



# Catalytic oxidative desulfurization performance of immobilized NMP. FeCl<sub>3</sub> ionic liquid on $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support



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## HIGHLIGHTS

- NMP.FeCl<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared as a novel recyclable supported catalyst for ODS system.
- True immobilization of NMP.FeCl<sub>3</sub> was confirmed by several characterization techniques.
- A facilitated desulfurization was attained by the novel catalyst in a solvent free system.
- 99% of DBT was removed at the found optimal operating conditions of ODS.
- Based on examination results, a plausible mechanism was proposed for desulfurization.

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## ABSTRACT

NMP.FeCl<sub>3</sub> (NMP = N-methyl-2-pyrrolidone, C<sub>5</sub>H<sub>9</sub>NO) ionic liquid (IL) was effectively immobilized on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a support and examined in the catalytic oxidative deep desulfurization (ODS) of BT, DBT and 4,6-DMDBT from model oil employing 30 wt.% H<sub>2</sub>O<sub>2</sub> as the oxidant reagent. The supported catalyst was prepared via a simple wet impregnation and the effective immobilization of IL was confirmed by FTIR, SEM, EDS, XRD, BET and BJH analysis. The maximum efficiency of 99% was achieved for ODS of DBT using supported IL at the loading amount of 10 wt.%, H<sub>2</sub>O<sub>2</sub>/sulfur molar ratio of 4, temperature of 40 °C, and duration of 90 min. The use of support material in this study resulted in using a lower amount of IL in ODS process. The ODS reactivity of the thiophenic compounds changed in the order of DBT > 4,6-DMDBT  $\gg$  BT. The catalyst was recycled for several times and showed no significant loss in the activity. Furthermore, based on GC–MS analysis of the products, desulfurization mechanism was surveyed and a reasonable pathway was proposed.

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## 1. Introduction

The sulfur compounds in the fuels cause acid rain and emission of SO<sub>x</sub> in the air after fuel combustion, which are dangerous for human and environmental health [1–3]. In order to eliminate the sulfur of fuels, severe environmental rules have been legislated all over the world [4,5]. The usual hydrodesulfurization (HDS) is well known to effectively treat sulfur-containing hydrocarbons at an appropriate industrial operating conditions; However, HDS requires high hydrogen pressures at high temperatures for deep desulfurization of some substituted benzothiophenes (BTs) and dibenzothiophenes (DBTs) to reach ultra-low sulfur fuels [6–8]. Therefore, some further methods such as extractive desulfurization [9], biodesulfurization [10], adsorptive desulfurization [11] and oxidative desulfurization (ODS) [12–15], have been introduced as

complementary processes to HDS for ultra-deep desulfurization. Among them, the ODS process is now nearing commercialization which is able to deeply desulfurize aromatic sulfur compounds under moderate reaction conditions and using H<sub>2</sub>O<sub>2</sub> having lower price than H<sub>2</sub> in HDS [16,17]. In the ODS process, at the first stage, sulfur compounds are oxidized to the sulfones products by a proper catalyst and oxidant. Then, the sulfones are extracted from the oil phase by an extractive solvent or solid adsorbent [18,19]. Recently, the use of several designed Ionic liquids (ILs) as an extractive solvent [20–22], oxidation catalyst [8,23] or both catalyst and extractive reagent [1,4,23] has been found to be highly effective in ODS process. The beneficial properties of ILs such as having a good ability to extract thiophenic compounds, immiscibility with the oil phase and thermal stability with a wide range of liquid temperature, have raise the consideration of ILs in ODS Process [24]. Furthermore, the combination of extractive and catalytic functions of ILs has been demonstrated to be an efficient and cost-effective method for ODS process [20,25,26]. For instance, [Bpy]

