Catalytic Oxidation Desulfurization over PTA-dispersed MIL-101 under Mild Conditions

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Abstract. With H_2O_2 as oxidant, phosphotungstic acid (PTA) was used as heterogeneous oxidation desulfurization catalyst via immobilizing on porous MIL-101. By combining the catalytic activity of PTA with the adsorption property of supporter MIL-101, 91.2% of dibenzothiophene (DBT) in model fuel has been removed. Even with benzene and p-xylene co-existed, 0.5PTA/MIL remained its activity in catalytic oxidation of DBT. However, when TBHP was used as an alternative of H_2O_2 in this reaction system, no conversion of dibenzothiophene (DBT) was detected.

1. Introduction

Since fossil fuel derived oils contain certain amount of refractory thiophenic sulfurs, the combustion of it would inevitably lead to catalyst deactivation and serious environmental problems [1]. Therefore, it is necessary to establish regulations to limit the contents of sulfur in gasoline and diesel. For example, the European Union has mandated to limit the S-level in commercial fuel to less than 10 ppmS [2,3].

Nowadays, the common method in chemistry industry for removing sulfur-containing compounds from hydrocarbons is hydrodesulfurization (HDS). However, it is difficult to remove aromatic thiophene and its derivatives through HDS due to their steric hindered nature on catalyst surface [2,4]. Meanwhile, rigorous operation conditions of HDS also bring about high investment, operating cost, and so on [5]. Thus, possible alternative strategies including adsorption [6,7], liquid-liquid extraction [8], oxidation [9] and combines of them were explored. Among these non-HDS methods, adsorption-catalytic oxidation appeared promising due to its high efficiency and mild operating conditions [10].

In oxy-desulfurization process, thiophenic sulfurs can be oxidized to their corresponding sulfoxides or sulfones by H_2O_2 [2], NO_2 [11] or *tert*-butyl-hydroperoxide (TBHP) [12] in the presence of catalyst. As a common acidic and oxidation catalysts, phosphotungstic acid (PTA) was often used to catalyze the oxidation of dibenzothiophene (DBT) [13]. However, low oxidation efficiency and recovery greatly limited its application. Recently, the emergence of chromium-based MIL-101 which possesses excellent thermal and hydrothermal stabilities and extraordinary adsorption ability, provides a chance to solve these problems through immobilizing PTA [14, 15]. It is expected that the immobilization of PTA over porous MIL-101 will improve its catalytic performance. Considering the fact that the activity of supported PTA depends mainly on the type of supporter, strength of interaction and active species loading amount, different supporters and proper loading of PTA were studied [16].

Beyond that, many studies have referred to the performance of different oxidants in the oxidation of aryl sulfides over MIL-101 [17,18]. Therefore, in this study we investigated the performance of both H_2O_2 and TBHP in the oxidation of DBT. As we all know, commercial fuels consist of alkanes, olefins and aromatics. Here, we firstly investigated the catalytic activity of PTA-dispersed MOFs in the oxidation of DBT with benzene and p-xylene co-existed which might promote the development of oxy-desulfurization technique in real fuel.

2. Experimental

2.1. Materials and reagents

Terephthalic acid (TPA) ($C_8H_6O_4$, ≥ 99%), Chromium (III) nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$, ≥ 99%), hydrated 12-tungstophosphoric acid ($H_3PW_{12}O_{40} \cdot xH_2O$, ≥ 96%), dibenzothiophene ($C_{12}H_8S$, ≥ 98%) and other chemicals and solvents were all purchased from commercial sources and used without further purification.

2.2. Preparation of Catalysts

MIL-101 was synthesized by a hydrothermal reaction of 2.4 g $Cr(NO_3)_3 \cdot 9H_2O$ with 1 g TPA, 1.2 mL hydrofluoric acid (HF, 5M), and 30 mL deionized water as reported [19]. The products (blue powder) obtained were doubly filtered off using glass filters with a pore size of 40 and 100 μm to remove the surplus TPA. Then a solvothermal treatment was sequentially performed using N, N-dimethylformamide (DMF), ethanol (95% EtOH with 5% H_2O), ammonium fluoride (1 M NH_4F) and hot water. Finally, the powder was dried overnight and then activated at 433 K under vacuum.

