



Oxidative desulfurization of fuel catalyzed by metal-based surfactant-type ionic liquids

Wenshuai Zhu^{a,b}, Guopeng Zhu^b, Huaming Li^{b,*}, Yanhong Chao^b, Yonghui Chang^a, Guangying Chen^a, Changri Han^{a,*}

^a College of Chemistry and Chemical Engineering, Hainan Normal University, Haikou 571158, PR China

^b College of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, PR China

ARTICLE INFO

Article history:

Received 9 February 2011

Received in revised form 2 July 2011

Accepted 5 July 2011

Available online 12 July 2011

Keywords:

Metal-based surfactant-type ionic liquid

Catalytic oxidation

Desulfurization

Hydrogen peroxide

Kinetics

ABSTRACT

Metal-based surfactant-type ionic liquids (MSILs) methyltri-*n*-octylammonium peroxomolybdate $[(\text{CH}_3)\text{N}(\text{n-C}_8\text{H}_{17})_3]_2\text{Mo}_2\text{O}_{11}$ and peroxotungstate $[(\text{CH}_3)\text{N}(\text{n-C}_8\text{H}_{17})_3]_2\text{W}_2\text{O}_{11}$ were synthesized and characterized, which have been extended to new families and generations of functionalized ILs. Here the MSILs were applied in removal of sulfur-containing compounds with H_2O_2 and possessed of the character of reaction-induced self-separation catalysis. The effects of $\text{H}_2\text{O}_2/\text{DBT}$ (molar ratio), oil/MSIL (mass ratio) and the agitation rate were studied to estimate the optimal conditions for the desulfurization system catalyzed by $[(\text{CH}_3)\text{N}(\text{n-C}_8\text{H}_{17})_3]_2\text{Mo}_2\text{O}_{11}$. The quaternary ammonium cation could transfer the catalytic active species to the aromatic sulfur compounds under the reaction conditions and higher oxidative reaction rate was achieved. Kinetic experiments revealed that the oxidative desulfurization reaction was in accordance with pseudo-first-order kinetics and the reaction rate constant and half-life were calculated. Furthermore, the oxidation reactivity of different substrates was in the following order: $\text{DBT} > 4,6\text{-DMDBT} > \text{BT}$. The MSIL $[(\text{CH}_3)\text{N}(\text{n-C}_8\text{H}_{17})_3]_2\text{Mo}_2\text{O}_{11}$ could be recycled for 10-times with a slight decrease in activity. $[(\text{CH}_3)\text{N}(\text{n-C}_8\text{H}_{17})_3]_2\text{Mo}_2\text{O}_{11}$ was also an efficient catalyst to remove the sulfur-containing compound in different solvents. Multiple reactions of oxidation desulfurization process were feasible and effective for prehydrodtreated gasoline.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Sulfur-containing compounds are undesirable in gasoline and diesel fuels because of the emission of SO_x gases leading to air pollution. In order to protect the human health and reduce the environmental hazards, environmental regulations that tend to limit the sulfur levels to very lower ones have already been introduced in many countries during the last few decades [1]. The specifications present a new and challenging task for the petroleum refining industry.

Much attention has been paid to low level sulfur approaching requirements for the deep desulfurization technologies currently. Hydrodesulfurization (HDS) can remove aliphatic and acyclic sulfur compounds quite efficiently when adopted at an industrial scale. However, conventional HDS has difficulty in reducing refractory sulfur-containing compounds such as dibenzothiophene (DBT) and its derivatives, including 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) since these compounds have a steric hindrance and their reactivity

with HDS catalysts are low [2–4]. Consequently, the development of non-HDS-type process is highly desirable worldwide, such as extraction [5–7], adsorption [8], oxidation [9–17], as well as bioprocess [18]. So is the progress of the combination of these approaches, such as ultrasound-assisted oxidation [19], solvent extraction and oxidation [20–22], photocatalytic oxidation [23] and microwave catalytic desulfurization [24]. Among these methods, oxidation desulfurization (ODS) has attracted more attention owing to its advantages such as mild reaction conditions ($<100^\circ\text{C}$ and atmospheric pressure) which present a promising post-treatment strategy to the conventional HDS [9–17,19–23]. In ODS process, sulfur compounds are oxidized to their corresponding sulfoxides and sulfones, which present slightly higher polar compounds than hydrocarbon molecules. The refractory DBT and its derivatives then can be oxidized more easily in the presence of various catalysts during desulfurization process. Moreover, these oxidized products can be removed by extraction with organic extractants or room temperature ionic liquids (RTILs) [25–28].

RTILs have received a great deal of attention and have been proven to be valuable and useful in a multitude of different applications owing to their unique characteristics, such as non-volatility, non-flammability, and high thermal stability [29,30]. Furthermore,

* Corresponding authors. Tel.: +86 0511 88791800; fax: +86 0511 88791708.
E-mail addresses: lihm@ujs.edu.cn (H. Li), hchr116@hainnu.edu.cn (C. Han).

RTILs have been described as ‘designer solvents’ since the introduction of structural functionalities on cations or anions. Their properties can be tuned by careful selection of ionic species so as to deliver different chemical and physical functionalities in the same compounds. Recently these functionalized ILs have been synthesized for specific purposes such as catalysis [31], organic synthesis [32,33] and separation of specific materials [34]. However, most of them have been emphasized on cationic substitutions with regard to the structural features, especially the employment of functional groups into imidazolium cations [35,36], while few studies emphasize on the design of anionic counterion. What’s more, these anion-functionalized ILs, by definition, can present the unique property or multi-functions as the cation-functionalized ILs do and open up the development of novel prosperities of ILs as well.

The transition metal peroxo compounds have attracted much attention for their application in catalytic studies [37–42]. Among them, peroxomolybdates or peroxotungstates have been proven as the most efficient catalysts, with hydrogen peroxide (H_2O_2) as an oxidant, in oxidation of allylic alcohols and olefins [43–45]. Furthermore, recently the characteristics of so-called reaction-controlled phase-transfer catalysts based on a combination of quaternary ammonium cations with active peroxo anions of molybdate or tungstate have been paid much attention to. For example, $[PMo_4O_{24}]^{3-}$ immobilized on the quaternary-ammonium poly (phthalazinone ether sulfone ketone) [46], $[\pi-C_5H_5NC_{16}H_{33}]_3\{PO_4[W(O)_2(O_2)]_4\}$ [47], $[\pi-C_5H_5NC_{16}H_{33}]_3\{PO_4(WO_3)_4\}$ [47] and $[\pi-C_5H_5NC_{16}H_{33}]_3[PW_4O_{32}]$ [48] have shown excellent activity for the homogeneous catalytic epoxidation of alkenes. All these molybdenum- and tungsten-based catalytic systems showed high efficiency of H_2O_2 utilization. Those which behaved as surfactant-type catalysts act efficiently in oxidizing propylene, alkenes, olefins and oleic acid. And after reaction, these catalysts could be filtered and reused like heterogeneous analogues, which endowed the unique reaction-controlled phase-transfer characteristic. Lambert et al. [49] have reported that amphiphilic salt peroxo tungstophosphate $\{PO_4[WO(O_2)_2]_4\}^{3-}$ with H_2O_2 , known as Venturello–Ishii chemistry, was an efficient and environmentally benign reaction system for epoxidation of 1-octene. And catalyst could be reused by ultrafiltration. Li and co-workers [50] have developed the catalytic oxidation efficiently in the emulsion systems, using the amphiphilic quaternary ammonium heteropolyoxotungstates which demonstrated high performances in the selective oxidation desulfurization process. Surfactant-type catalysts combining the quaternary ammonium cations with the anions of polyoxometalates have ability to form emulsion droplets, which perform as homogeneous catalysts in the interface of two immiscible liquids to achieve high activities and high H_2O_2 efficiency during the oxidative process.

