



## Kinetics and mechanism for oxidative desulfurization of fuels catalyzed by peroxy-molybdenum amino acid complexes in water-immiscible ionic liquids

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### ABSTRACT

Three peroxy-molybdenum amino acid complexes (PMAACs) were synthesized and characterized. Their catalytic activities for oxidation of dibenzothiophene (DBT) in extraction and catalytic oxidative desulfurization system (ECODS) were evaluated using different ionic liquids. Comparing with simple catalyst  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  in ECODS, PMAACs were effective wide-ranging catalysts and exhibited high desulfurization efficiency not only in water-miscible IL [bmim]BF<sub>4</sub> but also in water-immiscible [bmim]PF<sub>6</sub>, [omim]BF<sub>4</sub> and [omim]PF<sub>6</sub>. Especially 4,6-dimethyldibenzothiophene (4,6-DMDBT), the most difficult refractory compound in HDS, could be completely removed under optimal conditions. The reaction mechanism and desulfurization differences between using  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  catalyst and PMAACs in water-miscible and water-immiscible ionic liquids have been investigated and explained by UV-vis. Kinetic parameters of the oxidation of DBT, BT and 4,6-DMDBT were studied.

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### 1. Introduction

Recently, a novel liquid–liquid extraction and catalytic oxidative desulfurization system (ECODS) has been reported by our groups, which may develop a simple, safe, reproducible and environment friendly post-treatment to the traditional hydrosulfurization (HDS) in order to achieve ultra-deep desulfurization [1]. Some refractory sulfur compounds, such as dibenzothiophene (DBT) and its derivatives 4,6-dimethyldibenzothiophene (4,6-DMDBT) were difficult to remove via HDS. Oxidative desulfurization (ODS) has attracted wide attention for its advantages, such as complementarity to HDS and mild reaction conditions. The reactivity of DBT and its derivatives in ODS is reverse to that in HDS, and these S-compounds can easily be removed [2–4].

Various oxidative desulfurization systems have been reported in the literature before, such as, organic acid/H<sub>2</sub>O<sub>2</sub> [5–7], heteropolyacid/H<sub>2</sub>O<sub>2</sub> [8–11], polyoxometalates/H<sub>2</sub>O<sub>2</sub> [12–16], aldehyde/O<sub>2</sub> [17,18], TS-1/H<sub>2</sub>O<sub>2</sub> [19], ionic liquids/H<sub>2</sub>O<sub>2</sub> [20–25]. ODS processes usually were achieved through two steps. Firstly, sulfur compounds were selectively oxidized to sulfoxides and sulfones, which would then be removed by appropriate extractants or adsorbents [26–28]. ECODS with ionic liquids could reduce the

steps and develop a green and effective one-pot desulfurization method. DBT and its derivatives were extracted into ionic liquids and were oxidized to their corresponding sulfoxides and sulfones, which are highly polar and more easily stay in IL.

In our previous work, commercially available catalysts such as  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{H}_2\text{MoO}_4$ ,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ,  $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$ ,  $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40} \cdot 7\text{H}_2\text{O}$  and  $\text{Na}_3\text{PMo}_{12}\text{O}_{40} \cdot 7\text{H}_2\text{O}$  have been studied and exhibited high desulfurization efficiency in ECODS using water-miscible [bmim]BF<sub>4</sub>. In the case of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , detailed experiments were plotted including optimizing conditions, investigating different ionic liquids and suggesting the process of ECODS and so on [1]. However, this kind of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  catalyst exhibited low desulfurization in water-immiscible ionic liquid. As a new desulfurization system, there is still much room for the development of more efficient and wide-ranging catalysts in different ionic liquids.

Pioneering works indicated that catalyst active center was virtually molybdenum peroxide species [29,30]. In this work, molybdenum peroxide species were caught using three amino acid ligands, and three peroxy-molybdenum amino acid complexes (PMAACs) were synthesized and characterized. Their catalytic activities in ECODS were evaluated using different kinds of ionic liquids. Comparing with  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  catalyst in ECODS, PMAACs were effective wide-ranging catalysts and exhibited high desulfurization efficiency not only in water-miscible IL [bmim]BF<sub>4</sub> but also in water-immiscible [bmim]PF<sub>6</sub>, [omim]BF<sub>4</sub> and [omim]PF<sub>6</sub>. The

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reaction mechanism and desulfurization difference between using  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  catalyst and PMAACs in water-miscible and water-immiscible ionic liquids have been investigated and explained.

## 2. Experimental

### 2.1. Materials

Benzothiophene (BT), DBT, 4,6-DMDBT were purchased from Sigma–Aldrich. Other materials were commercial reagent grade and obtained from Shanghai Sinopharm Chemical Co., Ltd.

### 2.2. Characterization of catalysts

Elementary (C, H and N) analyses were performed using CHN-O-Rapid (Heraeus Corporation). The content of Mo was measured by the gravimetry. The content of active oxygen was measured by the iodine titration. Thermogravimetry and differential scanning (TG/DSC) were done on STA-449C Jupiter (NETZSCH Corporation, Germany). Sample weighing about 10 mg was heated from 30 to 750 °C at a heating rate of 10 °C/min in a dynamic air atmosphere. FT-IR spectrum was performed on a Nicolet FT-IR spectrophotometer (Nexus 470, Thermo Electron Corporation) using KBr disks at room temperature. UV–vis spectra were recorded on UV-2450 spectrophotometer (Shimadzu Corporation, Japan).

### 2.3. Preparation of catalysts [31]

Preparation of  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_2\text{H}_5\text{NO}_2$ : 30.0 mmol  $\text{MoO}_3$  was dissolved in 30 wt.%  $\text{H}_2\text{O}_2$  (30.0 mL) by stirring at 40 °C for 5 h. Gradual addition of 30.0 mmol glycine acid to the above solution under stirring produced the clear yellow solution. The solution was left at 5 °C, and after about 24 h the bright yellow crystals were obtained. The solid was filtered off, washed with 95% ethanol and dried in vacuo at 50 °C.