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FeCl<sub>4</sub> [27], [Otbim]CH<sub>3</sub>COO [28], [C<sub>4</sub>mip]FeCl<sub>4</sub> [29], [Hnmp]HCOO [30], [C<sub>5</sub>H<sub>9</sub>NO]FeCl<sub>3</sub> [31] and [C<sub>4</sub>mim]Cl/ZnCl<sub>2</sub> [32] have been used simultaneously as a homogenous catalyst and extracting solvent in ODS process. Above-mentioned ILs efficiently produce high active oxidizing agents by reacting with H<sub>2</sub>O<sub>2</sub> oxidant due to Lewis or Bronsted acidic properties [29]. Li et al. [5,31] designed and prepared some appropriate ILs of C<sub>5</sub>H<sub>9</sub>NO.FeCl<sub>3</sub>, C<sub>5</sub>H<sub>9</sub>NO.ZnCl<sub>2</sub> and C<sub>5</sub>H<sub>9</sub>NO.SnCl<sub>2</sub> for ODS process using H<sub>2</sub>O<sub>2</sub> as oxidant. Specially, C<sub>5</sub>H<sub>9</sub>NO-FeCl<sub>3</sub> having a low viscosity efficiently extracted the thiophenic sulfur compounds by both NMP rings and FeCl<sub>3</sub> groups [5,31]. Furthermore, FeCl<sub>3</sub> provided a higher proficiency to catalyze the reaction of H<sub>2</sub>O<sub>2</sub> to OH radicals [31]. However, the high consumption of expensive ILs and difficult recovery of them as well as the oil loss problem, were some disadvantages of homogenous ILs in ODS. In the recent researches, the immobilization of ILs on some solid supports has been introduced to decrease the required amount of expensive ILs in the process, facilitate the separation of catalyst from the reaction media, and to realize the application of them in the continuous and commercial reactors [33–38]. A high DBT desulfurization was achieved using supported [Bmim]FeCl<sub>4</sub>/SiO<sub>2</sub> [33], [Pmim]FeCl<sub>4</sub>/MCM-41 [34] and [Pmim]FeCl<sub>4</sub>/SBA-15 [35] catalysts with [Omim]BF<sub>4</sub> as an extractive solvent in ODS process. However, the regeneration of [Omim]BF<sub>4</sub> solvent in the mentioned heterogeneous systems would increase the process cost. Then, more active supported ILs have been designed and employed in the ODS without using any extractive solvent. The supported catalysts of [Bmim]<sub>12</sub>PW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> [36], [Bmim]<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> and [C<sub>16</sub>mim]<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub> [37] were referred to be high active in ODS process using H<sub>2</sub>O<sub>2</sub> as oxidant; These recyclable catalysts could adsorb the oxidation products from the oil phase, therefore no further extractive solvent was added in ODS process. However, the supporting of ILs on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, commercial support, has not been reported in the ODS process. There are only a few report describing supported IL on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for the other desulfurization processes namely gas phase desulfurization of n-butyl mercaptan [39] and extractive desulfurization of DBT and butylmercaptan [40]. In this work, a novel recyclable supported IL composed of NMP.FeCl<sub>3</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for the first time was synthesized, characterized and its ODS performance was investigated. FeCl<sub>3</sub> based IL had beneficial Lewis acidic properties to generate active oxidizing agent of OH radicals from hydrogen peroxide [31]. The aims of NMP.FeCl<sub>3</sub> supporting on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in this study have been the reduction of IL usage, facilitating the separation of the prepared solid catalyst from oil, and improving the ODS performance without adding any extractive solvent. The effects of process variables and catalyst recycling were also investigated.

## 2. Experimental

### 2.1. Materials

N-methyl-2-pyrrolidone (NMP), Anhydrous Iron (III) Chloride (FeCl<sub>3</sub>) were purchased from Fluka chemical company. Benzothiophene (BT), Dibenzothiophene (DBT), 4,6-Dimethyldibenzothiophene (4,6-DMDBT), n-Octane, H<sub>2</sub>O<sub>2</sub> (30 wt. % aqueous solution), 2- methyl naphthalene, ethyl acetate, hexadecane, dichloromethane, and methanol were supplied from Merck chemical company, Germany.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was purchased from Fluka chemicals Ltd. All the chemical materials were used without further purification.