Based on the above summarizations, a new family of metal-based surfactant-type ionic liquids (MSILs) were designed and prepared. These liquid catalysts composed of quaternary ammonium cation $[(CH_3)N(n-C_8H_{17})_3]^+$ pairing with polyoxometalates anions $[\{M=O(O_2)_2\}_2(\mu-O)]^{2-}$ ($M=W, Mo$), which were found to be room temperature ionic liquids, and could be applied in catalytic oxidation removal of refractory benzothiophene (BT), DBT and 4,6-DMDBT in model oil. Quaternary ammonium salts function as a surfactant and transfer polyoxometallic anions into the substrates between water/oil biphasic. MSILs possess of the character of reaction-induced self-separation catalysis [51], which could switch from heterogeneous to the emulsion phase in the reaction process and led to high catalytic activity. When the reaction was finished, the MSIL was separated from the emulsion phase and self-separated at the bottom of the flask.

2. Experimental

2.1. Materials

Commercially available 30 wt.% H_2O_2 , $Na_2MoO_4 \cdot 2H_2O$, $Na_2WO_4 \cdot 2H_2O$, dichloromethane, CH_3CN , *n*-octane and tetradecane were purchased from Sinopharm Chemical Reagent Co., Ltd. DBT, BT and 4,6-DMDBT were marketed by Sigma–Aldrich and were used without further purification. $[(CH_3)N(n-C_8H_{17})_3]Cl$ used in this work was a commercial product from Xiamen Pioneer Technology Inc. and was purified before use. FCC gasoline was obtained from Jiangdu petrification. Actual prehydrotreated gasoline was obtained from Jiangsu Jia Yu Xin Industrial Co., Ltd. Ionic liquids $[Bmim]BF_4$, $[Bmim]PF_6$, $[Omim]BF_4$, $[Omim]PF_6$ were purchased from Shanghai Chengjie Chemical Co., Ltd.

2.2. Instrumentation

All NMR spectra were recorded on a Bruker AV-400 spectrometer (Germany) using DMSO and TMS as solvent and reference, respectively. Chemical shifts (δ) were given in parts per million and coupling constants (J) in hertz. FT-IR spectra were performed on a Nicolet FT-IR spectrophotometer (Nexus 470, Thermo Electron Corporation) using KBr pellets at room temperature. TG/DSC was done on STA-449C Jupiter (NETZSCH Corporation, Germany). Sample weighing about 30 mg was heated from 30 °C to 800 °C at a heating rate 10 °C/min in a dynamic N_2 . Gas chromatography (Agilent 7890A, U.S.) was coupled with a flame ionization detector (GC-FID). HP-5 capillary column with 30 m \times 0.32 mm inner diameter \times 0.25 μ m film thickness was used for separation. Microcoulometric analyzer (WK-2D, Jiangsu Jiangfen Electroanalytical Instrument Co., Ltd., China).

2.3. Preparation of MSIL

$[(CH_3)N(n-C_8H_{17})_3]_2\{[Mo=O(O_2)_2]_2(\mu-O)\}$ (abbreviated as $[(CH_3)N(n-C_8H_{17})_3]_2Mo_2O_{11}$)

6 mL 30 wt.% H_2O_2 was added to the solution of $Na_2MoO_4 \cdot 2H_2O$ (1.33 g, 5.5 mmol) in 10 mL water while being stirred in an ice-water bath. The formed dark red solution was treated with dilute HCl until it just turned bright yellow (pH 4–5). $[(CH_3)N(n-C_8H_{17})_3]Cl$ (2.02 g, 5 mmol) was added dropwise with vigorous agitation at the room temperature. The mixture was stirred adequately for an additional reaction period of 2 h. After reaction, the liquid was separated and then washed with dichloromethane (2×10 mL). The solvent was evaporated under reduced pressure so as to provide a highly viscous liquid product. The liquid was stored at 40 °C *in vacuo*. Elemental analysis for $C_{50}H_{108}N_2Mo_2O_{11}$ ($[(CH_3)N(n-C_8H_{17})_3]_2Mo_2O_{11}$) calcd. (found): C, 54.33(53.53); H, 9.85(10.10); N, 2.53 (2.06). 1H NMR (400 MHz; DMSO) δ = 0.871 (3H, t), 1.271 (10H, s), 1.614 (2H, s), 2.966 (1H, s), 3.215 (2H, t); ^{13}C NMR (100 MHz; DMSO) δ = 14.38, 21.82, 22.17, 22.38, 22.52, 26.26, 26.36, 28.88, 28.92, 28.97, 29.05, 31.64, 47.99, 50.43, 60.98, 63.34, 64.06. FTIR ν_{max}/cm^{-1} : 966 ($\nu(Mo=O)$), 883 ($\nu(O-O)$), 783 ($\nu_{asym}(Mo_2O)$), 665 ($\nu_{sym}[Mo(O_2)]$), 586 ($\nu_{asym}[Mo(O_2)]$).

2.4. Preparation of MSIL

$[(CH_3)N(n-C_8H_{17})_3]_2\{[W=O(O_2)_2]_2(\mu-O)\}$ (abbreviated as $[(CH_3)N(n-C_8H_{17})_3]_2W_2O_{11}$)