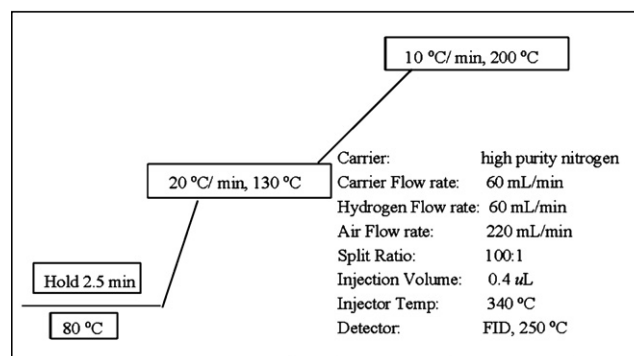
Preparation of  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_3\text{H}_7\text{NO}_2 \cdot \text{H}_2\text{O}$ : 30.0 mmol  $\text{MoO}_3$  was dissolved in 30 wt.%  $\text{H}_2\text{O}_2$  (30.0 mL) by stirring at 40 °C for 5 h. 30.0 mmol alanine dissolved in 20 mL deionized water was added gradually to the above solution under stirring and clear yellow solution was produced. A small portion of this solution was evaporated and the residue was left at 5 °C. After about 48 h, the yellow crystals were obtained. The solid was filtered off, washed with 95% ethanol and dried in vacuo at 50 °C.

Preparation of  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_5\text{H}_9\text{NO}_4 \cdot \text{H}_2\text{O}$ :  $\text{MoO}_3$  (30.0 mmol) was dissolved in 30 wt.%  $\text{H}_2\text{O}_2$  (40.0 mL) by stirring at 40 °C for 5 h. Gradual addition of 30.0 mmol glutamic acid to the above solution under stirring produced the clear yellow solution. The solution was left at 5 °C, and after about 24 h the bright yellow crystals were obtained. The solid was filtered off, washed with 95% ethanol and dried in vacuo at 50 °C.

### 2.4. Desulfurization experiments and analysis of sulfur content in simulated diesel

The extraction desulfurization experiments were carried out at 30 °C for 15 min. The extraction coupled with catalytic oxidative desulfurization experiments was carried out in a home-made 40 mL two-necked flask. The mixture, containing 5 mL of simulated diesel, 30 wt.%  $\text{H}_2\text{O}_2$ , 1 mL of ionic liquid and catalyst, was stirred vigorously.

After reaction was completed, the upper simulated diesel phase was withdrawn and analyzed by gas chromatography with *n*-tetradecane as internal standard, coupled with a flame ionization detector (GC-FID). A 15 m × 0.32 mm inner diameter × 1.0 μm film thickness SE-54 capillary column was used for separation. High purity nitrogen and hydrogen were used as carrier and fuel for FID,



Scheme 1. Chromatographic conditions for composition analysis.

respectively. Sample volume of 0.4 μL was injected without any solvent dilution. The temperature profile is given in Scheme 1.

## 3. Results and discussion

### 3.1. The composition of catalysts

The data of elemental analyses, the content of Mo and active oxygen of catalysts are listed in Table 1.

### 3.2. The TG/DSC of catalysts

TG/DSC of three catalysts under nitrogen is shown in Fig. 1. The results indicated that  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_2\text{H}_5\text{NO}_2$  excluded crystalline water because there was no mass loss under 100 °C, as shown in Fig. 1a.  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_2\text{H}_5\text{NO}_2$  decomposed with mass loss in the first step at 140.2 °C and the corresponding exothermic peak of DSC curve emerged, which indicated that peroxy species decomposed. Then, from 199.2 °C to 325.0 °C  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_2\text{H}_5\text{NO}_2$  went on decomposing, the mass loss of the second step attributed to the organic complex leaving. The final remainders were molybdenum oxide. To other catalysts (Fig. 1b and c), there was a mass loss of about 100 °C, which corresponded to the loss of water molecules weakly bound to catalysts. After 100 °C, TG/DSC curves showed a similar decomposition process as  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_2\text{H}_5\text{NO}_2$ .

### 3.3. The infrared spectra of catalysts

The IR spectra of complexes are shown in Table 2. There were four characteristic bands of  $\nu(\text{Mo}=\text{O})$ ,  $\nu(\text{O}-\text{O})$ ,  $\nu_{\text{sym}}[\text{Mo}(\text{O}_2)]$  and  $\nu_{\text{asym}}[\text{Mo}(\text{O}_2)]$ . As for  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_2\text{H}_5\text{NO}_2$ , strong band at 969  $\text{cm}^{-1}$  was assigned to  $\nu(\text{Mo}=\text{O})$  of terminal oxo group and near 878  $\text{cm}^{-1}$ , 860  $\text{cm}^{-1}$  were due to  $\nu(\text{O}-\text{O})$  of peroxy ligands. The bands at 654 and 579  $\text{cm}^{-1}$  were probably due to asymmetric and symmetric stretches of the  $\text{Mo}(\text{O}_2)$  unit. Similar results were obtained by the literature [31]. The general similarity of infrared spectra of  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_3\text{H}_7\text{NO}_2 \cdot \text{H}_2\text{O}$  and  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_5\text{H}_9\text{NO}_4 \cdot \text{H}_2\text{O}$  suggested a similar structure for all three anions in Table 2.

