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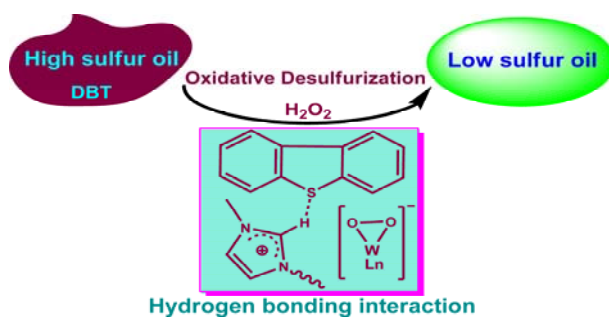
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The peroxotungsten anions-based ionic liquid-type catalysts were highly efficient for the deep desulfurization of model oil with H_2O_2 under mild and solvent-free conditions.



The Deep Oxidative Desulfurization Catalyzed by Ionic Liquid-type Peroxotungsten Catalyst

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Abstract: The new peroxotungsten anions-based ionic liquid-type catalysts were synthesized and characterized by the methods of NMR, IR, and TG etc. Then, these salts were used as catalyst for the deep desulfurization of model oil containing dibenzothiophene (DBT) with H₂O₂ as an oxidant. The effects of temperature, H₂O₂/DBT molar ratio, and the catalyst loading on the desulfurization activity have been investigated in detail. The present catalysts showed excellent desulfurization activity under solvent-free and mild reaction conditions. Moreover, this catalyst could be recycled at least ten times without any decrease in activity. It was found that the H-bonding interaction between H₂-proton in imidazolium and basic S atom in DBT molecule played a very important role in enhancing catalytic activity. On the basis of activity measurement and characterization of the catalyst, the reaction mechanism of oxidation desulfurization has been suggested.

Keywords: Peroxotungsten Anion, Hydrogen bond, Desulfurization, Epoxidation

1 Introduction

With the development of the automobile industry, desulfurization in fuels has been attracting more and more attention as the consideration both in industry and environment in the world. The combustion of sulfur-containing compounds in transportation fuels was the main reason for the formation of smog, sour gases, and acid rain. Therefore, developing novel and green processes to convert these sulfur-containing compounds into other innocuous forms has already been attracting more and more attention over the world.^{1,2}

Up to now, the traditional of process for the desulfurization of fuels in industry was known as hydrodesulfurization (HDS), which was efficient in removing thiol, sulfides, and disulfides from fuels, but less effective for dibenzothiophene (DBT) and its derivatives.³⁻⁵ Additionally, HDS required a harsh reaction conditions such as high temperature, high pressure with a suitable catalyst. In order to overcome these problems, oxidative desulfurization (ODS) has been explored intensively in past decades, since the reaction was highly efficient to remove sulfur compounds under mild conditions. Reported oxidative desulfurization catalysts included peroxometalate,⁶⁻⁸ metal oxides hybrids,⁹⁻¹¹ ionic liquid,¹²⁻¹⁴ molecular sieves¹⁵⁻¹⁷ and so on. Especially, peroxometalate anion-based catalyst tended to be more attractive due to their high reactivities, selectivities and stabilities for the H₂O₂-based ODS in the past years.

It is known that ionic liquids possess many desirable properties such as high thermal stability, nonvolatility, and good solubility.¹⁸⁻¹⁹ They also show good extraction ability for aromatic sulfur-containing compounds, and are immiscible with aliphatic liquids such as fuel oil. Therefore, it can effectively eliminate further environmental and safe problems.²⁰⁻²¹ Of late years, some peroxometalate anion-based salts have been used as catalyst, ionic liquid as solvent or extractant for desulfurization reaction.²²⁻²⁵ In this aspect, three hexatungstates which were dissolved in the hydrophobic 1-octyl-3-methylimidazolium hexafluorophosphoric ([Omim]PF₆) ionic liquid forming a water-in-IL emulsion system with H₂O₂ had been reported.²⁶ This desulfurization system could reach a high conversion with a good recyclability.

In addition, a lanthanide-containing polyoxometalate has also been used as a desulfurization catalyst with 30% H₂O₂ as oxidant, and ionic liquid as an extraction solvent.^{27, 28} In most previous research, a hydrophobic ionic liquid was normally needed to extract sulfur-containing compounds in these systems. Up to now, there were few reports about peroxometalate anion-based catalyst applied in the desulfurization reaction without any other extractants. In this regard, several surfactant-type polyoxometalate-based ionic liquids had been synthesized and investigated on their oxidative desulfurization for model oil by using H₂O₂ as the oxidant without other extractant.²⁹ Besides, an amphiphilic catalyst composed of peroxotungsten anion and quaternary ammonium cation had also reported for the selective oxidation of S containing molecules present in diesel to sulfones in W/O emulsion systems.³⁰ These work offered an alternative for oxidative desulfurization of actual prehydrotreated fuel. Although the desulfurization reaction could be performed under mild conditions with excellent desulfurization efficiency for dibenzothiophene and its derivatives, an emulsion was formed in these catalytic systems, which possibly resulted in difficult separation of oil after reaction. Thus there was still much room for improving the oxidative desulfurization catalysts. For example, more easy procedure to recover the catalyst and meanwhile desulfurization reaction under more mild reaction and solvent-free conditions will be highly desirable.

Our group had employed peroxometalate anion-based ionic liquids as the catalysts for the epoxidation of olefins with a good conversion and selectivity.³¹⁻³⁴ Based on these previous investigations, in this paper we synthesized and characterized the novel ionic liquid-type catalysts which were composed of tungsten peroxy anion complexes and alkyl imidazolium cation. Then the novel catalysts were employed for the oxidative desulfurization without any other extractants. It was found that there was a hydrogen bonding interaction between DBT and imidazolium cation, which promoted the oxidation of DBT molecules under mild reaction conditions. Moreover, the catalyst could be reused conveniently at least ten times without any significant decrease in the activity.

2 Experimental

2.1 Materials

All solvents (A.R. grade) were dried with the standard methods. Commercially available H₂O₂ (30% in water), ethyl acetate, ethanol, 1-octane, ether and 1-methyl imidazole were purchased from Sinopharm Chemical Reagent Co. Ltds. Na₂WO₄·2H₂O, 2-picolinic acid, dibenzothiophene (DBT), cetyltrimethylammonium chloride, Tetrabutylammonium chloride 1-dodecyl chloride, 1-hexadecyl chloride, were purchased from Sigma-Aldrich and used without further purification.