A solution of $Na_2WO_4 \cdot 2H_2O$ (1.81 g, 5.5 mmol) in 10 mL water was placed. Treated with 6 mL 30 wt.% H_2O_2 a yellow solution was presented, to which dilute HCl was added dropwise until the solution just turned colorless (pH 2–3). $[(CH_3)N(n-C_8H_{17})_3]Cl$ (2.02 g, 5 mmol) was added dropwise with vigorous agitation at the room temperature for 2 h. After the reaction, the liquid was separated

and washed with dichloromethane (2×10 mL). Then a slightly yellow and highly viscous liquid was produced after the solvent was evaporated under reduced pressure. The product was stored at 40°C *in vacuo*. Elemental analysis for $\text{C}_{50}\text{H}_{108}\text{N}_2\text{W}_2\text{O}_{11}$ ($[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]_2\text{W}_2\text{O}_{11}$) calcd. (found): C, 46.88(47.06); H, 8.50(8.92); N, 2.19 (2.20). ^1H NMR(400 MHz; DMSO) $\delta = 0.866$ (3H, t), 1.288 (10H, m), 1.610 (2H, s), 3.008 (1H, s), 3.235 (2H, t), 3.457 (1H, s). ^{13}C NMR (100 MHz; DMSO) $\delta = 14.37, 21.87, 22.25, 22.36, 22.54, 22.73, 22.97, 26.26, 26.77, 28.93, 28.94, 29.01, 29.05, 29.21, 29.28, 31.50, 31.67, 31.83, 48.11, 50.56, 55.40, 60.88, 63.16, 65.36, 68.38$. FTIR $\nu_{\text{max}}/\text{cm}^{-1}$: 978 ($\nu(\text{W}=\text{O})$), 815 ($\nu(\text{O}-\text{O})$), 747 ($\nu_{\text{asym}}(\text{W}_2\text{O})$), 619 ($\nu_{\text{sym}}[\text{W}(\text{O}_2)]$), 562 ($\nu_{\text{asym}}[\text{W}(\text{O}_2)]$).

2.5. Preparation of $\text{K}_2\{[\text{W}=\text{O}(\text{O}_2)_2]_2(\mu\text{-O})\}$ (abbreviated as $\text{K}_2\text{W}_2\text{O}_{11}$)

$\text{K}_2\text{W}_2\text{O}_{11}$ was prepared as a white crystal according to [52]. FTIR $\nu_{\text{max}}/\text{cm}^{-1}$: 966.7 (W=O), 853.8 (O–O), 763.7 ($\nu_{\text{asym}}(\text{W}_2\text{O})$), 616.6 ($\nu_{\text{sym}}[\text{W}(\text{O}_2)]$), 538.8 ($\nu_{\text{asym}}[\text{W}(\text{O}_2)]$), 448.4 ($\nu_{\text{sym}}(\text{W}_2\text{O})$).

2.6. Preparation of different model oils

2.932 g DBT was dissolved in 1000 mL *n*-octane to form the model oil, the sulfur content of which was $500 \mu\text{g mL}^{-1}$. Other kinds of model oil were prepared with the same method—by dissolving BT and 4,6-DMDBT in *n*-octane with sulfur contents of $250 \mu\text{g mL}^{-1}$ and $250 \mu\text{g mL}^{-1}$, respectively.

2.7. Procedure for the desulfurization of model oils and actual gasoline

Desulfurizations were performed with the MSILs in a homemade 40 mL two-necked flask. After the required amounts of MSILs were added to the flask, 30 wt.% H_2O_2 and 5 mL model oil were poured into the mixture, and then the mixed solution was then stirred vigorously at 30°C for 2 h in an oil bath. After the reaction, the upper phase (model oils or actual gasoline) was periodically withdrawn and separated by centrifugation before analyzing for sulfur content. The different substrate concentrations in model oil were determined using GC-FID with tetradecane as the internal standard. Carrier gas was high purity nitrogen and flow rate was 25 mL/min . Hydrogen and air flow rates were 30 mL/min and 400 mL/min , respectively. The GC process for DBT and BT started at 100°C and the temperature was raised to 200°C at 15°C/min . The GC process for 4,6-DMDBT started at 100°C and the temperature was raised to 160°C at 20°C/min and then raised to 230°C at 25°C/min . The injector temperature was 250°C and detector temperature was 300°C . And the total sulfur content in actual gasoline was tested by microcoulometry.

3. Results and discussion

3.1. Catalysts preparation and characterization

The MSILs were synthesized based on Ref. [52] and their structures have been proven by IR and NMR. The spectrum data from FTIR analysis was used to describe the obtained compounds and to determine the purity of the synthesized salts. The NMR technique of ^1H and ^{13}C presented the pure products without unexpected signals. Both the ^1H and the ^{13}C NMR spectra confirmed the identity of the obtained MSILs $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]_2\text{Mo}_2\text{O}_{11}$ and $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]_2\text{W}_2\text{O}_{11}$.

The thermal stability of $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]\text{Cl}$, $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]_2\text{Mo}_2\text{O}_{11}$ and $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]_2\text{W}_2\text{O}_{11}$ (Fig. 1) was characterized by TG–DSC. These results demonstrated that MSILs had no crystalline water because there was no mass loss and no endothermic peak around 100°C [45]. Compared with the

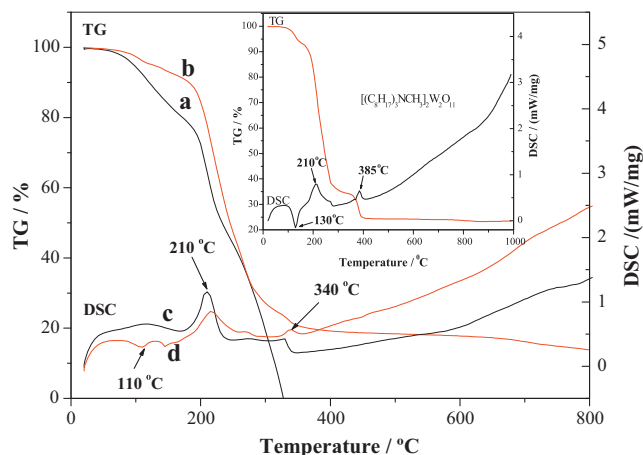


Fig. 1. TG–DSC of $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]\text{Cl}$ (a, c), $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]_2[\text{Mo}_2\text{O}_{11}]$ (b, d) and $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]_2[\text{W}_2\text{O}_{11}]$ (insert).

material $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]\text{Cl}$ (Fig. 1a and c), when $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]_2\text{Mo}_2\text{O}_{11}$ was decomposed there was a mass loss from 100°C to 150°C and the corresponding exothermic peak on DSC curve emerged at 110°C in the first step, which demonstrated the decomposition of peroxy species (Fig. 1b and d). After 200°C there was two mass loss on TG curve, which may be attributed to the decomposition of the quaternary ammonium organic cation $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]^+$. Until about 500°C , this decomposition came to an end gradually. And the final remainder after 800°C was the molybdenum oxide. The TG–DSC curves of $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]_2\text{W}_2\text{O}_{11}$ were given with a similar decomposition process (Fig. 1(insert)).

In the following step, these synthesized MSILs were employed for oxidative desulfurization. The conversion of DBT, BT and 4,6-DMDBT in the model oil was used to calculate the removal of sulfur compounds.