### 3.4. Investigation of the different desulfurization systems

DBT was chosen as a sulfur compound representative of the main refractory sulfur-containing compounds in fuel by HDS treatment. Peroxy-molybdenum amino acid complex  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_2\text{H}_5\text{NO}_2$  was used as a catalyst to investigate the removal of DBT in [Bmim]BF<sub>4</sub> and [Bmim]PF<sub>6</sub>. The conversion of DBT in simulated diesel was used to calculate the removal of sulfur. When [Bmim]BF<sub>4</sub> and [Bmim]PF<sub>6</sub> were used as extractants for DBT-containing simulated diesel at 30 °C, the S-removal only reached 13.6% and 11.1%. With the addition of  $\text{H}_2\text{O}_2$  in [Bmim]BF<sub>4</sub> and

**Table 1**  
Elementary analyses, gravimetry and the content of active oxygen of catalysts.

Entry	Catalyst	Data	C%	H%	N%	Mo%	O%
1	MoO(O <sub>2</sub> ) <sub>2</sub> ·C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	Exp.	8.96	2.40	4.94	34.90	11.88
		Calc.	9.57	2.01	5.58	35.66	11.90
2	MoO(O <sub>2</sub> ) <sub>2</sub> ·C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub> ·H <sub>2</sub> O	Exp.	12.29	2.98	5.42	34.28	11.58
		Calc.	12.73	3.20	4.95	33.90	11.31
3	MoO(O <sub>2</sub> ) <sub>2</sub> ·C <sub>5</sub> H <sub>9</sub> NO <sub>4</sub> ·H <sub>2</sub> O	Exp.	18.02	3.45	3.96	27.51	9.69
		Calc.	17.61	3.25	4.11	28.13	9.38

[Bmim]PF<sub>6</sub>, the S-removal of 31.5% and 39.2% was achieved after chemical oxidation, respectively. Both [Bmim]BF<sub>4</sub> and [Bmim]PF<sub>6</sub> were immiscible with simulated diesel. However, aqueous hydrogen peroxide could be dissolved in [Bmim]BF<sub>4</sub> and bi-phasic system

was formed, in which the oil phase was the upper layer and IL phase was the lower layer. To [Bmim]PF<sub>6</sub>, tri-phasic system was formed, in which the oil phase was the upper layer, aqueous hydrogen peroxide as oxidizing agent was in the middle and IL phase was the lowest layer.

In our previous work [1], we have reported that Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O as a catalyst revealed a deep removal of DBT from simulated diesel in water-miscible [Bmim]BF<sub>4</sub> (99.0%), however, this commercially available catalyst exhibited low removal of DBT in water-immiscible [Bmim]PF<sub>6</sub> (69.8%). In this work, removal of DBT increased to 99.2% in water-immiscible ionic liquid [Bmim]PF<sub>6</sub> using peroxo-molybdenum amino acid complex MoO(O<sub>2</sub>)<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> as a catalyst and remained 99.0% in water-miscible ionic liquid [Bmim]BF<sub>4</sub> (Table 3, Entry 4). The results indicated that PMAAC played a significant role in the ECODS, which exhibited high catalytic activity not only in the bi-phase reaction system, but also in the tri-phase reaction system. As for other PMAACs, the results indicated that high desulfurization efficiency was achieved in other water-immiscible ionic liquids.

The oxidative desulfurization system merely containing catalyst and H<sub>2</sub>O<sub>2</sub> led to 2.0–3.4% S-removal in the absence of IL, which could be attributed to the self-decomposition of most hydrogen peroxide under 70 °C in the presence of catalyst. According to experimental observation, large numbers of small oxygen bladders were observed by naked eyes and hydrogen peroxide decomposed completely in very short time in the presence of PMAACs. These results also demonstrated that ionic liquids not only served as extractant and reaction medium but also acted as stabilizing agent of hydrogen peroxide in reaction.

### 3.5. The mechanism and desulfurization difference of ECODS

In order to interpret the desulfurization difference between using Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O catalyst and PMAACs in water-miscible and water-immiscible ionic liquids, DBT was selected as a sulfur compound representative of those in fuel, and the process and mechanism of oxidative desulfurization in water-miscible [Bmim]BF<sub>4</sub> and water-immiscible [Bmim]PF<sub>6</sub> were investigated by UV–vis spectra. As shown in Fig. 2a, the UV–vis spectrum of [Bmim]BF<sub>4</sub> was the same as that of [Bmim]BF<sub>4</sub>/Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, but was different from the UV–vis spectrum of [Bmim]BF<sub>4</sub>/MoO(O<sub>2</sub>)<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>. Both [Bmim]BF<sub>4</sub> and [Bmim]BF<sub>4</sub>/Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O had no peak from 300 nm to 400 nm wavelength, which indicated that Na<sub>2</sub>MoO<sub>4</sub> did not dissolve in IL. However, the UV–vis spectrum of [Bmim]BF<sub>4</sub> mixed with MoO(O<sub>2</sub>)<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> had a peak at 348 nm wavelength (Mo=O) [31]. The results showed MoO(O<sub>2</sub>)<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> dissolved in IL and the peak of 348 nm was exhibited by the catalyst in IL. To the UV–vis spectra of [Bmim]PF<sub>6</sub>, [Bmim]PF<sub>6</sub>/Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O and [Bmim]PF<sub>6</sub>/MoO(O<sub>2</sub>)<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>, the same rule of the above results could be applied (Fig. 2b).

