTA anions encapsulated in the mesocages of amine functionalized MOFs MIL-101(Cr)-NH_2 have been prepared using anionic exchange approach. The obtained catalyst showed excellent activity for oxidative desulfurization under mild conditions. Furthermore, the catalyst is easily recoverable and can be reused several times without leaching or loss of activity due to the electrostatic interaction of PTA with the amine groups of MIL-101(Cr)-NH_2. Therefore, PTA@MIL-101(Cr)-NH_2 as heterogeneous catalyst has great potential for further industrial application.

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Notes and references

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Electronic Supplementary Information (ESI) available: Detailed synthetic processes of MIL-101(Cr)-NH_2, MIL-101(Cr)-NO_2 and characterization methods of catalyst and catalytic performance, control experiments procedures and results, FT-IR spectra, TEM, SEM, TG.
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PTA@MIL-101(Cr)-NH_2 has been prepared via anion exchange method, which showed high catalytic activity for oxidative desulfurization under mild condition.