2.2 Method

All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen. All NMR spectra were recorded on a Bruker Avance III 400 instrument (400 MHz for ¹H) by using CDCl₃ as solvent and TMS as reference. Chemical shifts (δ) are given in parts per million and coupling constants (J) in hertz. The elemental analysis of C, H, N was performed on an Elementar Vario EI III Elementa and ICP-AES analysis of W on Vanan 710 instrument, respectively. FT-IR spectra were recorded at room temperature on a Nicolet Fourier transform infrared spectrometer (Magna 550). A perkin Elmer Pyris Diamond was used in the current study for the thermogravimetric analysis(TGA) measurements. A constant heating rate of 10 °C/min was used under N₂ atmosphere. The products were analyzed by Shimadzu GC-2014 equipped with a HP-5 column (30 m, 0.25 mm i.d.) and an FID detector.

2.3 Catalyst preparation

Synthesis of ionic liquid [C₁₂mim][Cl], [C₁₆mim][Cl]

The 1-dodecyl-3-methylimidazolium chloride ([C₁₂mim][Cl]) was synthesized according to the conventional method.³⁵ Equal molar amounts of 1-methyl imidazole and 1-dodecyl chloride were added to an autoclave with stirring at 90 °C for 48 h under a 0.7 MPa N₂ atmosphere. After the reaction, the crude products were washed with ethyl acetate and dried under the vacuum at 60 °C for 2 h. ¹H NMR (400-MHz,

CDCl₃) δ =10.8 (s, H, CH), 7.5(s, H, CH), 7.3(s, H, CH), 4.3(t, 2H, CH₂), 4.1(t, 3H, CH₃), 1.9(s, 2H, CH), 1.3 (m, 18H, CH₂), 0.9(t, 3H, CH₃).

[C₁₆mim][Cl] was synthesized as the same procedure as [C₁₂mim][Cl] except that 1-dodecyl chloride was replaced by 1-hexadecyl chloride. ¹H NMR (400-MHz, CDCl₃) δ =10.7 (s, H, CH), 7.4(s, H, CH), 7.3(s, H, CH), 4.3(t, 2H, CH₂), 4.1(t, 3H, CH₃), 1.9(s, 2H, CH), 1.3 (m, 26H, CH₂), 0.9(t, 3H, CH₃).

Synthesis of [C₁₂mim][W(O)(O)₂(C₅H₄NCO₂)] ([C₁₂mim][PyW]) and [C₁₆mim][W(O)(O)₂(C₅H₄NCO₂)] ([C₁₆mim][PyW])

Catalysts were prepared conveniently in one-pot method. A solution of 2-picolinic acid (0.74 g, 6 mmol) in 1 mL of water was added to a solution of tungstic acid (1.5 g, 6 mmol) dissolved in 7.5 mL of 30% hydrogen peroxide chilled to 0 °C. The resulting solution was then stirred overnight at room temperature to afford tungsten peroxo complexes.³⁶ Then a solution of [C₁₂mim][Cl] in 3 mL of ethanol was added dropwise into the above aqueous solution. A white precipitate was formed immediately. After stirring for 24 h under room temperature, the precipitate was filtered off and washed with water and ethanol, and then dried under the vacuum to afford slightly yellow powder. (Yield: 80%). Mp=76.5 °C. ¹H NMR (400-MHz, CDCl₃) δ =9.1 (s, H, CH), 8.4(d, H, CH), 8.1(d, H, CH), 7.9(t, H, CH), 7.5(t, H, CH), 7.4(s, H, CH), 7.3(s, H, CH), 4.3(t, 2H, CH₂), 4.1(t, 3H, CH₃), 1.9(s, 2H, CH), 1.3 (m, 18H, CH₂), 0.9(t, 3H, CH₃). (Found: C, 40.63; H, 5.35; N, 6.20; W, 25.87%; C₂₂H₃₆N₃O₇W requires C, 41.39; H, 5.68; N, 6.20; W, 28.80%).

[C₁₆mim][PyW] was also synthesized in a similar way as that of [C₁₂mim][PyW] except that the solution of [C₁₂mim][Cl] was replaced by [C₁₆mim][Cl]. (Yield: 90%). Mp=82.3 °C. ¹H NMR (400-MHz, CDCl₃) δ =9.1 (s, H, CH), 8.4(d, H, CH), 8.1(d, H, CH), 7.9(t, H, CH), 7.5(t, H, CH), 7.3(s, H, CH), 7.2(s, H, CH), 4.3(t, 2H, CH₂), 4.1(t, 3H, CH₃), 1.9(s, 2H, CH), 1.3 (m, 26H, CH₂), 0.9(t, 3H, CH₃). (Found: C, 44.39; H, 5.72; N, 5.88; W, 23.74%; C₂₆H₄₄N₃O₇W requires C, 44.97; H, 6.39; N, 6.05; W, 26.47%).

Synthesis of [CTA][W(O)(O)₂(C₅H₄NCO₂)] ([CTA][PyW]) and [TBA][W(O)(O)₂(C₅H₄NCO₂)] ([TBA][PyW])

[CTA][PyW] was prepared by the same procedure with cetyltrimethylammonium chloride (CTAC) as the precipitant. (Yield: 90%). Mp=84.2 °C. ¹H NMR (400-MHz, CDCl₃) δ=8.4(d, H, CH), 8.1(d, H, CH), 7.9(t, H, CH), 7.5(t, H, CH), 3.4(t, 2H, CH₂), 3.3(s, 9H, CH₃), 1.8(s, 2H, CH), 1.3 (m, 26H, CH₂), 0.9(t, 3H, CH₃). (Found: C, 43.82; H, 6.89; N, 3.80; W, 24.80%; C₂₅H₄₇N₂O₇W requires C, 44.72; H, 7.05; N, 4.17; W, 27.38%).

[TBA][PyW] was prepared by the same procedure with tetrabutylammonium chloride (TBAC) as the precipitant. (Yield: 80%). Mp=75.1 °C. ¹H NMR (400-MHz, CDCl₃) δ=8.4(d, H, CH), 8.1(d, H, CH), 7.9(t, H, CH), 7.5(t, H, CH), 3.3(m, 8H, CH₂), 1.7(m, 8H, CH₂), 1.8(m, 8H, CH₂), 1.0 (t, 9H, CH₃). (Found: C, 37.90; H, 6.01; N, 3.94; W, 25.80%; C₂₂H₄₁N₂O₇W requires C, 41.98; H, 6.57; N, 4.45; W, 29.21%).