Though there were two (oil and IL phases) or more phases (oil, aqueous and IL phases) in all ECODS, the oxidation reaction virtually occurred in IL phase. In the case of [Bmim]BF<sub>4</sub>, substrate, catalysts (Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O or MoO(O<sub>2</sub>)<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>) and oxidant were all in IL phase during the reaction process. So this reaction was homogeneous-like and exhibited high sulfur removal

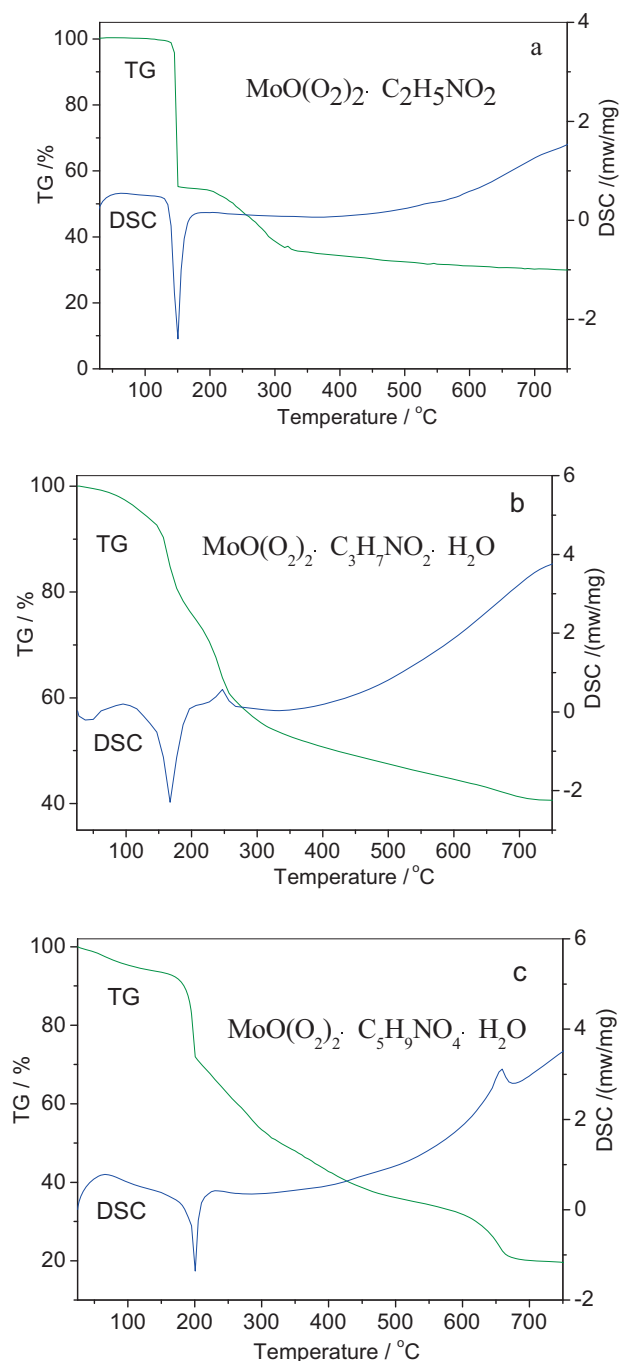
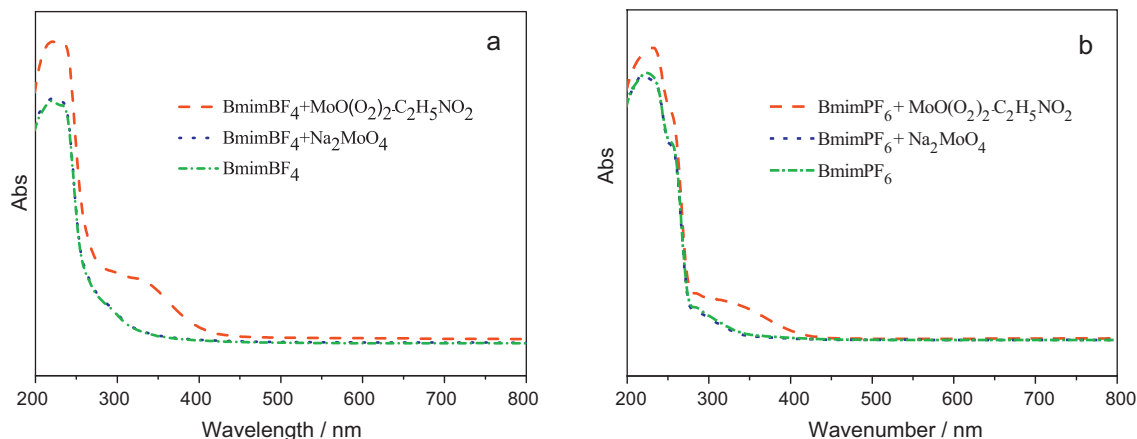


Fig. 1. TG–DSC of catalysts.

**Table 2**  
Data of IR spectra of catalysts.

Entry	Catalyst	IR (cm <sup>-1</sup> )			
		$\nu(\text{Mo}=\text{O})$	$\nu(\text{O}-\text{O})$	$\nu_{\text{sym}}[\text{Mo}(\text{O}_2)]$	$\nu_{\text{asym}}[\text{Mo}(\text{O}_2)]$
1	$\text{MoO}(\text{O}_2)_2 \cdot \text{C}_2\text{H}_5\text{NO}_2$	969	878, 860	579	654
2	$\text{MoO}(\text{O}_2)_2 \cdot \text{C}_3\text{H}_7\text{NO}_2 \cdot \text{H}_2\text{O}$	964	894, 852	558	611
3	$\text{MoO}(\text{O}_2)_2 \cdot \text{C}_5\text{H}_9\text{NO}_4 \cdot \text{H}_2\text{O}$	976	913, 866	558	628

**Fig. 2.** UV-vis spectra of [Bmim]BF<sub>4</sub> and [Bmim]PF<sub>6</sub> system.

(Scheme 2a). Ionic liquid not only served as an extractant and reaction medium but also acted as stabilizing agent of hydrogen peroxide in reaction.

However, [Bmim]PF<sub>6</sub> was immiscible with aqueous hydrogen peroxide, so Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O and the oxidant were partitioned with [Bmim]PF<sub>6</sub> and the reaction was heterogeneous-like (Scheme 2b). Ionic liquids only served as an extractant, which could not prevent H<sub>2</sub>O<sub>2</sub> from self-decomposing. The catalyst and H<sub>2</sub>O<sub>2</sub> touched directly and led to H<sub>2</sub>O<sub>2</sub> decomposing drastically side-reaction. So low catalytic activity of [Bmim]PF<sub>6</sub>/Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O was attributed to the low utilization of H<sub>2</sub>O<sub>2</sub>.