3.2. Different effects of the catalytic system on desulfurization

Many types of oxidative desulfurization systems based on transition metal salts present in fuels have been already reported, such as $\text{H}_2\text{O}_2/\text{M-TMA}$ ($\text{M} = \text{W}, \text{Mo}$) [13], $\text{H}_2\text{O}_2/\text{Na}_2\text{HPW}_{12}\text{O}_{40}$ [27] and $\text{H}_2\text{O}_2/\text{H}_3\text{PW}_6\text{Mo}_6\text{O}_{40}$ [41]. However, the main problem lies in biphasic reaction: an oil phase with the sulfur-containing compound and an organic solvent that contains aqueous H_2O_2 that is not soluble in the oil phase. Here we carried out the oxidative desulfurization of DBT using phase transfer catalysts to provide a green and highly active oxidation process of fuel oil.

Table 1 showed the different effects of the catalytic system on desulfurization. Both MSILs $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]_2\text{Mo}_2\text{O}_{11}$ and $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]_2\text{W}_2\text{O}_{11}$ with oxidant H_2O_2 had high catalytic activity for oxidation of DBT. The sulfur conversion was 96.1%

Table 1
Comparison of different desulfurization systems on sulfur conversion.

Entry	Different desulfurization systems	S-conversion of different desulfurization systems (%)	
		Catalyst	Catalyst + H_2O_2
1	$[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]_2\text{Mo}_2\text{O}_{11}$	3.3	96.2
2	$[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]_2\text{W}_2\text{O}_{11}$	4.3	86.7
3	$[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]\text{Cl}$	6.6	7.4
4	$\text{K}_2\text{W}_2\text{O}_{11}$	1.1	2.3
5	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	0.8	1.1
6	$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	0.9	1.5

Experimental conditions: O/S = 8 (molar ratio); oil/MSIL (mass ratio) = 40; $t = 2$ h; $T = 30^\circ\text{C}$; agitation rate = 500 rpm.

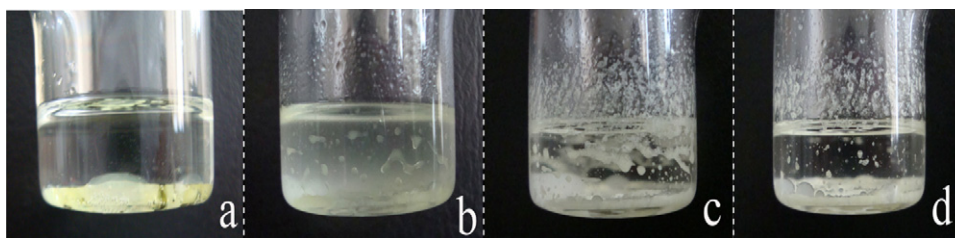


Fig. 2. Different stages of the catalytic oxidation desulfurization over MSIL $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]_2\text{Mo}_2\text{O}_{11}$ with H_2O_2 . (a) Before the reaction, $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]_2\text{Mo}_2\text{O}_{11}$ (pale yellow viscous liquid) at the bottom of the flask, H_2O_2 in the middle lay and model oil (transparent liquid) in the upper layer; (b) emulsification system after the reaction proceeding 10 min with agitation; (c) biphasic desulfurization system was observed after 1 h; (d) after the reaction was finished, the MSIL sticking to sidewall was self-separated at the bottom of the flask. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and 86.7%, respectively. When the cation or the anion was used as an independent catalytic system (Entries 3–6), the application could not promote the reaction obviously. These reasons of high catalytic activity of MSILs lay in efficient mass transfer, which was caused by the emulsion properties of the quaternary ammonium cation across the phasic boundaries [53]. On the basis of our previous work [54], emulsion system composed of quaternary ammonium cations and polyoxometallic anions presented the oxidation accomplishment completely. During the desulfurization reaction (oil/MSIL=40:1 and $\text{H}_2\text{O}_2/\text{DBT}$ (O/S=8)), the lipophilic quaternary ammonium cation could act as phase transfer reagent. $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]^+$ has long lipophilic alkyl chain and can easily transfer the active peroxy species, which were formed by the reaction between hydrophilic $\text{Mo}_2\text{O}_{11}^{2-}$ and H_2O_2 , into substrates (Fig. 2). Further advantages were that no co-surfactant was needed and deep desulfurization (96.2%) could be achieved. It was reported that $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]^+$ showed the efficient potential for alcohol oxidation and epoxidation of alkenes [40,43]. Herein it was found to be favorable for stabilizing the emulsion system and for transferring the catalytic species to the aromatic sulfur compound under the optimal reaction conditions and to result in higher oxidative reaction rate.

3.3. Supposed mechanism of reaction system

During the reaction, the ODS system formed an emulsion using $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]_2\text{Mo}_2\text{O}_{11}$ with H_2O_2 at room temperature and then the MSIL was able to be self-separated at the end of the reaction (Fig. 2). In Fig. 2a, MSIL $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]_2\text{Mo}_2\text{O}_{11}$, H_2O_2 and model oil were added in the flask before the reaction. After reaction for 10 min, emulsification of the desulfurization system was observed by the presence of the quaternary ammonium cation from the MSIL itself (Figs. 2b and 3). The MSIL could be dispersed well into the substrate phase during the oxidation reaction of DBT. More interestingly, the emulsification gradually got weaker and weaker as the reaction went on until biphasic desulfurization system was observed (Fig. 2c). When the reaction was finished, the MSIL was separated from the oil phase and self-separated at the bottom of the flask (Fig. 2d). The feature of this liquid catalyst that contained the lipophilic cation and hydrophilic anion was amphiphilic, which made it play an essential role in the formation of the emulsion and oxidation of DBT, respectively. Moreover, the recovery of the heterogeneous catalyst was convenient for the ODS system.

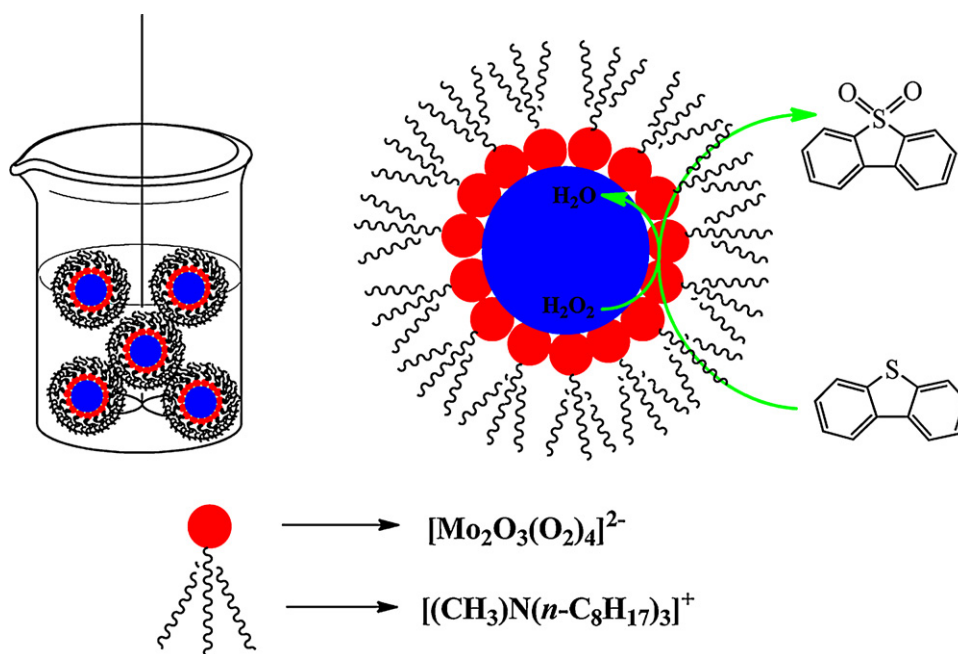


Fig. 3. Supposed catalytic oxidation desulfurization using MSIL $[(\text{CH}_3)\text{N}(n\text{-C}_8\text{H}_{17})_3]_2[\text{Mo}_2\text{O}_{11}]$ and oxidant H_2O_2 in emulsion droplets.