2.4 Typical procedure for oxidative desulfurization and epoxidation reaction

The solution of DBT in n-octane was used as model oil with a S-content 1000 ppm. The oxidation reaction was carried out in a 50 mL Schlenk flask equipped with a reflux condenser and a thermometer. After [C₁₆mim][PyW] (0.0031 mmol) was added, 5 mL of the model oil, 30% H₂O₂ (0.064mL), and internal standard (n-dodecane) were charged into the Schlenk flask (n_{DBT}/n_{catalyst}/n_{H₂O₂} = 50:1:200, molar ratio). Then, the reaction mixture was stirred at 50 °C for 2 h and cooled down to room temperature. The upper clear solution was withdrawn and determined by GC with an internal standard. After washing with n-octane and ether respectively, and drying at 50 °C for 1h under reduced pressure, the catalyst could be reused for the next catalytic recycle. The solid product dibenzothiophene sulfone (DBTO₂) could be separated from the bottom phase by filtration. Then, DBTO₂ was extracted by acetonitrile, and further purified by recrystallization at 0 °C to afford white needle crystal.

The *cis*-cyclooctene epoxidation was carried out in a 25 mL Schlenk flask equipped with a reflux condenser and a thermometer. After 0.02 mmol catalyst was added, 1 mmol *cis*-cyclooctene, 1.5 mmol H₂O₂ was then charged into the Schlenk

flask. Then the reaction mixture was stirred at 60 °C for 6 h and then cooled down to room temperature. The products were extracted thrice with cyclohexane. The resulting organic layer was dried with MgSO₄ and then analyzed by using GC.

2.5. Adsorption of DBT on catalysts

The adsorption of DBT on catalyst was performed by using our reported similar method.³⁷ After DBT (0.15 mmol) was dissolved in 5 mL n-octane, the [CTA][PyW] or [C₁₆mim][PyW] (0.03 mmol) catalyst was added to the n-octane solution and the solution was stirred vigorously at 50 °C. The decrease of DBT concentration in n-octane was monitored by using GC with n-dodecane as an internal standard until the adsorption was saturated.

2.6 The hot filtration experiments for oxidative desulfurization

After adding 0.003125 mmol [C₁₆mim][PyW], 5 mL of the model oil, 0.064 mL 30% H₂O₂ and n-dodecane(internal standard), the mixture was heated up to reaction temperature and stirred vigorously for 1 h. And then, the catalyst was rapidly filtered out with hot filter funnel from the reaction mixture under reaction temperature, the remaining filtrate was allowed to continue on reaction after adding fresh H₂O₂.

3 Results and discussion

3.1 Catalyst preparation and characterization

[C₁₂mim][Cl] was synthesized easily according to the previously reported method,³⁵ while tungsten peroxo anion-based catalyst was prepared through ionic exchange (Scheme 1). Because [C₁₂mim][PyW] did not dissolved in water, HCl as a by-product can be removed easily by washing fully the catalyst. Sequentially, [C₁₆mim][PyW], [TBA][PyW] and [CTA][PyW] were obtained in a similar method. On the basis of the analysis of ¹H NMR, elemental analysis of C, H, N and ICP-AES analysis of W, the ionic liquid-type catalysts have been synthesized successfully.

<Insert Scheme 1>

The synthesized catalysts were firstly characterized with FT-IR. As shown in Fig.

1a, the main bands of [C₁₆mim][PyW] are 3430(OH) cm⁻¹, 1609(C-N) cm⁻¹, 1468, 1394(C-H) cm⁻¹ and 1167(MeN) cm⁻¹ which were assigned to the vibrations of imidazolium cation, and 1706 cm⁻¹, 951 cm⁻¹, 850 cm⁻¹, 583 cm⁻¹, and 556 cm⁻¹ were ascribed to the vibrations of C=O, W=O, O-O, W(O₂)(asym) and W(O₂)(sym), respectively, which indicated that the anion structure was retained in ionic liquid-type catalyst. The FT-IR spectrum of [C₁₂mim][PyW] catalyst was very similar to that of [C₁₆mim][PyW]. However, a small red-shift of the wavenumber from 1706 cm⁻¹ to 1690 cm⁻¹ (C=O vibration) was observed when the imidazolium cation was replaced by the quaternary ammonium cations probably due to the interaction between the different cations and anion (Fig. 1a-1d).

<Insert Fig. 1>

The thermal stability of the catalysts was also examined by using TGA method. As shown in Fig. 1S, for ionic liquid-type [C₁₆mim][PyW] catalyst, a slight loss around 100-200 °C resulted from water removal and obvious weight loss of nearly 47% around 200-350 °C was result of the decomposition of the imidazolium-based cation. The further weight loss was the decomposition of anion of the catalyst. The overall weight loss was in accordance with the result of ICP-AES analysis of W. The [C₁₂mim][PyW] catalyst had very similar decomposition trend with that of [C₁₆mim][PyW] due to the similar cations and same anion, but quaternary ammonium salts like [CTA][PyW] and [TBA][PyW] showed a slightly lower thermal decomposition temperature, implied lower thermal stability than that of the imidazolium cation salts (Fig. 1S).

3.2 Catalytic performance

Firstly, the effect of different cations in the tungsten peroxo complex on the desulfurization activity of DBT has been investigated. In the present work, a tungsten peroxo anion [PyW]⁻ was combined with four different countercations and applied for the desulfurization of DBT with H₂O₂ as an oxidant (Scheme 2). As shown in Fig. 2, the imidazolium-based catalysts showed higher catalytic activity than that of quaternary ammonium-based catalysts. After reacting for 2 h, both of the

imidazolium-based catalysts afforded excellent DBT conversions, and especially [C₁₆mim][PyW] almost provided a complete conversion, which implied that the efficiency of sulfur removal increased with increasing alkyl chain length. It was understandable that the catalyst with a longer alkyl chains had stronger hydrophobic interaction with the substrates (DBT) by van der Waals force, which was favorable to the absorption/coordination of DBT and reaction of the substrates. Nevertheless, although the hydrophobicity of [CTA][PyW] and [C₁₆mim][PyW] was almost the same, the former afforded much lower activity than the latter, which implied that DBT molecules could coordinate or absorb more easily on active tungsten peroxy anions in the presence of imidazolium cations.

The adsorption of DBT over [CTA][PyW] and [C₁₆mim][PyW] catalysts was carried out to identify the role of cations in catalysis. As shown in Fig. 3, the DBT molecule exhibited significantly different adsorption rate over the two catalysts. After adsorption for 30 min at 50 °C, the concentration of DBT in n-octane was decreased from 0.03 mmol/mL to 0.023 mmol/mL due to the adsorption of DBT on [C₁₆mim][PyW], while the concentration of DBT only decreased a little on [CTA][PyW]. Interestingly, the adsorption capacity of DBT on [C₁₆mim][PyW] was nearly equimolar with the amount of [C₁₆mim][PyW] used (the ratio of the absorbed DBT to [C₁₆mim][PyW]=1:1). The adsorption result indicated clearly that [C₁₆mim][PyW] was more accessible to adsorb/coordinate the DBT molecules, as compared with [CTA][PyW], and then promoting desulfurization reaction.