Then the supported catalysts were prepared through impregnating 500 mg MIL-101 obtained before into 500 mg/50 mL, 250 mg/50 mL and 50 mg/50 mL PTA aqueous solution, respectively [14,16]. After stirring for 12 h at room temperature, the solids were separated and washed by water. Then the obtained powder were dried and activated at 433 K under vacuum and designated as PTA/MIL, 0.5PTA/MIL and 0.1PTA/MIL.

2.3. Characterization of the Catalysts

XRD patterns were collected using Cu Kα radiation on Rigaku D/max 2200/PC diffractometer (Rigaku Corporation, Japan). Bruker AXS S4 PIONEER X-ray fluorescence (XRF) spectrometer was used to obtain the elemental composition of samples. FT-IR spectra were recorded on a Bio-Rad FTS 155 FTIR spectrometer in KBr pellets under atmospheric conditions.

2.4. General Procedure of the Oxidative Removal of DBT

Before reaction, catalysts were firstly degassed under vacuum at 150 °C for 4h, and then kept in a desiccator. Model fuels were prepared by dissolving calculated amount of DBT in n-octane and resulting in 500 ppmS. The concentrations of DBT can be determined by gas chromatography (Agilent 6890A, Agilent Corporation) equipped with flame ionization detector.

In the oxidation reactions, catalysts and hexadecyl trimethyl ammonium bromide (CTAB) were used in contents of 7.5 mg/mL and 10 mg/3 mL, respectively. Then a 30% solution of H_2O_2 in water was added to start the reaction with O/S molar ration 50. During the reactions, series of samples were with draw from system and separated from catalysts in specific intervals, and then DBT concentrations were measured.

In addition, hydrocarbon-soluble oxidant TBHP was applied to study the performance of different oxidants in catalytic oxidation of DBT. Finally, in order to clarify the negative effects of poisonous aromatics on DBT conversion, we firstly introduced benzene and p-xylene into 500 ppmS model fuels in content of aromatics/n-octane (1:99, 5:95 and 15:85 vol.), respectively. Then the conversion of DBT was discussed.

3. Results and Discussion

3.1. Physical Properties of the Catalysts

As shown in Fig. 1, the XRD patterns indicated that MIL-101 and 0.5PTA/MIL are crystals and in good agreement with those reported [20,21]. Comparing with the XRD pattern of PTA, distinct peaks standing for PTA emerged at $2\theta = 7°$ in 0.5PTA/MIL [22]. The elemental composition determined by XRF analysis was shown in Table 1. The loading amount of PTA varied from 11.76

to 61.11%.

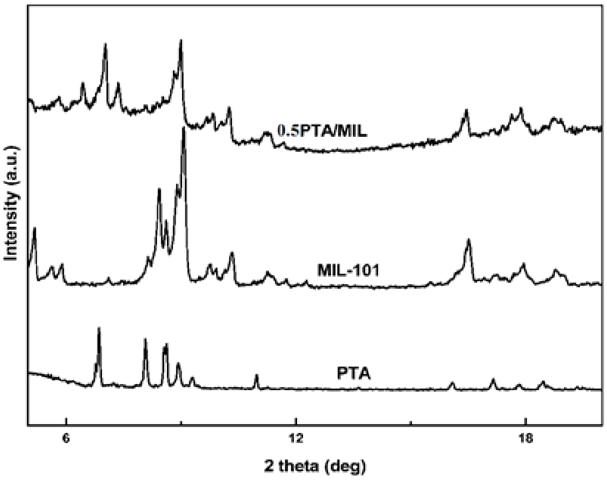

Fig. 1. XRD patterns of MIL-101 and 0.5PTA/MIL.

Table 1. XRF results of PTA-dispersed MIL-101(Cr) materials.

Samples	W, wt.%	Cr, wt.%	P, wt.%	PTA, wt.%
PTA/MIL	65.43	22.04	1.35	32.94
0.5PTA/MIL	51.97	33.09	1.00	20.64
0.1PTA/MIL	15.02	44.12	0.27	4.89
2PTA@MIL	2.15	48.87	0.19	0.74

In Fig. 2, a broad adsorption band represented –OH stretching of the strongly bonded water in the PTA-containing samples appeared at 3440 cm^{-1}, while the sharp peak at 1640 cm^{-1} stood for the crystal water of PTA. The bands at 881 and 983 cm^{-1} corresponded to the W-O-W vibrations and W=O stretching, respectively [23]. Besides those bands, the bands at 1080 and 594 cm^{-1} were related to the P=O stretching in unsubstituted PTA and O-P-O vibration [24,25].