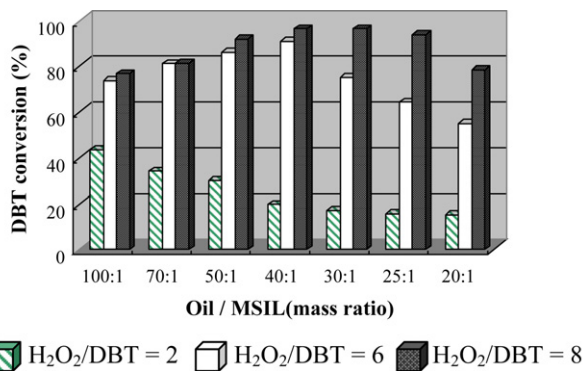


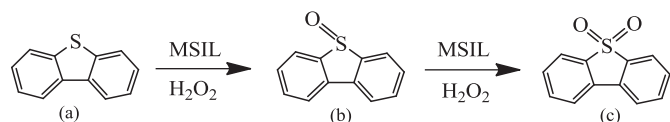
Fig. 4. The effect of O/S (molar ratio) and oil/MSIL (mass ratio) on conversion of DBT. Experimental conditions: $t = 2$ h; $T = 30$ °C; agitation rate = 500 rpm.

3.4. The effect of H_2O_2/DBT (molar ratio) and oil/MSIL (mass ratio) on conversion of DBT

To investigate the effect of the amount of oxidizing agent and the emulsion properties, experiments on the effect of H_2O_2/DBT (O/S) (molar ratio) and oil/MSIL (mass ratio) at temperature 30 °C were carried out. O/S of 2, 6, 8 and oil/MSIL of 100:1, 70:1, 50:1, 40:1, 30:1, 25:1 and 20:1 are plotted in Fig. 4. According to the stoichiometric reaction, 2 mol of H_2O_2 are consumed for oxidation of 1 mol of DBT to its corresponding sulfone, as shown in Scheme 1. When O/S molar ratio was increased from 2 to 8, DBT conversion increased at different oil/MSIL ratios. When the mass ratio of oil/MSIL increased from 20:1 to 100:1 at O/S = 2, the sulfur conversion of DBT increased slowly to 43.2%. When O/S = 6, DBT conversion increased from 54.7% at oil/MSIL = 20:1–90.8% at oil/MSIL = 40:1. Then it was found to decrease obviously when oil/MSIL > 40:1. There exhibited a similar trend of DBT conversion at O/S = 8. Under the reaction conditions of oil/MSIL = 40:1 and O/S = 8, the MSIL brought forth the highest desulfurization activity (96.2%). As oil/MSIL = 20:1, DBT conversion decreased to 76.5%.

3.5. The effect of the agitation rate on DBT conversion

The appropriate magnetic agitation rate is favored with the stability of the emulsion droplets formed by emulsifying agent. If the agitation rate is set at a low value, the MSIL $[(CH_3)N(n-C_8H_{17})_3]_2[Mo_2O_{11}]$ as an emulsifying agent could not be neatly distributed in the phase interface. On the other hand, if set at a high value, the emulsion droplets formed by the emulsifying agent may be damaged because of severe contacts between the magnet and the wall of the flask. These results summarized in Table 2 shows the effect of the agitation rate on DBT conversion. With the agitation rate (rpm) increasing, the DBT conversion increased from 66.7% at 100 rpm to 96.2% at 500 rpm. When the rate was set at 750 rpm, there was a slight increase (DBT conversion increased to 97.2%) of DBT removal. However, if the agitation rate was set at 1000 rpm, DBT oxidation will be slowed down and the DBT conversion decreased to 96.5%. Hence, 500 rpm was applied in all desulfurization experiments.



Scheme 1. Pathways of dibenzothiophene (DBT) oxidation: (a) DBT, (b) DBT S-oxide (sulfoxide) (DBTO), (c) DBT S, S-dioxide (sulfone) (DBTO2).

Table 2
The effect of the agitation rate on DBT conversion.

Entry	The agitation rate (rpm)	Sulfur conversion (%)
1	100	66.7
2	250	72.3
3	375	90.5
4	500	96.2
5	750	97.2
6	1000	96.5

Experimental conditions: oil/MSIL (mass ratio) = 40; O/S = 8 (molar ratio); $t = 2$ h; $T = 30$ °C.

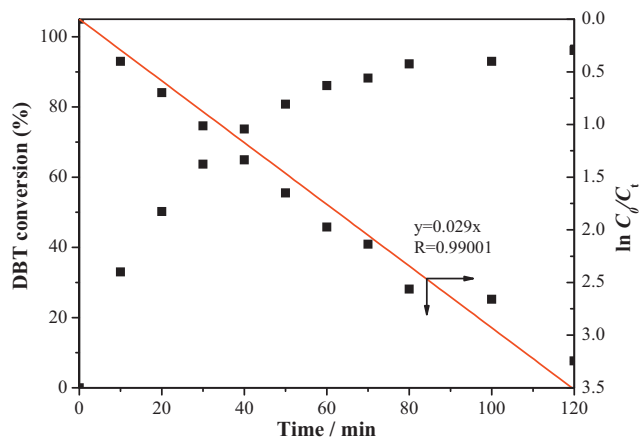


Fig. 5. Time-course variation of DBT conversion and $\ln(C_0/C_t)$. Experimental conditions: $T = 30$ °C; oil/MSIL (mass ratio) = 40; O/S = 8 (molar ratio); agitation rate = 500 rpm.