<Insert Scheme 2>

<Insert Fig. 2>

<Insert Fig. 3>

Sequentially, the possible interaction between DBT molecules and imidazolium ring was further clarified through ¹H NMR measurement. As shown in Fig. 4, the proton chemical shift at H2, H4, H5 of imidazolium ring in [C₁₆mim][PyW] were 9.13, 7.26 and 7.23 ppm in CDCl₃, respectively. However, after [C₁₆mim][PyW] was added with DBT in CDCl₃, the proton chemical shift changed obviously. Especially, the proton chemical shift at H2 position of imidazolium ring moved downfield

considerably (from 9.13 to 9.32). The resonance signal of H5 and H4 ring protons also showed slight shift but their changes of the chemical shift are much smaller than that of the proton H2. The variation of chemical shifts could be explained by several contributions such as aromatic ring current effect (π - π), hydrogen bonding effect, C-H- π interaction between cation and thiophene ring, anion effect, dilution effect and electrostatic field effect. In this investigation, the proton H2 was moved downfield which was different from reported research that aromatic ring current effect was the dominate factor where proton H2 was moved upfield.³⁸ It is well known that the formation of a hydrogen bond will cause a proton chemical shift (H2) to move to lower field. The change in chemical shift is indicative of the formation of a substantial hydrogen bond.³⁹ On the basis of the above discussion, it was demonstrated that the strong H-bonding interaction between the acidic proton H2 and basic S atom existed, resulting in fast adsorption of DBT on imidazolium ring and thus easy accessibility to catalytically active tungsten peroxo anion. In contrast, it was observed that all resonance signal of [CTA][PyW] exhibited almost no any changes under the same condition. This strongly suggested that there was no significant interaction between quaternary ammonium cation (CTA) and DBT molecules. This was the reason why [C₁₆mim][PyW] afforded much higher desulfurization efficiency than [CTA][PyW].

<Insert Fig. 4>

The effect of temperature on the catalyst/H₂O₂ system was screened. As shown in Fig. 5, the conversion of DBT increased with the reaction temperature at the same reaction time. It was obvious that a higher reaction temperature was favorable to the oxidation of DBT and the desulfurization efficiency was increased sharply when reaction temperature was over 40 °C. In the view of economizing the energy and the nonproductive decomposition of hydrogen peroxide at high temperature, the reaction temperature of 50 °C was chosen for further investigation in the present work.

<Insert Fig. 5>

Further, DBT/catalyst molar ratio ranged from 30:1 to 100:1 was examined for the desulfurization reaction. As shown in Fig. 6A, the reaction rate increased with the rise of molar ratio of DBT/Catalyst. The sulfur removal increased slightly when the

ratio of DBT/catalyst decreased from 50:1 to 30:1. In the view of the desulfurization efficiency and catalyst cost, 50:1 was chosen as the appropriate ratio of DBT/catalyst. The result showed that a suitable molar ratio of DBT to Catalyst was important for the desulfurization.

H₂O₂ is a green oxidant compared with other organic oxidant. In order to optimize the reaction conditions and elucidate the influence of the amount of H₂O₂ on the desulfurization, different molar ratios of H₂O₂ to DBT were screened under the reaction conditions of reaction temperature 50 °C, model oil (S content 1000 ppm) 5 mL, molar ratio of DBT/catalyst 50:1. As shown in Fig. 6B, the reaction rate was dependent obviously on H₂O₂/DBT molar ratios, As H₂O₂/DBT increased from 3:1 to 4:1, the removal efficiency of DBT increased correspondingly but higher H₂O₂/DBT molar ratio can not improve the removal efficiency of DBT. In contrast, if H₂O₂/DBT molar ratio was further increased up to 6, the removal efficiency of DBT decreased considerably. For example, DBT could be almost completely removed when the molar ratios of H₂O₂/DBT (4:1 and 5:1) after reaction 2h, but the removal of DBT only reached 61.9% at the molar ratios of H₂O₂/DBT (6:1) under the same condition. Because the present oxidant was 30% H₂O₂ aqueous solution, the more addition of H₂O₂ induced that the larger amount of water was introduced into the reaction system, which affected significantly the reaction environment. As the reaction system was composed of three-phase, which was consisted of water, n-octane phase and catalyst. When the amount of H₂O₂ was increased, the mass transfer efficiency was decreased to some extent, which might lower the catalytic activity.^{23,24,40}

<Insert Fig. 6>

The recycling of the [C₁₆mim][PyW] was investigated under the reaction conditions of temperature 50 °C, model oil (S content 1000 ppm) 5 mL, molar ratio of H₂O₂/DBT/catalyst 200:50:1. As shown in Fig. 2S, the present catalyst could be reused at least ten times without decreasing the catalytic activity in the desulfurization of DBT. The amount of leaching W detected by ICP-AES was only about 5 ppm in the n-octane phase, which illustrated clearly that the present catalyst was highly leaching-resistant for the desulfurization reaction. After reaction, the product (DBTO₂)

was isolated and then characterized by ^1H NMR and FT-IR. As shown in Fig. 3S, the ^1H NMR of the recovered DBTO₂ is the same as that of standard DBTO₂.^{41,42} The specific infrared absorption of DBTO₂ at 1169 and 1289 cm^{-1} was seen and can be attributed to sulfone groups (Fig. 4S).

In order to identify further whether the leaching W species played a crucial role in oxidative desulfurization reaction of DBT, a fast hot filtration experiment was carried out under the reaction temperature. As shown in Fig 7, after reaction for 1 h, the catalyst was filtrated out, and residual n-octane phase continued on the reaction after adding fresh H₂O₂, no further DBT was converted to the corresponding product. This result proved that the trace of leaching W had no activity for desulfurization.

<Insert Fig. 7>

In the next step, the [C₁₆mim][PyW] and [CTA][PyW] catalysts were extended to catalyze epoxidation of *cis*-cyclooctene with 30% aqueous H₂O₂ as the oxidant under solvent-free condition at 60 °C (Scheme 3). As shown in Fig. 8, there was almost no significant difference of catalytic activity between [C₁₆mim][PyW] and [CTA][PyW]. After reacting 6 h, *cis*-cyclooctene could be converted to the corresponding epoxide with about 80% conversion and 100% of selectivity to epoxide. This result was quite different with that of the oxidative desulfurization reaction, in which the imidazolium-based catalyst had a higher catalytic activity. Combined with the previous characterization of ^1H NMR (Fig. 4), we can realize further that the interaction between ionic liquid-type catalyst and substrate was very important to the desulfurization reaction. The similar epoxidation activity was obtained since no basic S atom (compared with DBT) existed in *cis*-cyclooctene molecules and thus the interaction between *cis*-cyclooctene and the imidazolium of [C₁₆mim][PyW] was weak. The same anion and the similar hydrophobicity of [C₁₆mim][PyW] and [CTA][PyW] led to the almost same epoxidation activity under the same reaction conditions.

