



# Graphene-like boron nitride anchored Brønsted acid ionic liquids as metal-free catalyst for advanced oxidation process

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## ABSTRACT

Catalytic oxidation of aromatic sulfur compounds for separation from fuel oils has turned to be an important theme in environmental protection. However, most current reports focused on metal-based catalysts, resulting in high costs and potential secondary pollution to fuel oils. In this work, three metal-free Brønsted acid ionic liquids were prepared and anchored onto graphene-like hexagonal boron nitride (G-h-BN) to gain metal-free, heterogeneous catalysts. The heterogenization process not only provided convenience to recycling of the catalysts, but also supplied a sharply decreased ILs dosage. Notably, the prepared catalyst [Bmim]<sub>2</sub>H<sub>2</sub>PO<sub>4</sub>/G-h-BN held the best catalytic activity, a ~100% of catalytic activity can be gained in catalytic oxidation of 4,6-dimethyldibenzothiophene (4,6-DMDBT), which has been regarded as the most stubborn sulfide in industrial hydrodesulfurization (HDS). It was also found that distractors in fuels showed almost no influence on catalytic oxidation of 4,6-DMDBT. Besides, the catalytic oxidation product was also investigated to propose a possible reaction mechanism. The heterogeneous metal-free catalyst were recycled for 5 times without significant decrease in catalytic performance.

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## Introduction

Advanced oxidation processes (AOPs) have been regarded as an efficient strategy in removing organic pollutants in water, fuel oils and some other media for environmental remediation [1–3]. The pathway can be operated at near-ambient temperature and pressure, which is an economical method from both the fundamental and a technical points of view [1,2]. Among all AOPs, catalytic oxidation of sulfur compounds in fuel oils is an important one (Oxidative desulfurization, ODS), because of the combustion of sulfides in fuel oils will result in serious air pollution with the emission of SO<sub>x</sub> but hydrodesulfurization (HDS) process is less active to aromatic sulfur compounds and requires harsh operating conditions [4,5]. A core topic in the ODS process is seeking for a proper catalyst with high activity.

Up to date, diverse catalysts, such as ionic liquids (ILs) [6–9], organic acids [10], polyoxometalates [11–13], and metal oxides [14–17], etc., have been developed in ODS systems. Among those

reported highly-active catalysts, ILs, especially task-specific ILs (TSILs), have gained increasing attentions due to their excellent dissolving capacity to both inorganic and organic compounds, adjustable acidity, high stability, etc. However, most current reported TSILs for ODS are metal-based ones, resulting in secondary pollution to fuel oils and higher costs. To settle this issue, a small amount of reports have been focused on metal-free TSILs, especially acidic TSILs. The reason that acidic TSILs have been developed is because of the Lewis alkalinity of sulfides in fuel oils. Zhao and his co-authors reported utilization of [Hnmp]BF<sub>4</sub> as the extractant and catalyst for ODS and a ~100% catalytic can be gained [18]. Lv presented a [Hnmp]HCOO TSIL for ODS with satisfying catalytic activity [19]. However, giving an insight to previous reports, an inevitable shortage is that the large consumption amount of TSILs (Table 1), resulting in a higher costs. The large consumption amount of TSILs mainly originates from the poor exposure and low contact area between TSILs and reactants. Additionally, the homogenous catalyst also struggles from separation difficulty, leading to recycling disadvantages.

To settle this problem, heterogenization of TSILs has been considered as an efficient strategy for constructing heterogeneous catalyst. The heterogenization process can hold the both advantages of high catalytic activity of TSILs and recycling convenience

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**Table 1**  
Catalytic performance of Acidic TSILs in previous reports.

Entry	Catalyst	Sulfur compounds	Catalytic activity	Amount of catalyst	REF
1	[BMIM][HSO <sub>4</sub> ]	4,6-DMDBT	~80%	$V_{\text{modeloil}}/V_{\text{IL}} = 2:1$	[37]
2	[EimC <sub>4</sub> SO <sub>3</sub> H]NTf <sub>2</sub>	DBT	>99%	$m_{\text{modeloil}}/m_{\text{IL}} = 2:1$	[38]
3	1-(2-methoxy)ethyl-3-carboxymethyl imidazolium bis(trifluoromethanesulfonyl) imidate	DBT	>99%	$V_{\text{IL}} = 1 \text{ mL (1 g oil)}$	[39]
4	[Hnmp]HCOO	4,6-DMDBT	~80%	$V_{\text{IL}}/V_{\text{modeloil}} = 1:10$	[19]
5	[Hnmp]BF <sub>4</sub>	DBT	100%	$V_{\text{modeloil}}/V_{\text{IL}} = 1:1$	[18]
6	[HCPL][TFA]	DBT	100%	$m_{\text{modeloil}}/m_{\text{IL}} = 1:1$	[40]
7	[BMIm]HSO <sub>4</sub>	DBT	100%	$m_{\text{IL}} = 3 \text{ g (5 mL oil)}$	[41]
8	[(CH <sub>2</sub> ) <sub>2</sub> COOHmim][HSO <sub>4</sub> ]	4,6-DMDBT	95.1%	2.5 mmol	[42]
9	[Bmim]H <sub>2</sub> PO <sub>4</sub> /G-h-BN	4,6-DMDBT	100%	$m(\text{catalyst}) = 0.05 \text{ g (} m_{\text{IL}} = 0.0025 \text{ g, 5 mL oil)}$	This work

of supports. Currently, alumina [20], mesoporous silica [21], metal organic frameworks (MOFs) [22] and carbon nanotubes [23], etc. and some other materials with high specific surface areas have been widely applied in heterogenization of TSILs [24–26]. Although these supports provide convenience in separation, the less exposed active sites drives the heterogeneous catalysts are less than the original homogeneous ones. Accordingly, preparation of a satisfying catalyst with durative high activity and favorable recycling ability is rather important. More recently, layer structural materials have been found to be a potential option because of their high SSAs and special layer-structures, keeping them away from easily-blocked porous structure [27–29]. Among all those layered materials, graphene-like hexagonal boron nitride (G-h-BN), known as “white graphene”, has been regarded as a favorable one. Compared with graphene, G-h-BN holds better thermal-stability and resistance to chemical corrosion. Indeed, G-h-BN has been widely employed as supports for synthesizing heterogeneous catalysts with excellent catalytic activity and promising durability [30–36].