3.6. Kinetics of oxidation of DBT in *n*-octane by H_2O_2

To study kinetics of oxidation of DBT with $[(CH_3)N(n-C_8H_{17})_3]_2[Mo_2O_{11}]$ as the catalyst, samples were taken out from oil phase and measured with a GC-FID to determine sulfur content in the reaction course. The time-course variation of DBT conversion was shown in Fig. 5. When the oxidation of DBT in *n*-octane is assumed to be the pseudo-first-order reaction [14], the sulfur content of model oil will meet with Eqs. (1) and (2):

$$\ln\left(\frac{C_0}{C_t}\right) = kt \quad (1)$$

$$t_{1/2} = \frac{0.693}{k} \quad (2)$$

C_0 and C_t are for the sulfur content of model oil at time zero and time t (s), respectively, and k is for the pseudo-first-order rate constant (min^{-1}). Half-life ($t_{1/2}$ (min)) is calculated using Eq. (2), which is derived from Eq. (1) by replacing C_t with $C_0/2$. Time-course variation of $\ln(C_0/C_t)$ was shown in Fig. 5. We have calculated k and $t_{1/2}$, which were 0.029 min^{-1} and 23.9 min, respectively. Herein the results of oxidation of DBT in *n*-octane by H_2O_2 have supported the pseudo-first-order kinetics procedure.

Table 3
Recycling of MSIL $[(CH_3)N(n-C_8H_{17})_3]_2[Mo_2O_{11}]$ over desulfurization.

Cycle	DBT conversion (%)	Cycle	DBT conversion (%)
1	96.2	6	93.9
2	97.5	7	93.1
3	96.3	8	89.7
4	95.4	9	87.5
5	94.4	10	85.4

Experimental conditions: oil/MSIL (mass ratio) = 40; O/S = 8 (molar ratio); $T = 30$ °C; $t = 2$ h; agitation rate = 500 rpm.

Table 4
Oxidative desulfurization in different solvents.

Entry	Solvents	DBT conversion (%)	
		$[(\text{CH}_3\text{N}(\text{n-C}_8\text{H}_{17})_3)_2[\text{Mo}_2\text{O}_{11}]]$	$[(\text{CH}_3\text{N}(\text{n-C}_8\text{H}_{17})_3)_2[\text{W}_2\text{O}_{11}]]$
1	None	83.1	68.3
2	CH_3OH	56.3	17.8
3	CH_3CN	80.6	54.8
4	$[\text{Bmim}]\text{BF}_4$	96.8	83.1
5	$[\text{Omim}]\text{BF}_4$	97.8	85.9
6	$[\text{Bmim}]\text{PF}_6$	94.9	45.7
7	$[\text{Omim}]\text{PF}_6$	99.7	98.1

Experimental conditions: oil/MSIL (mass ratio) = 50; O/S = 6 (molar ratio); $t = 2$ h; $T = 30^\circ\text{C}$; $V(\text{solvent}) = 1$ mL; agitation rate = 500 rpm.

3.7. The effect of different substrates on sulfur conversion

To investigate the desulfurization performance of the MSIL $[(\text{CH}_3\text{N}(\text{n-C}_8\text{H}_{17})_3)_2[\text{Mo}_2\text{O}_{11}]]$ on other sulfur compounds besides DBT, experiments combined with catalytic oxidation of different aromatic sulfur compounds (BT and 4,6-DMDBT) were carried out under the same conditions. As shown in Fig. 6, the sulfur conversion of BT and 4,6-DMDBT was 52.0% and 73.2% after 240 min in ODS system, respectively. From the data, it was obvious that the sulfur conversion through ODS process decreased in the order of $\text{DBT} > 4,6\text{-DMDBT} > \text{BT}$. These results may be attributed to the difference of both aromatic π -electron density of sulfur compounds and steric hindrance around the sulfur atoms. The desulfurization performance increased with the increase of the aromatic π -electron density. Among DBT, BT and 4,6-DMDBT, π -electron density on the sulfur atom of BT was the lowest [2], and so was the lowest catalytic reactivity. The difference between π -electron density of DBT and 4,6-DMDBT was not very significant, but the conversion of 4,6-DMDBT was much lower than that of DBT due to the domination of the influence of steric hindrance.

3.8. The recycling of MSIL

The possibility of the recycling of MSIL $[(\text{CH}_3\text{N}(\text{n-C}_8\text{H}_{17})_3)_2[\text{Mo}_2\text{O}_{11}]]$ was investigated in ODS system. After oxidative desulfurization reaction, MSIL could be separated by decantation and recycled. And fresh H_2O_2 and model oil were added into the original reaction flask for the next run. The data shown in Table 3 indicated that the MSIL could be recycled several times with an unnoticeable decrease in DBT conversion. DBT conversion still remains 93.1% even after seven consecutive cycles. However,

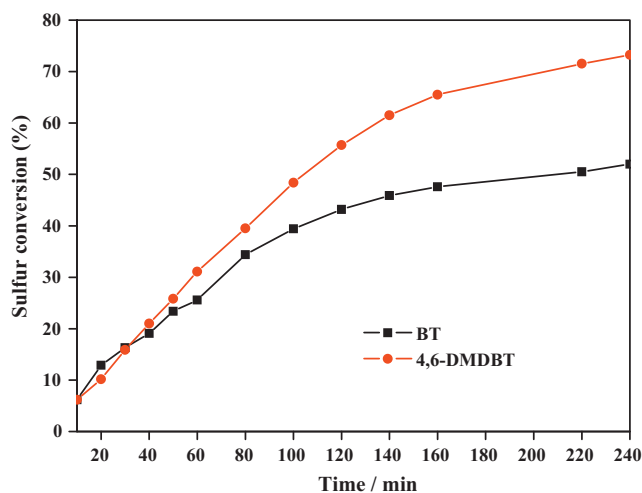


Fig. 6. The effect of sulfur species on sulfur conversion. Experimental conditions: O/S = 8 (molar ratio); oil/MSIL (mass ratio) = 40; $T = 30^\circ\text{C}$; agitation rate = 500 rpm.

the conversion dropped to 89.7% in the next cycle. There was no sulfone visible in the IL phase at the end of first cycle. After three cycles some white precipitates came out and were in the IL phase, which led to the decrease of sulfur removal. When the reaction was carried out in a large scale (10 times), DBT conversion decreased from 96.2% to 85.4%. The recycled catalyst could be reused for at least seven reaction cycles with a slight activity drop.

3.9. Extraction combined with oxidation desulfurization using different solvents

Solvents have a great effect on the catalytic ability of the polyoxometallates. The solvent effect was investigated for the nature of MSILs during oxidation of DBT using H_2O_2 as the oxidant. Here both organic solvents and conventional ILs were chosen as reaction solvents. Experiments shown in Table 4 indicated DBT conversion in different organic solvents. As observed, the catalytic activity of the peroxomolybdenum anion-containing catalyst was superior to that of the corresponding peroxotungsten analogue in different organic solvents. We speculated that it may be attributed to the nature of the Mo and W atom of MSILs [22]. There was a relatively higher desulfurization activity when CH_3CN was used compared with CH_3OH (Entry 2, Entry 3). This behavior might be related to the protic (CH_3OH) or aprotic (CH_3CN) character of the solvents [28]. On the other hand, the two MSILs presented limited catalytic abilities for the deep desulfurization within CH_3OH as well as CH_3CN during the oxidation process.