<Insert Scheme 3>

<Insert Fig. 8>

3.3 Proposed mechanism for the desulfurization reaction system

On the basis the experimental results and discussion above, the desulfurization process of DBT catalyzed by [C₁₆mim][PyW] was proposed in Scheme 4. First, the oxidant H₂O₂ could continuously provided active oxygen to the active peroxo species in the hydrophilic group of catalyst and DBT was absorbed to cation through a hydrogen bond interaction between imidazolium ring (H2 position) and S atom of DBT. Then, the active peroxo species was transferred to the substrate molecules. Thus a continuous oxidize of DBT to the corresponding product (DBTO₂) was observed. The polarity of sulfur compound was increased after oxidation. With increasing recycle runs, the sulfones were precipitated gradually and accumulated in the lower phase.

<Insert Scheme 4>

4 Conclusion

In summary, we had synthesized a new peroxotungsten anions-based ionic liquid catalyst for deep desulfurization of DBT in model oil using H₂O₂ as the oxidant successfully under solvent-free conditions. The sulfur removal of DBT can reach 99.0% over [C₁₆mim][PyW] catalyst under mild conditions. It was demonstrated that there was a hydrogen bond interaction between H2 position of imidazolium cation and S atom of DBT molecules, which played a crucial role in enhancing desulfurization efficiency. The present catalyst [C₁₆mim][PyW] can be recycled ten times with an unnoticeable decrease in activity. In summary, this process provides a novel and effective way to remove sulfur from model oil. For these advantages, this ionic liquid-type catalyst will be constructed for the promising, green catalytic system.

Acknowledgements

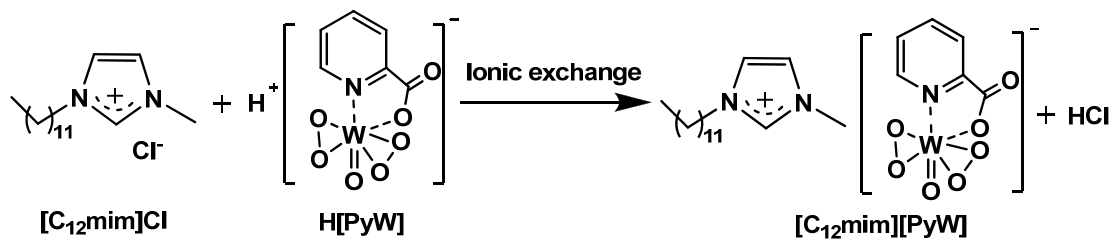
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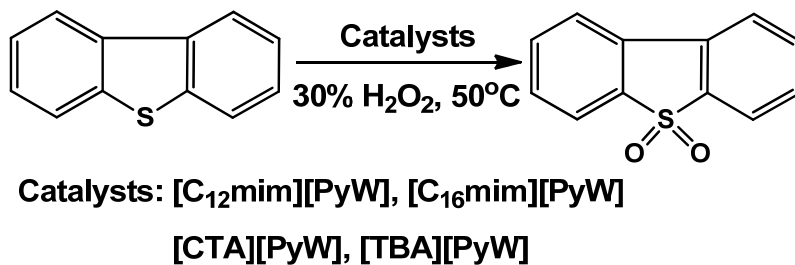
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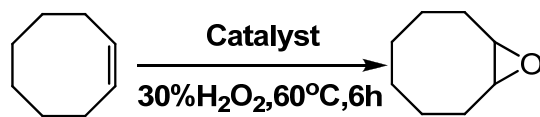
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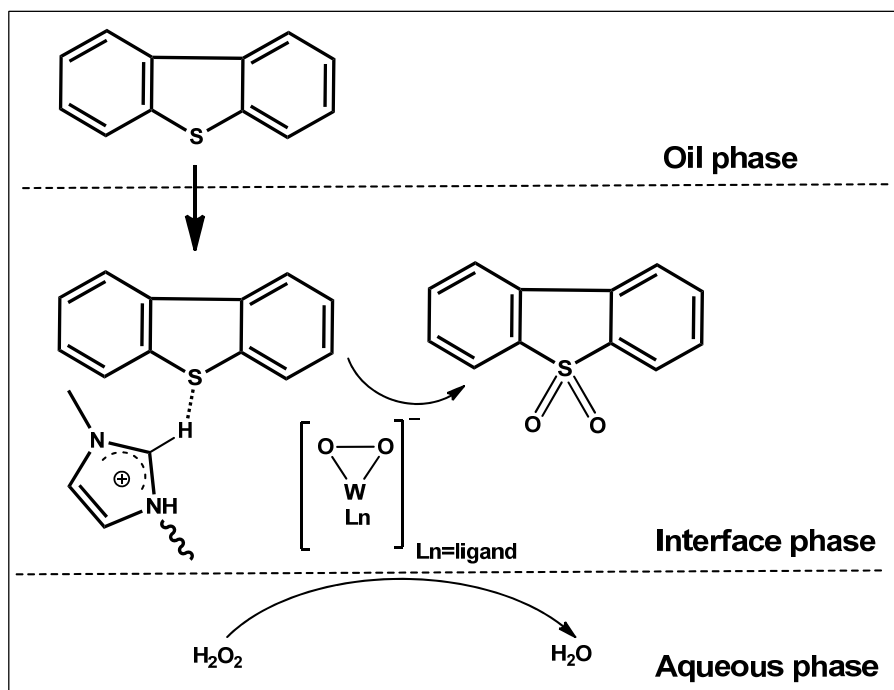
Scheme 1 The synthetic route of an ionic liquid catalyst.



Scheme 2 The oxidative desulfurization of DBT over different catalysts.



Scheme 3 Epoxidation of *cis*-cyclooctene



Scheme 4. Proposed reaction mechanism for the desulfurization of DBT.