In the case of MoO(O<sub>2</sub>)<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> as a catalyst, it exhibited high desulfurization efficiency in [Bmim]PF<sub>6</sub> because the catalyst could dissolve in IL but aqueous hydrogen peroxide could not. The catalyst and H<sub>2</sub>O<sub>2</sub> were partitioned, and H<sub>2</sub>O<sub>2</sub> decomposition slowed down. The oxidation of DBT virtually occurred with molybdenum peroxide species [29,30]. MoO(O<sub>2</sub>)<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> catalyst could transfer active oxygen of H<sub>2</sub>O<sub>2</sub> to IL phase. DBT was extracted into IL and MoO(O<sub>2</sub>)<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> was also in IL phase. So the reaction was homogeneous-like (Scheme 2c), which led to high catalytic reactivity. Ionic liquid also served as an extractant and reaction medium.

**Table 3**  
Different desulfurization systems of model diesel oil.<sup>a</sup>

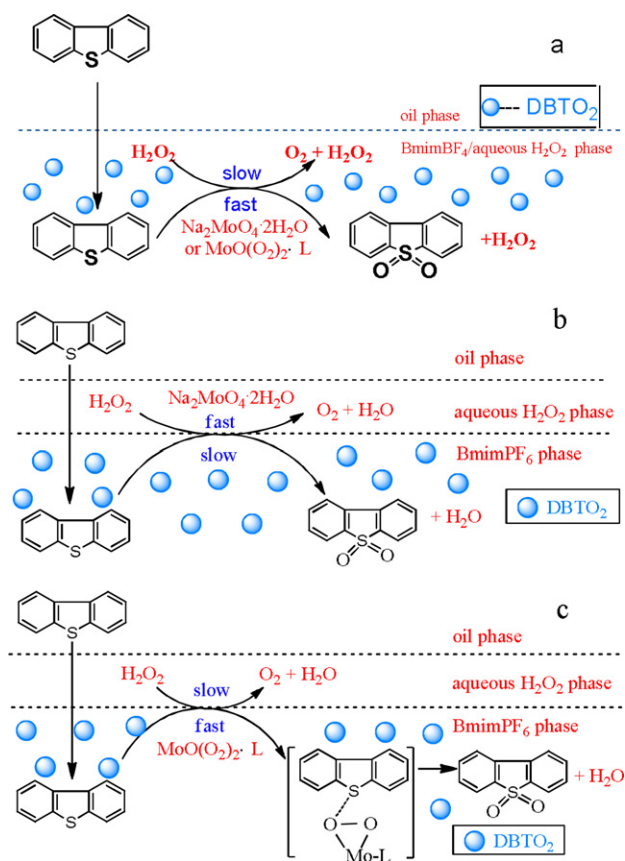
Entry	Desulfurization system	Sulfur removal (%)		
		[Bmim]BF <sub>4</sub>	[Bmim]PF <sub>6</sub>	Without IL
1 <sup>b</sup>	IL	13.6	11.1	–
2	IL/H <sub>2</sub> O <sub>2</sub>	31.5	39.2	–
3 <sup>c</sup>	IL/Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O/H <sub>2</sub> O <sub>2</sub>	99.0	69.8	4.1
4	IL/Catalyst I/H <sub>2</sub> O <sub>2</sub>	99.0	99.2	2.0
5	IL/Catalyst II/H <sub>2</sub> O <sub>2</sub>	98.8	99.1	2.8
6	IL/Catalyst III/H <sub>2</sub> O <sub>2</sub>	98.9	99.2	3.4

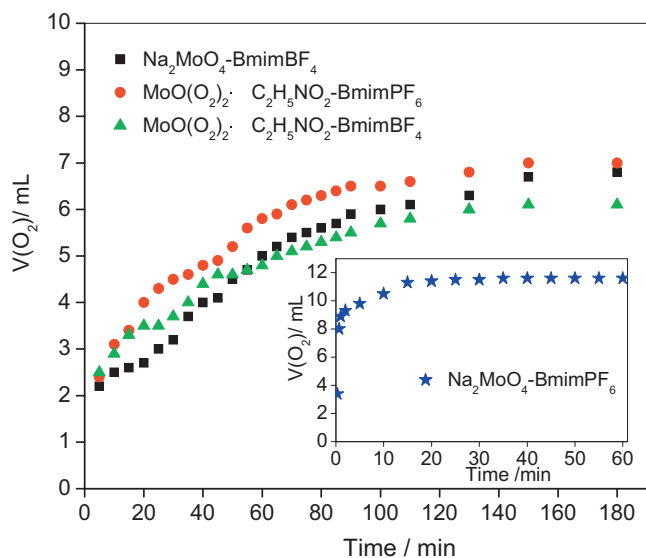
<sup>a</sup> Reaction conditions: Catalyst I = MoO(O<sub>2</sub>)<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>, Catalyst II = MoO(O<sub>2</sub>)<sub>2</sub>·C<sub>3</sub>H<sub>7</sub>NO<sub>2</sub>·H<sub>2</sub>O, Catalyst III = MoO(O<sub>2</sub>)<sub>2</sub>·C<sub>5</sub>H<sub>9</sub>NO<sub>4</sub>·H<sub>2</sub>O,  $t = 3$  h,  $T = 70$  °C,  $V(\text{simulated diesel}) = 5$  mL,  $V(\text{IL}) = 1$  mL,  $(n(\text{DBT})/n(\text{Catalyst})) = 10$ ,  $(n(\text{H}_2\text{O}_2)/n(\text{DBT})) = 4$ .