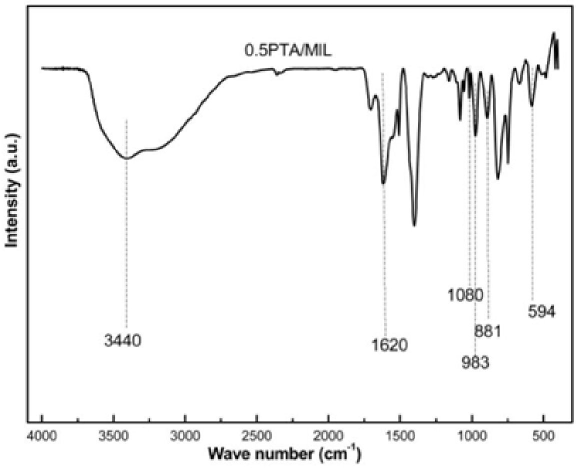

Fig. 2. FT-IR spectra of 0.5PTA/MIL.

3.2. Adsorption and catalytic oxidation of DBT

As shown in Fig. 3 and Table 2, when MIL-101 and PTA-loaded catalysts were present, adsorption took place firstly as reported [3,26]. Generally, the adsorption capacity of DBT decreased in the order of MIL~0.1PTA/MIL > 0.5PTA/MIL > PTA/MIL >> 0.5PTA/Na-Y. To explore the effect of carriers on oxidation, catalytic activity of Na-Y with equal amount of PTA loaded was measured. Compared with the 87.6% reduction over 0.5PTA/MIL, only 4.8% of DBT was converted over

0.5PTA/Na-Y. Basing on the similar amount of PTA introduced, the lower activity of 0.5PTA/Na-Y could be ascribed to the strong interaction between PTA and Na-Y [16].

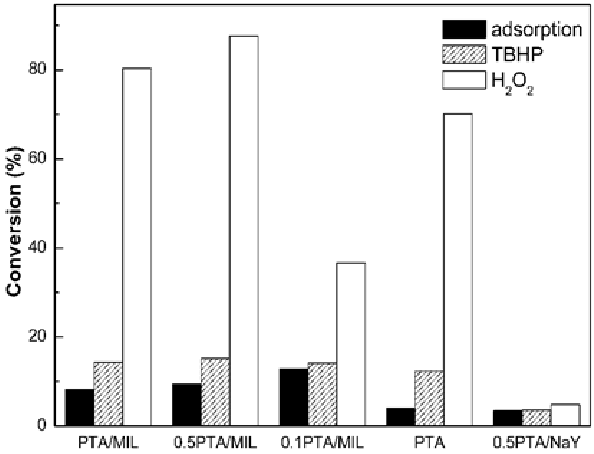

Fig. 3. Reduction of DBT over different materials through adsorption and oxidation using TBHP or H_2O_2 as oxidant. Conditions: phase transfer agent, 0 (adsorption) or 10 mg (oxidation), O/S = 0 (adsorption), 4 (TBHP) or 50 (H_2O_2) (molar ratio), concentration of catalyst, 7.5 mg/mL solution, reaction time, 4 h, ambient temperature.

Beyond that, it is worth noting that the activity of 0.5PTA/MIL was better than that of homogeneous PTA (87.6% vs 70.1%) which indicated the benefits of MIL-101 caused by coordinatively unsaturated sites (CUS) [17]. In addition, to obtain the optimal loading amount of PTA content on oxidation process, DBT was oxidized by catalysts with various PTA loaded. Interestingly, the result was not absolutely consistent with the loading amount of PTA. The conversion of DBT over 0.5PTA/MIL was higher than 0.1PTA/MIL and PTA/MIL. Therefore, appropriate amount of PTA introduced also play a crucial role in the oxidation of DBT [16].

Table 2. The adsorption capacities of DBT and catalytic oxidation conversations of DBT with TBHP or H_2O_2 over different catalysts. Conditions: phase transfer agent, 10 mg, O/S (H_2O_2) = 50 (molar ratio), concentration of catalyst, 7.5 mg/mL solution, reaction time, 4 h, ambient temperature.