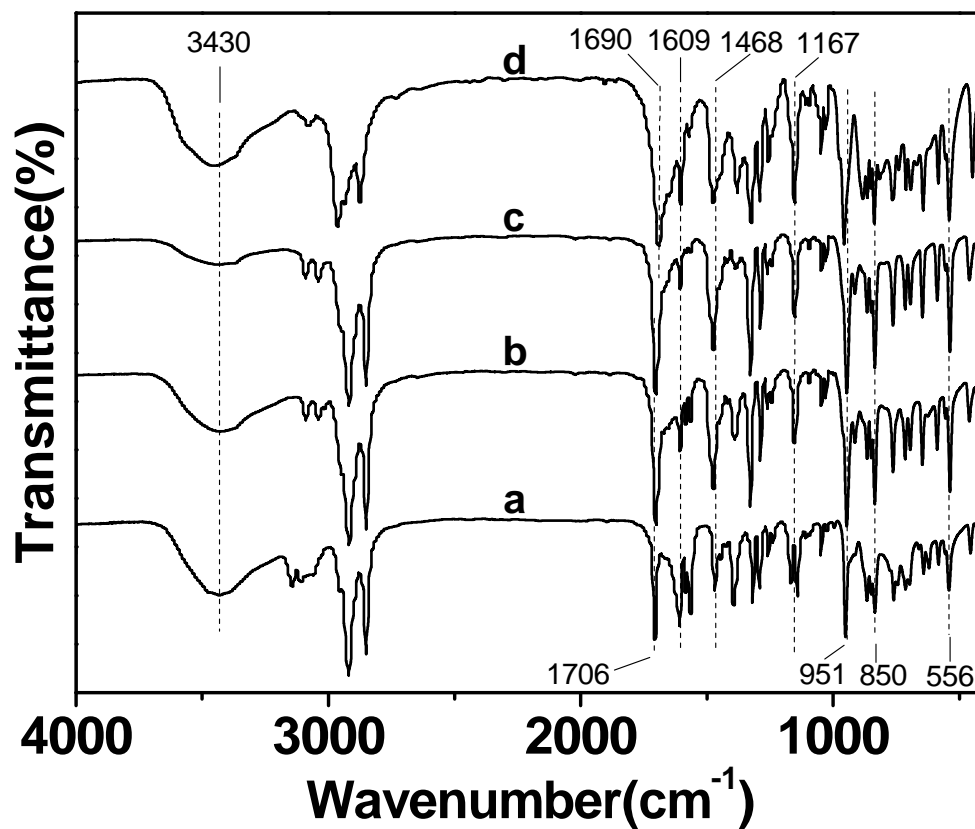


Fig. 1 FT-IR spectra of (a) [C₁₆mim][PyW]; (b) [C₁₂mim][PyW]; (c) [CTA][PyW]; (d) [TBA][PyW].

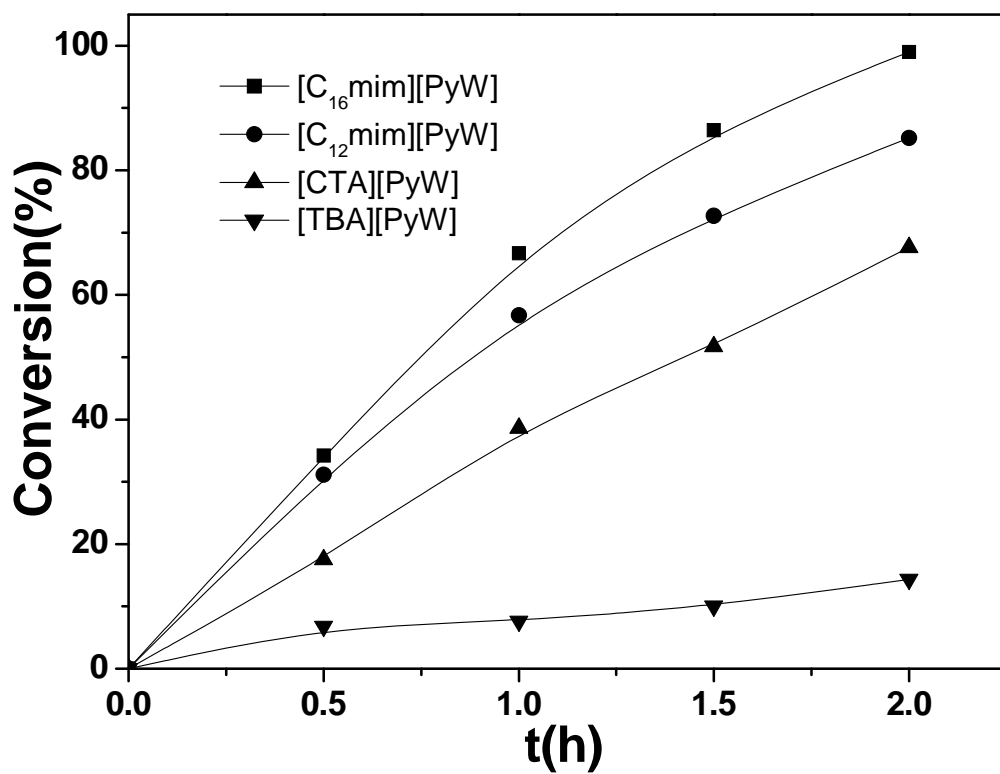


Fig. 2 Time profile of desulfurization of DBT catalyzed with different catalysts. Reaction condition: model oil = 5 mL (S-content 1000 ppm), T = 50 °C, n(DBT)/n(Catalyst)/n(H₂O₂) = 50:1:200 (molar ratio).

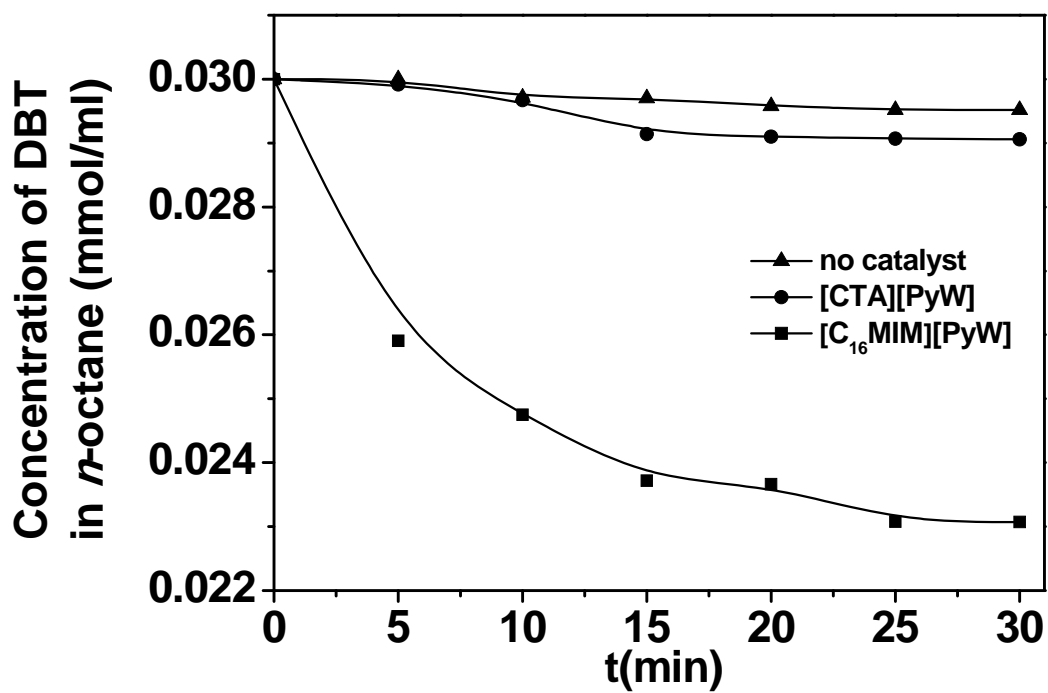


Fig. 3 The concentration changes of DBT in n-octane in the presence of different catalysts. Experimental condition: T = 50 °C, 5mL n-octane, 0.15 mmol DBT, n(DBT)/(Catalyst)=5:1 (molar ratio).