Previous work [55–57] was reported that extraction and catalytic oxidation desulfurization (ECODS) with RTILs exhibited high catalytic activity in the desulfurization. Here we tested the catalytic activity of MSILs for the oxidative desulfurization using four conventional RTILs $[\text{Bmim}]\text{BF}_4$, $[\text{Omim}]\text{BF}_4$, $[\text{Bmim}]\text{PF}_6$ and $[\text{Omim}]\text{PF}_6$ to develop an environmentally friendly process (Entries 4–7). The results indicated that the advantage of this process over the desulfurization exhibited much higher DBT conversion percentages with RTILs than those with polar organic solvents under the same conditions. Furthermore, $[(\text{CH}_3\text{N}(\text{n-C}_8\text{H}_{17})_3)_2[\text{Mo}_2\text{O}_{11}]]$ was more efficient catalyst for the sulfur removal in longer alkyl chains $[\text{Omim}]\text{BF}_4$ and $[\text{Omim}]\text{PF}_6$, where the conversions could reach 97.8% and 99.7%, respectively. From the table, it could be found that solvents, especially RTILs, had a significant effect on the MSILs over oxidative desulfurization.

3.10. Oxidative desulfurization of FCC gasoline and prehydrotreated gasoline

Multiple reactions of the ODS process were applied to the actual FCC gasoline and prehydrotreated gasoline. The sulfur-containing compounds in the gasoline can be oxidized with MSIL $[(\text{CH}_3\text{N}(\text{n-C}_8\text{H}_{17})_3)_2[\text{Mo}_2\text{O}_{11}]]$. Oxidative desulfurization of actual gasoline was done under optimal experimental conditions: 5 mL gasoline, $T = 30^\circ\text{C}$, $V(\text{H}_2\text{O}_2) = 64 \mu\text{L}$, $m([(CH_3)N(n-$

$C_8H_{17}_3)_2Mo_2O_{11}$) = 0.178 g. To FCC gasoline, the sulfur content decreased from 341 to 204 ppmw S after four rounds of reaction in the absence of extractant. When 1 mL [Bmim]BF₄ ionic liquid was combined as extractant, the sulfur content could reach 105 ppmw after four rounds of reaction. The lower sulfur removal lay in the complicated sulfur compounds (containing thiols, thiophene, dibenzothiophene and alky-substituted DBTs, etc.) in FCC gasoline. However, to prehydrotreated gasoline, multiple reactions of the ODS process could remove sulfur compounds efficiency because the hydrotreatment greatly improved the quality of the fuels. For example, thiols and thiophene could be easily removed in HDS process, which were refractory in ODS process. The sulfur species mainly remained DBT and alky-substituted DBTs in prehydrotreated gasoline, which were easily be oxidized in ODS process. In the presence of 1 mL [Bmim]BF₄ as extractant, the sulfur content decreased from 150 to 30 ppmw after two rounds of reaction and the color of ionic liquid phase was deepened a lot. With the increase of reaction steps, the gasoline became more transparent and clearer. After the three-round reaction, the dark yellow color of gasoline faded and sulfur content was only 12 ppmw (sulfur removal, 92%). So multiple reactions of oxidation desulfurization process were feasible and effective for prehydrotreated gasoline.

4. Conclusion

Two MSILs [(CH₃)N(*n*-C₈H₁₇)₃)₂Mo₂O₁₁ and [(CH₃)N(*n*-C₈H₁₇)₃)₂W₂O₁₁ have been synthesized and used as the catalysts for deep desulfurization in the presence of H₂O₂. Under the optimal reaction conditions of oil/MSIL = 40:1, O/S = 8, reaction temperature: 30 °C and agitation at 500 rpm, the MSIL [(CH₃)N(*n*-C₈H₁₇)₃)₂Mo₂O₁₁ brought forth the highest desulfurization activity (96.2%). The amphiphilic nature of this liquid catalyst played an essential part in the formation of the emulsion and recycling oxidation of DBT. The sulfur conversion follows the pseudo-first-order kinetics with the reaction rate constant and half-life of 0.029 min⁻¹ and 23.9 min, respectively. The oxidation reactivity of the different substrates was as following: DBT > 4,6-DMDBT > BT. Moreover, [(CH₃)N(*n*-C₈H₁₇)₃)₂Mo₂O₁₁ could be recycled with a slight decrease in sulfur removal. RTILs had a significant effect on MSILs over oxidative desulfurization both in model oils and in actual prehydrotreated gasoline.

Acknowledgements

This work was financially supported by the National Nature Science Foundation of China (No. 21076099, 20876071), Specialized Research Fund for the Doctoral Program of Higher Education of China (No. 20103227110016) Postdoctoral Foundation of China (No. 20090461067, No. 201003556) and Jiangsu Province (No. 1001025C), Advanced Talents of Jiangsu University (No. 09JDG063).