<sup>b</sup> The mixture was stirred at 30 °C for 15 min.

<sup>c</sup> Results from previous work [1].

In order to validate these results, the experiments of decomposition of hydrogen peroxide were plotted. Only catalyst, hydrogen peroxide and ionic liquid were mixed under the simulated desulfurization reaction condition to study oxygen evolution. The data

**Scheme 2.** ECODS mechanism using different catalysts in [Bmim]BF<sub>4</sub> and [Bmim]PF<sub>6</sub>.



**Fig. 3.** Investigating the decomposition of hydrogen peroxide. Reaction conditions:  $T = 70^\circ\text{C}$ ,  $V(\text{IL}) = 1\text{ mL}$ ,  $n(\text{Catalyst}) = 0.156\text{ mmol}$ ,  $V(\text{H}_2\text{O}_2) = 100\ \mu\text{L}$ .

in Fig. 3 showed that hydrogen peroxide decomposed drastically in  $[\text{Bmim}]\text{PF}_6/\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}/\text{H}_2\text{O}_2$  tri-phase reaction system and 8.9 mL and 11.3 mL oxygen were collected in 1 min and 15 min, respectively. After 1 h, hydrogen peroxide could not be detected with potassium iodide starch test paper in  $[\text{Bmim}]\text{PF}_6$ . The results indicated that a majority of hydrogen peroxide could not take part in the oxidation, which led to lower sulfur removal (69.8%). In the case of other reaction systems, hydrogen peroxide self-decomposition became calm. The results showed that these reaction systems became moderate and catalyst could make full use of hydrogen peroxide. In a word, PMAAC played an important role in extraction and catalytic oxidative desulfurization, which exhibited high desulfurization not only in water-miscible but also in water-immiscible IL.

### 3.6. Influence of removal of DBT in simulated diesel

Removal of DBT with  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_2\text{H}_5\text{NO}_2$  as a catalyst in water-immiscible ionic liquid ( $[\text{Bmim}]\text{PF}_6$ ) in various conditions was studied and listed in Table 4. The results indicated that the higher the reaction temperature was and the longer the time was, the greater the removal of DBT was. DBT removal was 48.0% at  $30^\circ\text{C}$  and increased to 99.2% at  $70^\circ\text{C}$ . DBT removal can reach 91.9% in 1 h and can be increased to 98.4% extending 2 h. After 3 h, DBT was nearly completely removed under the temperature of  $70^\circ\text{C}$ , with a removal of 99.2%. The data also showed that the amount of catalysts made the positive contribution to the oxidation reactivity. When the ratio of  $n(\text{DBT})/n(\text{Catalyst})$  was 50 and 20, the catalytic

**Table 4**  
Investigation of different desulfurization conditions.

Entry	Temperature ( $^\circ\text{C}$ )	Time (h)	$n(\text{DBT})/n(\text{Catalyst})^a$	$n(\text{H}_2\text{O}_2)/n(\text{DBT})^a$	IL (mL)	S-removal (%)
1	30	3	10	4	1	48.0
2	50	3	10	4	1	88.0
3	70	3	10	4	1	99.2
4	70	1	10	4	1	91.9
5	70	2	10	4	1	98.4
6	70	3	50	4	1	55.8
7	70	3	20	4	1	82.5
8	70	3	10	2	1	72.6
9	70	3	10	3	1	91.2
10	70	3	10	4	2	100

<sup>a</sup> Molar ratio.

**Table 5**  
Influence of the nature of the IL on the removal of DBT.

IL	S-removal (%)	
	$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	$\text{MoO}(\text{O}_2)_2 \cdot \text{C}_2\text{H}_5\text{NO}_2$
$[\text{Bmim}]\text{BF}_4$	99.0	99.0
$[\text{Omim}]\text{BF}_4$	67.6	98.7
$[\text{Bmim}]\text{PF}_6$	69.8	99.2
$[\text{Omim}]\text{PF}_6$	77.8	99.3

Reaction conditions:  $V(\text{simulated diesel}) = 5\text{ mL}$ ,  $(n(\text{DBT})/n(\text{Catalyst})) = 10$ ,  $(n(\text{H}_2\text{O}_2)/n(\text{DBT})) = 4$ ,  $T = 70^\circ\text{C}$ ,  $t = 3\text{ h}$ ,  $V(\text{IL}) = 1\text{ mL}$ .

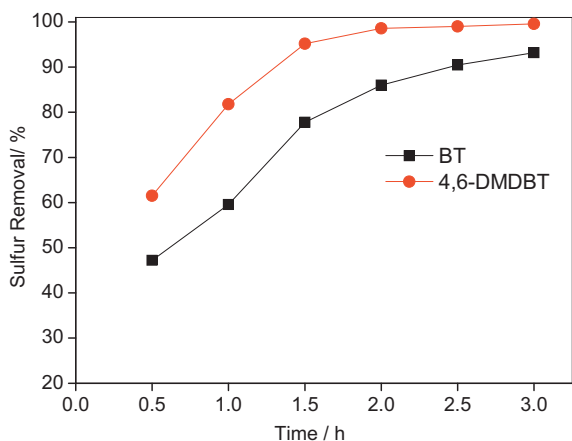
active centers were not enough to catalyze the reaction and the removal of DBT was only 55.8% and 82.5%, respectively. When the amount was increased ( $n(\text{DBT})/n(\text{Catalyst}) = 10$ ), the sulfur removal can get to 99.2%. The amount of IL was a vital parameter to influence the desulfurization efficiency. Without IL, the sulfur removal was nearly equal to zero. With 1 mL and 2 mL ILs, the sulfur removal reached 99.2% and 100.0%, respectively. These results indicated that the larger amount of IL led to the higher desulfurization. The added amount of  $\text{H}_2\text{O}_2$  and the catalyst had a great influence on the reaction. When the ratio of  $n(\text{H}_2\text{O}_2)/n(\text{S})$  was up from 2.0 to 4.0, the sulfur removal increased sharply from 72.6% to 99.2%. Because there were competing reactions between the DBT oxidation by  $\text{H}_2\text{O}_2$  and the self-decomposition of  $\text{H}_2\text{O}_2$ , and twice stoichiometric amount of  $\text{H}_2\text{O}_2$  could get high sulfur removal, which could be testified in mechanism section.