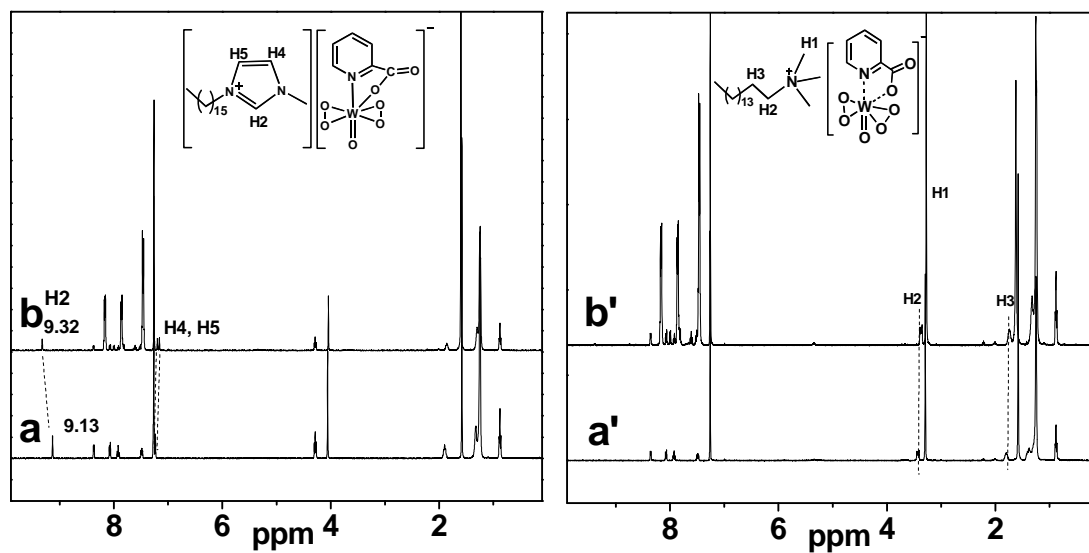


Fig. 4 ¹H NMR signal assignment of the protons of (a) [C₁₆mim][PyW], (b) [C₁₆mim][PyW] + DBT and (a') [CTA][PyW], (b') [CTA][PyW] + DBT.

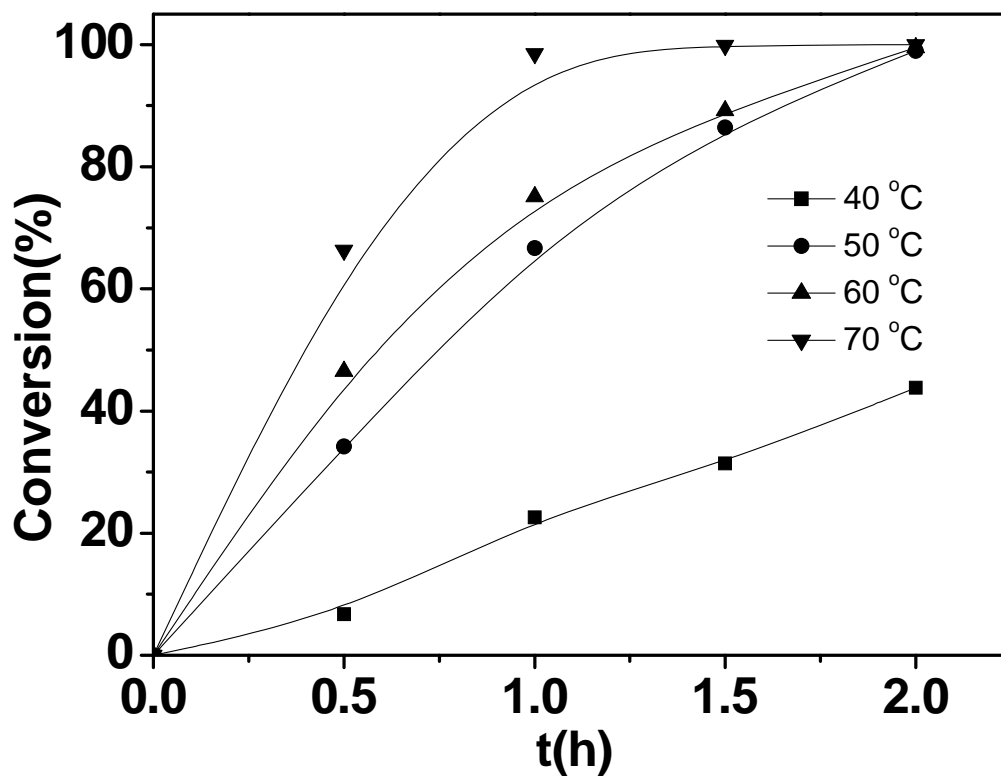


Fig. 5 Time profile of desulfurization of DBT with different temperature over catalyst $[C_{16}mim][PyW]$. Reaction condition: model oil = 5 mL (S-content 1000 ppm), $T = 50\text{ }^{\circ}C$, $n(DBT)/n(Catalyst)/n(H_2O_2) = 50:1:200$ (molar ratio).