References

- [1] P.S. Kulkarni, C.A.M. Afonso, *Green Chem.* 12 (2010) 1139–1149.
- [2] S. Otsuki, T. Nonaka, N. Takashima, W.H. Qian, A. Ishihara, T. Imai, T. Kabe, *Energy Fuels* 14 (2000) 1232–1239.
- [3] C.S. Song, *Catal. Today* 86 (2003) 211–263.
- [4] F.M. Collins, A.R. Lucy, C. Sharp, *J. Mol. Catal. A: Chem.* 117 (1997) 397–403.
- [5] A. Bösmann, L. Datsevich, A. Jess, A. Lauter, C. Schmitz, P. Wasserscheid, *Chem. Commun.* (2001) 2494–2495.
- [6] J. Eßer, P. Wasserscheid, A. Jess, *Green Chem.* 6 (2004) 316–322.
- [7] N.H. Ko, J.S. Lee, E.S. Huh, H. Lee, K.D. Jung, H.S. Kim, M. Cheong, *Energy Fuels* 22 (2008) 1687–1690.
- [8] R.T. Yang, A.J. Hernández-Maldonado, F.H. Yang, *Science* 301 (2003) 79–81.
- [9] J.L. García-Gutiérrez, G.A. Fuentes, M.E. Hernández-Terán, P. García, F. Murrieta-Guevara, F. Jiménez-Cruz, *Appl. Catal. A: Gen.* 305 (2006) 15–20.
- [10] H.Y. Lü, J.B. Gao, Z.X. Jiang, F. Jing, Y.X. Yang, G. Wang, C. Li, *J. Catal.* 239 (2006) 369–375.
- [11] Y.N. Zhang, L. Wang, Y.L. Zhang, Z.X. Jiang, C. Li, *Chin. J. Catal.* 32 (2011) 235–239.
- [12] A.M. Dehkordi, Z. Kiaei, M.A. Sobati, *Fuel Process. Technol.* 90 (2009) 435–445.
- [13] M.C. Capel-Sanchez, P. Perez-Presas, J.M. Campos-Martin, J.L.G. Fierro, *Catal. Today* 157 (2010) 390–396.
- [14] A. Di Giuseppe, M. Crucianelli, F. De Angelis, C. Crestini, R. Saladino, *Appl. Catal. B: Environ.* 89 (2009) 239–245.
- [15] J.Z. Gui, D. Liu, Z.L. Sun, D.S. Liu, D. Min, B. Song, X.L. Peng, *J. Mol. Catal. A: Chem.* 331 (2010) 64–70.
- [16] H.Y. Lü, Y.N. Zhang, Z.X. Jiang, C. Li, *Green Chem.* 12 (2010) 1954–1958.
- [17] F. Al-Shahrani, T.C. Xiao, S.A. Llewellyn, S. Barri, Z. Jiang, H.H. Shi, G. Martinie, M.L.H. Green, *Appl. Catal. B: Environ.* 73 (2007) 311–316.
- [18] M. Soleimani, A. Bassi, A. Margaritis, *Biotechnol. Adv.* 25 (2007) 570–596.
- [19] Z.L. Wu, B. Ondruschka, *Ultrason. Sonochem.* 17 (2010) 1027–1032.
- [20] W.H. Lo, H.Y. Yang, G.T. Wei, *Green Chem.* 5 (2003) 639–642.
- [21] F.T. Li, R.H. Liu, J.H. Wen, D.S. Zhao, Z.M. Sun, Y. Liu, *Green Chem.* 11 (2009) 883–888.
- [22] S.E. Jacobson, D.A. Muccigrosso, F. Mares, *J. Org. Chem.* 44 (1979) 921–924.
- [23] J. Zhang, D.S. Zhao, L.Y. Yang, Y.B. Li, *Chem. Eng. J.* 156 (2010) 528–531.
- [24] Z.S. Wei, G.H. Zeng, Z.R. Xie, *Energy Fuels* 23 (2009) 2947–2951.
- [25] H. Gómez-Bernal, L. Cedeño-Caero, A. Gutiérrez-Alejandre, *Catal. Today* 142 (2009) 227–233.
- [26] D.S. Zhao, Z.M. Sun, F.T. Li, R. Liu, H.D. Shan, *Energy Fuels* 22 (2008) 3065–3069.
- [27] W. Trakarnpruk, K. Rujiraworawut, *Fuel Process. Technol.* 90 (2009) 411–414.
- [28] L.F. Ramírez-Verduzco, J.A. De los Reyes, E. Torres-García, *Ind. Eng. Chem. Res.* 47 (2008) 5353–5361.
- [29] R.D. Rogers, K.R. Seddon, *Science* 302 (2003) 792–793.
- [30] H. Olivier-Bourbigou, L. Magna, D. Morvan, *Appl. Catal. A: Gen.* 373 (2010) 1–56.
- [31] M.F. Sellin, P.B. Webb, D.J. Cole-Hamilton, *Chem. Commun.* (2001) 781–782.
- [32] A.C. Cole, J.L. Jensen, I. Ntai, K.L.T. Tran, K.J. Weaver, D.C. Forbes, J.H. Davis Jr., *J. Am. Chem. Soc.* 124 (2002) 5962–5963.
- [33] X.M. Liu, J.X. Zhou, X.W. Guo, M. Liu, X.L. Ma, C.S. Song, C. Wang, *Ind. Eng. Chem. Res.* 47 (2008) 5298–5303.
- [34] S.G. Lee, *Chem. Commun.* (2006) 1049–1063.
- [35] T.L. Merrigan, E.D. Bates, S.C. Dorman, J.H. Davis Jr., *Chem. Commun.* (2000) 2051–2052.
- [36] J.H. Davis Jr., *Chem. Lett.* 33 (2004) 1072–1077.
- [37] C. Venturello, R. D'aloisio, J.C.J. Bart, M. Ricci, *J. Mol. Catal.* 32 (1985) 107–110.
- [38] Y. Ishii, K. Yamawaki, T. Yoshida, T. Ura, M. Ogawa, *J. Org. Chem.* 52 (1987) 1868–1870.
- [39] K. Yamaguchi, C. Yoshida, S. Uchida, N. Mizuno, *J. Am. Chem. Soc.* 127 (2005) 530–531.
- [40] K. Sato, M. Aoki, J. Takagi, R. Noyori, *J. Am. Chem. Soc.* 119 (1997) 12386–12387.
- [41] R. Wang, G.F. Zhang, H.X. Zhao, *Catal. Today* 149 (2010) 117–121.
- [42] D.C. Duncan, R.C. Chambers, E. Hecht, C.L. Hill, *J. Am. Chem. Soc.* 117 (1995) 681–691.
- [43] I.V. Kozhevnikov, G.P. Mulder, M.C. Steverink-de Zoete, M.G. Oostwal, *J. Mol. Catal. A: Chem.* 134 (1998) 223–228.
- [44] X.Y. Shi, J.F. Wei, *J. Mol. Catal. A: Chem.* 229 (2005) 13–17.
- [45] A.J. Bailey, W.P. Griffith, B.C. Parkin, *J. Chem. Soc. Dalton Trans.* (1995) 1833–1837.
- [46] Z.H. Weng, J.Y. Wang, S.H. Zhang, C. Yan, X.G. Jian, *Appl. Catal. A: Gen.* 339 (2008) 145–150.
- [47] Z.W. Xi, N. Zhou, Y. Sun, K.L. Li, *Science* 292 (2001) 1139–1141.
- [48] Y. Ding, W. Zhao, H. Hua, B.C. Ma, *Green Chem.* 10 (2008) 910–913.
- [49] A. Lambert, P. Plucinski, I.V. Kozhevnikov, *Chem. Commun.* (2003) 714–715.
- [50] J.B. Gao, S.G. Wang, Z.X. Jiang, H.Y. Lu, Y.X. Yang, F. Jing, C. Li, *J. Mol. Catal. A: Chem.* 258 (2006) 261–266.
- [51] Y. Leng, J. Wang, D.R. Zhu, X.Q. Ren, H.Q. Ge, L. Shen, *Angew. Chem. Int. Ed.* 48 (2009) 168–171.
- [52] N.J. Campbell, A.C. Dengel, C.J. Edwards, W.P. Griffith, *J. Chem. Soc. Dalton Trans.* (1989) 1203–1208.
- [53] H.Y. Lü, J.B. Gao, Z.X. Jiang, Y.X. Yang, B. Song, C. Li, *Chem. Commun.* (2007) 150–152.
- [54] W.S. Zhu, H.M. Li, X.Y. He, Q. Zhang, H.M. Shu, Y.S. Yan, *Catal. Commun.* 9 (2008) 551–555.
- [55] 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.
- [56] 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.
- [57] L.N. He, H.M. Li, W.S. Zhu, J.X. Guo, X. Jiang, J.D. Lu, Y.S. Yan, *Ind. Eng. Chem. Res.* 47 (2008) 6890–6895.