### 2.2. Preparation of the catalyst

The supported catalyst (NMP.FeCl<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) was prepared via a two-step method (Scheme 1); First, NMP.FeCl<sub>3</sub> IL was synthesized

via reacting FeCl<sub>3</sub> with NMP, then it was supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by a wet impregnation method. The preparation procedures were as follows: an adequate amount of anhydrous FeCl<sub>3</sub> was mixed with NMP (NMP/FeCl<sub>3</sub> molar ratio: 1/0.3) under a vigorous stirring for 3 h. To complete dissolution, FeCl<sub>3</sub> was added dropwise in several steps, while the reaction temperature was kept at 0 °C [31]. The impurities were eliminated from the produced IL using vacuum evaporation. The viscosity of the obtained IL was 28.5 mpa.s at 25 °C and its color was dark brown as shown in Scheme 1. A simple wet impregnation method was used to immobilize IL on the support [39,41]. For this purpose, NMP.FeCl<sub>3</sub> IL was diluted by dichloromethane in a 20 ml flask equipped with a condenser and then the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was added to the mixture and stirred vigorously for 3 h at room temperature. Afterwards, the solvent was evaporated by a vacuum rotary evaporator at 50 °C, then the solid was dried for 24 h under vacuum at 80 °C to obtain yellow supported IL (NMP.FeCl<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) (Scheme 1).

### 2.3. Catalyst characterization techniques

Fourier transform infrared (FTIR) spectra of the catalysts (KBr pellets) was recorded using PerkinElmer FT-IR spectrometer. X-ray diffraction (XRD) patterns of the catalysts was observed by Bruker D8 diffractometer with high-intensity Cu/K $\alpha$  radiation (1.5406 Å; 40 kV; 30 mA) and the step scan technique at 2 $\theta$  angles of 10–90°. Surface morphology of the catalyst was investigated using field emission scanning electron microscopy (SEM) by Tescan-VEGA, Czech. Energy dispersive spectroscopy (EDS) was taken to conduct the elemental analysis. Bruauer-Emmett-Teller (BET) method was utilized to measure the specific surface area and pore volume of the catalysts by means of Accelerated Surface Area and Porosity (ASAP 2010, Micromeritics). The pore-size distribution was assessed by adsorption branch of the isotherm with the Barrett-Joyner-Halenda (BJH) method. The oxidation products were characterized by GC-MS analysis (Varian, Saturn 2200, GC/MSD; VF-5 MS column, 30 m  $\times$  250  $\mu$ m id  $\times$  0.25  $\mu$ m; temperature program: 150 °C for 2 min, temperature rising of 10 °C/min up to 280 °C, 280 °C for 30 min; injector temperature: 280 °C). The amount of IL loading on the support material and its dissolution in the oil phase were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Spectro Arcos analyzer. The viscosity of the IL was measured by an Anton Paar AMVn viscometer.

### 2.4. Oxidative desulfurization method and analysis

The oxidative desulfurization experiments were performed in a 25 mL glass batch reactor equipped with a condenser, magnetic stirrer and a water bath for temperature control at atmospheric pressure. The model oil containing DBT in n-octane (containing 500 ppmw sulfur) was prepared and used as the feedstock in the reactor. The prepared NMP.FeCl<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was added into the reaction mixture of model oil and H<sub>2</sub>O<sub>2</sub> under vigorous mixing (stirring speed of 1000 rpm) at a constant temperature. After a specified reaction time, the sample of oil phase was taken out for GC analysis. The oxidation of sulfur compounds was evaluated by Agilent 7890A gas chromatograph (Manufactured by Agilent Co. Ltd.) using a flame ionization detector (GC-FID). Hexadecane was used as internal standard for ODS efficiency measurements. A HP-5 capillary column (30 m length and 0.32 mm inner diameter) was used for separation. N<sub>2</sub> was used as carrier gas at a flow rate of 5 mL/min. The column temperature was elevated with the rate of 10 °C/min from 200 up to 280 °C and then kept constant for 5 min. The temperatures of injector and detector were set at 280 and 300 °C, respectively, and the injection volume for all samples was 1  $\mu$ L.

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