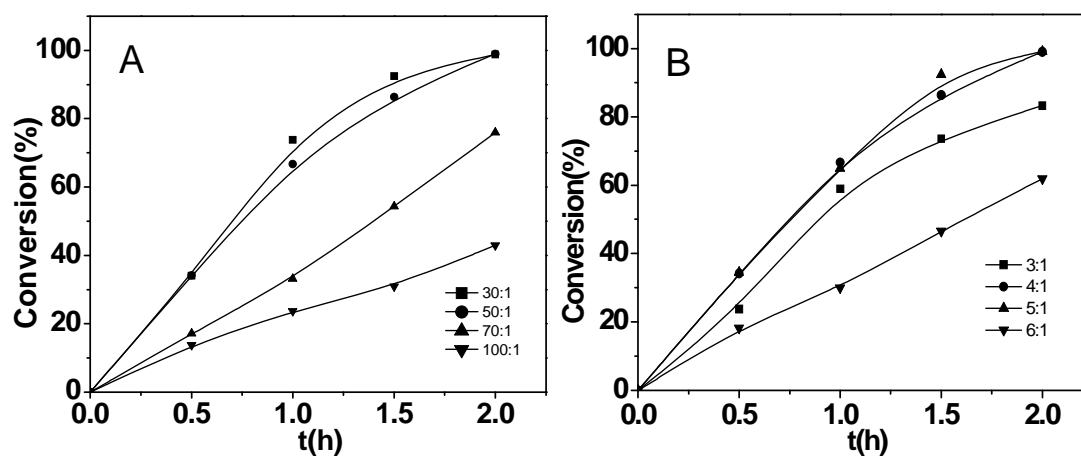


Fig. 6 A) Time profile of desulfurization of DBT with different DBT/Catalyst molar ratio. Reaction condition: model oil = 5 mL (S-content 1000 ppm), $T = 50\text{ }^{\circ}\text{C}$, $n(\text{DBT})/n(\text{H}_2\text{O}_2) = 1:4$ (molar ratio); B) Time profile of desulfurization of DBT with different $\text{H}_2\text{O}_2/\text{DBT}$ molar ratio. Reaction condition: model oil = 5 mL (S-content 1000 ppm), $T = 50\text{ }^{\circ}\text{C}$, $n(\text{DBT})/n(\text{Catalyst}) = 50:1$ (molar ratio).

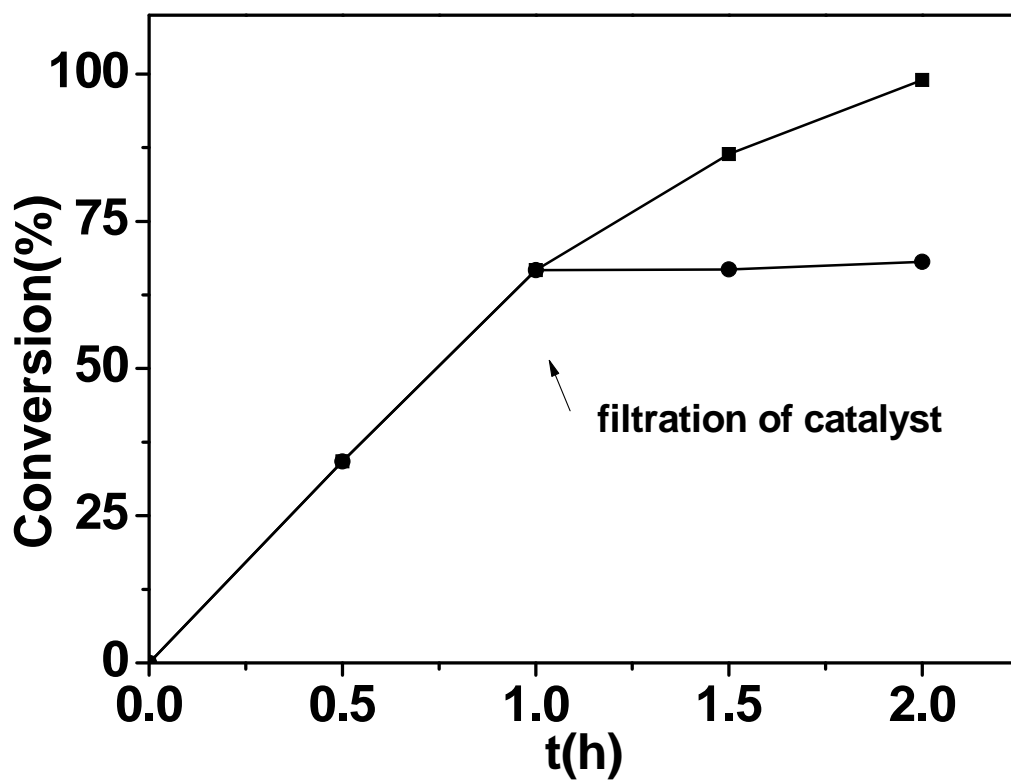


Fig. 7 Time profile of reaction and fast hot filtration test of DBT catalyzed with $[C_{16}mim][PyW]$. Reaction condition: model oil = 5 mL (S-content 1000 ppm), $T = 50$ °C, $n(DBT)/n(Catalyst)/n(H_2O_2) = 50:1:200$ (molar ratio).

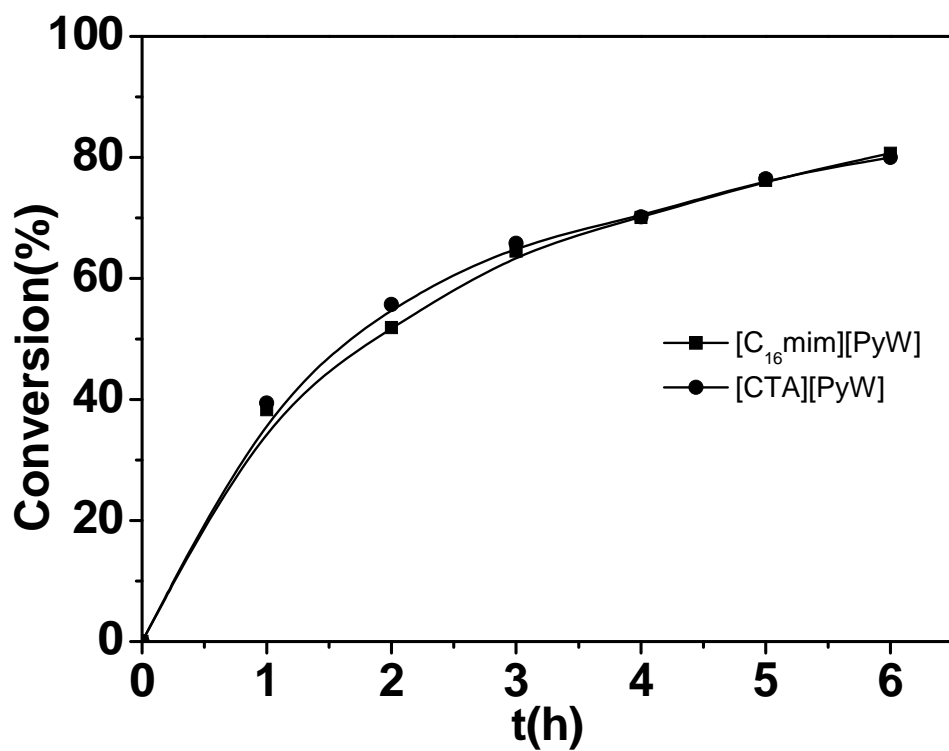


Fig. 8 Time profile of epoxidation of *cis*-cyclooctene catalyzed with different catalysts. Reaction condition: T = 60 °C, 0.02 mmol catalyst, 1 mmol *cis*-cyclooctene, 1.5 mmol 30% H_2O_2 .