### 3.7. Investigation of desulfurization in different ionic liquids

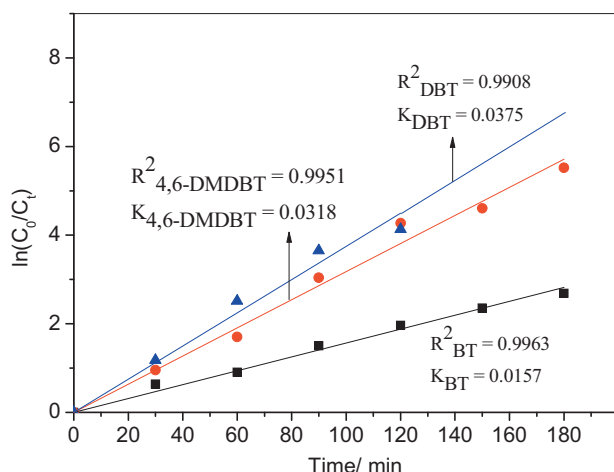
Compared with the desulfurization effect of simple catalyst  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_2\text{H}_5\text{NO}_2$  in water-miscible and water-immiscible ionic liquids, the results (Table 5) indicated that the simple catalyst exhibited high sulfur removal in water-miscible ionic liquid and low sulfur removal in water-immiscible ionic liquids. However, PMAACs showed high sulfur removal not only in water-miscible ionic liquid but also in water-immiscible ionic liquids. ECODS with  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  as a catalyst only led to 67.6%, 69.8% and 77.8% sulfur removal in  $[\text{Omim}]\text{BF}_4$ ,  $[\text{Bmim}]\text{PF}_6$ , and  $[\text{Omim}]\text{PF}_6$ . As for the  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_2\text{H}_5\text{NO}_2$  catalyst, there was an obvious increase of sulfur removal in three ionic liquids, reaching 98.7%, 99.2% and 99.3%, respectively. The results indicated PMAACs were effective and wide-ranging catalysts in different ionic liquids.

### 3.8. ECODS of different sulfur compounds in simulated diesel

4,6-DMDBT is very difficult to remove in HDS due to stereo hindrance. In our previous work [1], we have reported that  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  as a catalyst in ECODS revealed 61.0% and 89.5% desulfurization in 8 h to remove BT and 4,6-DMDBT, respectively. The results indicated that the activity of simple Mo-species was not high. In this paper,  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_2\text{H}_5\text{NO}_2$  as a catalyst exhibited



**Fig. 4.** ECODS of different sulfur substrates in oil. Reaction conditions:  $V(\text{simulated diesel}) = 5 \text{ mL}$ ,  $m(\text{Catalyst}) = 0.04 \text{ g}$ ,  $V(\text{H}_2\text{O}_2) = 64 \mu\text{L}$ ,  $T = 70^\circ\text{C}$ ,  $t = 3 \text{ h}$ ,  $V(\text{IL}) = 1 \text{ mL}$ .



**Fig. 5.** Pseudo-first-order kinetics for oxidation of different substrates.

high activity and effective wide-ranging to different sulfur compounds such as DBT, BT and 4,6-DMDBT. The results in Fig. 4 showed that in ECODS, to BT, the sulfur content could be lowered from 250 ppm to 16.9 ppm while to 4,6-DMDBT, the sulfur content can be lowered from 250 ppm to 1 ppm under optimizing conditions. Especially 4,6-DMDBT, the most difficult refractory compound in HDS, could be completely removed in 3 h in ECODS, which contains  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_2\text{H}_5\text{NO}_2$ .

### 3.9. Kinetics study of sulfur compound catalytic oxidation

Experiments to obtain kinetic parameters of the oxidation of sulfur compounds were performed using  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_2\text{H}_5\text{NO}_2$  as a catalyst in BmimPF<sub>6</sub>. Reaction kinetics were great important parameters in ECODS. The rate constant for the apparent consumption of S-compound was obtained from the pseudo-first-order equation.

$$-\frac{dC_t}{dt} = kC_t \quad (1)$$

$$\ln \frac{C_0}{C_t} = kt \quad (2)$$

where  $C_0$  and  $C_t$  were the sulfur concentrations at time zero and time  $t$  (min) and  $k$  was the first-order rate constant ( $\text{min}^{-1}$ ). The plot of  $\ln(C_0/C_t)$  against  $t$ , a straight line with slope  $k$  was obtained (Fig. 5). Half-lives were calculated by  $t_{1/2} = \ln 2/k$ , which was derived

from Eq. (2) by replacing  $C_t$  with  $C_0/2$ . The apparent rate constants of DBT, BT and 4,6-DMDBT were  $0.0375 \text{ min}^{-1}$ ,  $0.0157 \text{ min}^{-1}$ ,  $0.0318 \text{ min}^{-1}$  and the half-lives were 18.48 min, 44.14 min and 21.79 min, respectively.