Catalysts	**Reduction, %**		
	Adsorption	**TBHP oxidation**	**H_2O_2 oxidation**
MIL	13.2	12.3	13.8
4PTA@MIL	14.8	12.0	16.8
2PTA@MIL	15.4	14.0	16.4
1PTA@MIL	14.0	13.6	14.9
PTA/MIL	8.2	14.4	80.3
0.5PTA/MIL	9.5	15.1	87.6
0.1PTA/MIL	12.8	14.2	36.7
0.5PTA/NaY	3.4	3.5	4.8
PTA	4.0	12.3	70.1

In Fig. 4, the process of catalytic oxidation of DBT was monitored and could be well described by pseudo-second-order kinetics equation. As shown in Table 3, when O/S = 75 the conversion of DBT reached 94.2% while DBT reduction was 41.8% with O/S = 12.5. This might be ascribed to the formation of uniform oil-in-water emulsions system with higher O/S molar ratio [14]. Furthermore, from Table 3, it can be found that 99.8% of DBT was removed with 12.5 mg catalyst/mL solution. However, in the control test, no reduction of DBT was detected when TBHP was used as oxidant. As analyzed by Young Kyu Hwang, the decomposition of TBHP in this system generate alkylperoxy andalkyloxy radicals which could not oxidize DBT [17].

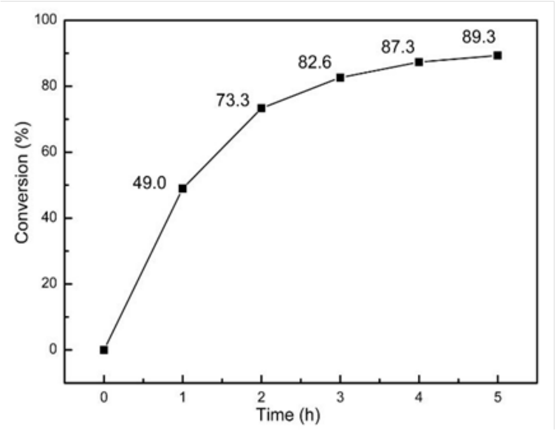

Fig. 4. Variation of DBT removal with reaction time with H_2O_2 over 0.5PTA/MIL catalyst. Conditions: phase transfer agent, 20 mg, O/S = 50 (molar ratio), concentration of catalyst, 7.5 mg/mL solution, reaction time, 5 h, ambient temperature.

Fig. 5 described the influence of benzene and p-xylene on the oxidization of DBT in H_2O_2-0.5PTA/MIL-CTAB system. In sharp contrast to the great decrease over PTA/AC, the introduction of both benzene and p-xylene reduced the conversion of DBT slightly. The DBT removal decreased as the aromatics added, and the influence of benzene was greater than p-xylene. When 1% (vol.) benzene and p-xylene was added respectively, the conversion of DBT was 83.7 and 84.1%. As the amount of benzene and p-xylene increased to 15% (vol.), only 76.6 and 81.1% of DBT was removed. However, comparing with the decrease of conversion over other catalysts [27], 0.5PTA/MIL remained most of its catalytic performance.

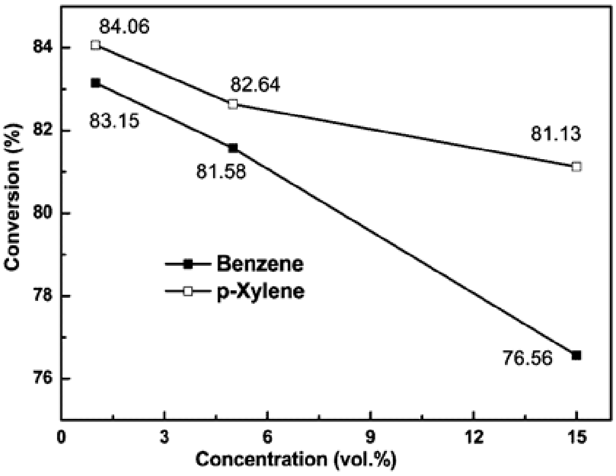

Fig. 5. Effect of aromatics benzene and p-xylene on the conversation of DBT. Conditions: phase transfer agent, 10 mg, concentration of catalyst, 7.5 mg/mL solution, O/S = 50 (molar ratios), reaction time, 4 h, ambient temperature.

4. Conclusions

Generally, the oxidation of DBT applying PTA-dispersed MIL-101 as heterogeneous catalysts has been investigated systematically. It was found that the oxidation of DBT proceed rapidly over PTA-dispersed MIL-101 under mild condition. Meanwhile, it is interesting to find that TBHP could not be used as an oxidant under the same conditions as H_2O_2. The presence of aromatics didn’t decrease the conversion of DBT greatly which suggested that sulfur removal from real fuel would be a possible and promising application for MOFs.

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