In this work, we presented three metal-free TSILs ([Bmim]H<sub>2</sub>PO<sub>4</sub>, [Bmim]HSO<sub>4</sub> and [Bmim]HCOO), and were anchored onto G-h-BN with rather high specific surface areas to obtain heterogeneous catalysts. The as-gained metal-free catalysts were carefully characterized by a series of analysis methods. The heterogenization process not only provided recycling performance to the catalysts, but also impelled the catalysts to be a more reactive species than original TSILs. What is noteworthy is that the prepared catalysts showed high catalytic activity to 4,6-DMDBT, which has been long regarded as a stubborn sulfides in HDS. Moreover, the catalytic ability of [Bmim]H<sub>2</sub>PO<sub>4</sub>/G-h-BN was hardly affected by distractors, giving a potential practical application. The prepared most active catalyst were recycled for 5 times without significant decrease in catalytic performance.

## Experimental

### Materials

Boric acid (H<sub>3</sub>BO<sub>3</sub>, A.R. grade), urea (CO(NH<sub>2</sub>)<sub>2</sub>, A.R. grade), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30 wt.%), *n*-octane (A.R. grade), methanol (A.R. grade), methane acid (HCOOH, 98%), sulphuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 85%), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, AR grade), tetrachloromethane (CCl<sub>4</sub>, AR grade), and 1-N-Butyl-3-Methylimidazolium Chloride ([Bmim]Cl) were obtained from Shanghai Sinopharm Chemical Reagent Co., Ltd., Tetradecane (99%), dibenzothiophene (DBT, 98%), benzothianaphthene (BT, 99%), 3-methylbenzothianaphthene (3-MBT, 96%), and 4,6-dimethyldibenzothiophene (4,6-DMDBT 97%) were purchased from Sigma-Aldrich without further purification.

### Catalysts preparation process

#### Synthesis of G-h-BN

Typically, 10 mmol of H<sub>3</sub>BO<sub>3</sub> and 300 mmol of urea were placed in a 100 mL of beaker, and a mixture of DI water and methanol (volume ratio of 1:1) was added subsequently. Afterwards, the breaker was heated to 60 °C and kept at this temperature until the total removal of solution to obtain a solid mixture. Then, the mixture was transferred to a tube furnace and heated to 900 °C with a ramping rate of 5 °C/min; additional two hours heating at this temperature was employed. The heating process was carried out under a N<sub>2</sub> atmosphere protection. Finally, the white powder G-h-BN was obtained.

#### Synthesis of Brønsted acid ionic liquids

A dichloromethane solution by dissolving 8.7335 g of [Bmim]Cl in 75 mL of CH<sub>2</sub>Cl<sub>2</sub> followed by adding equimolar phosphoric acid dropwise with magnetic stirring continuously. After stirring for 24 h, the solvent and the reaction product (HCl) were removed in a rotary evaporator. The obtained colorless viscous liquid was [Bmim]H<sub>2</sub>PO<sub>4</sub> after drying in a vacuum at 50 °C overnight. [Bmim]HSO<sub>4</sub> and [Bmim]HCOO were synthesized with the same method by replacing H<sub>3</sub>PO<sub>4</sub> with H<sub>2</sub>SO<sub>4</sub> and HCOOH, respectively.

#### Synthesis of heterogeneous catalysts

0.01 g of [Bmim]H<sub>2</sub>PO<sub>4</sub> and 0.19 g of G-h-BN were mixed with 20 mL of ethanol as solvent. Afterwards, the mixture was kept magnetic stirring vigorously for 24 h in an oil bath with a reflux condenser at 85 °C. After stirring, the mixtures were dried at 150 °C after filtering by a vacuum suction filtration. The obtained white powder was [Bmim]H<sub>2</sub>PO<sub>4</sub>/G-h-BN with a [Bmim]H<sub>2</sub>PO<sub>4</sub> loading amount of 5 wt.%. [Bmim]HSO<sub>4</sub>/G-h-BN and [Bmim]HCOO/G-h-BN with loading amount of 5 wt.% were synthesized with the same method, respectively.

### Characterization

A Nicolet Nexus 470 Fourier transform infrared spectrometer with KBr pellets at room temperature was employed for determination of Fourier transform infrared (FT-IR) spectra. Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) were determined using BaSO<sub>4</sub> as the reflectance standard material on a Shimadzu UV-2450, which is equipped with spherical diffuse reflectance accessory. An ESCALAB250 (Thermo VG, UK) was used for recording X-ray photoelectron spectroscopy (XPS). X-ray diffraction (XRD) was performed on a D8 Advance X-ray diffraction using Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) in the range of  $2\theta = 10\text{--}80^\circ$ . The Raman spectra was recorded by a Thermo Scientific DXR Smart Raman spectrometer with an excitation light of 532 nm. Morphology characterization (Transmission electron microscopy [TEM]) was carried out with a Hitachi H-700 Transmission electron microscope. The final products of oxidative desulfurization pro-

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