## 4. Conclusion

Three peroxy-molybdenum amino acid complexes  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_2\text{H}_5\text{NO}_2$ ,  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_3\text{H}_7\text{NO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{MoO}(\text{O}_2)_2 \cdot \text{C}_5\text{H}_9\text{NO}_4 \cdot \text{H}_2\text{O}$  were synthesized and characterized by elementary (C, H and N) analyses, TG/DSC and FT-IR which were effective wide-ranging catalysts in the liquid-liquid extraction and catalytic oxidative desulfurization system using different ionic liquids. Under the optimal reaction conditions, the removal of DBT, BT and 4,6-DMDBT reached 99.2%, 93.2% and 99.6%, respectively. Kinetic parameters of the oxidation of sulfur compounds were studied. The apparent rate constants of DBT, BT and 4,6-DMDBT were  $0.0375 \text{ min}^{-1}$ ,  $0.0157 \text{ min}^{-1}$ ,  $0.0318 \text{ min}^{-1}$  and the half-lives were 18.48 min, 44.14 min and 21.79 min, respectively. The reaction mechanism and difference of desulfurization efficiency using simple molybdate catalysts and peroxy-molybdenum amino acid complexes in water-miscible and water-immiscible ionic liquids have been investigated and explained in detail by UV-vis.

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## References

- [1] W.S. Zhu, H.M. Li, X. Jiang, Y.S. Yan, J.D. Lu, L.N. He, J.X. Xia, Green Chem. 10 (2008) 641–646.
- [2] D.S. Zhao, J.L. Wang, E.P. Zhou, Green Chem. 9 (2007) 1219–1222.
- [3] J. Gao, S. Wang, Z. Jiang, H. Lu, Y. Yang, F. Jing, C. Li, J. Mol. Catal. A: Chem. 258 (2006) 261–266.
- [4] J.M. Campos-Martin, M.C. Capel-Sanchez, J.L.G. Fierro, Green Chem. 6 (2004) 557–562.
- [5] S. Otsuki, T. Nonaka, N. Takashima, W.H. Qian, A. Ishihara, T. Imai, T. Kbae, Energy Fuels 14 (2000) 1232–1239.
- [6] G.X. Yu, S.X. Lu, H. Chen, Z.N. Zhu, Energy Fuels 19 (2005) 447–452.
- [7] M. Te, C. Fairbridge, Z. Ring, Appl. Catal. A: Gen. 219 (2001) 267–280.
- [8] F.M. Collins, A.R. Lucy, C. Sharp, J. Mol. Catal. A: Chem. 117 (1997) 397–403.
- [9] K. Yazu, Y. Yamamoto, T. Furuya, K. Miki, K. Ukegawa, Energy Fuels 15 (2001) 1535–1546.
- [10] L.N. Yang, J. Li, X.D. Yuan, J. Shen, Y.T. Qi, J. Mol. Catal. A: Chem. 262 (2007) 114–118.
- [11] X.M. Yan, P. Mei, J.H. Lei, Y.Z. Mi, L. Xiong, L.P. Guo, J. Mol. Catal. A: Chem. 304 (2009) 52–57.
- [12] H.Y. Lü, J.B. Gao, Z.X. Jiang, F. Jing, Y.X. Yang, G. Wang, C. Li, J. Catal. 239 (2006) 369–375.
- [13] C. Komintarachat, W. Trakarnpruk, Ind. Eng. Chem. Res. 45 (2006) 1853–1856.
- [14] D. Huang, Z. Zhai, Y.C. Lu, L.M. Yang, G.S. Luo, Ind. Eng. Chem. Res. 46 (2007) 1447–1451.
- [15] F. Al-Shahrani, T.C. Xiao, S.A. Llewellyn, S.B.Z. Jiang, H.H. Shi, G. Martinie, M.L.H. Green, Appl. Catal. B: Environ. 73 (2007) 311–316.
- [16] X. Jiang, H.M. Li, W.S. Zhu, L.N. He, H.M. Shu, J.D. Lu, Fuel 88 (2009) 431–436.
- [17] S. Murata, K. Murata, K. Kidena, M. Nomura, Energy Fuels 18 (2004) 116–121.
- [18] T.V. Rao, B. Sain, S. Kafola, B.R. Nautiyal, Y.K. Sharma, S.M. Nanoti, M.O. Garg, Energy Fuels 21 (2007) 3420–3424.
- [19] L. Kong, G. Li, X. Wang, B. Wu, Energy Fuels 20 (2006) 896–902.
- [20] W.H. Lo, H.Y. Yang, G.T. Wei, Green Chem. 5 (2003) 639–642.
- [21] W.S. Zhu, H.M. Li, X. Jiang, Y.S. Yan, J.D. Lu, J.X. Xia, Energy Fuels 21 (2007) 2514–2516.
- [22] L. Lu, S.F. Cheng, J.B. Gao, G.H. Gao, M.Y. He, Energy Fuels 21 (2007) 383–384.

- [23] F.T. Li, R.H. Liu, J.H. Wen, D.S. Zhao, Z.M. Sun, Y. Liu, *Green Chem.* 11 (2009) 883–888.
- [24] H.M. Li, L.N. He, J.D. Lu, W.S. Zhu, X. Jiang, Y. Wang, Y.S. Yan, *Energy Fuels* 23 (2009) 1354–1357.
- [25] H. Olivier-Bourbigou, L. Magna, D. Morvan, *Appl. Catal. A: Gen.* 373 (2010) 1–56.
- [26] Y. Shiraishi, T. Hirai, *Energy Fuels* 18 (2004) 37–40.
- [27] X.L. Ma, A.N. Zhou, C.S. Song, *Catal. Today* 123 (2007) 276–284.
- [28] A. Ishihara, D.H. Wang, F. Dumeignil, H. Amano, E.W. Qian, T. Kabe, *Appl. Catal. A: Gen.* 279 (2005) 279–287.
- [29] Y. Usui, K. Sato, *Green Chem.* 5 (2003) 373–375.
- [30] W.S. Zhu, H.M. Li, X.Y. He, Q. Zhang, H.M. Shu, Y.S. Yan, *Catal. Commun.* 9 (2008) 551–555.
- [31] D. Cirila, V. Nikola, A.J. Bradley, L.R. Myunghi, S. Ekk, *Inorg. Chem.* 36 (1997) 1798–1805.