



# Polymeric cation and isopolyanion ionic self-assembly: Novel thin-layer mesoporous catalyst for oxidative desulfurization

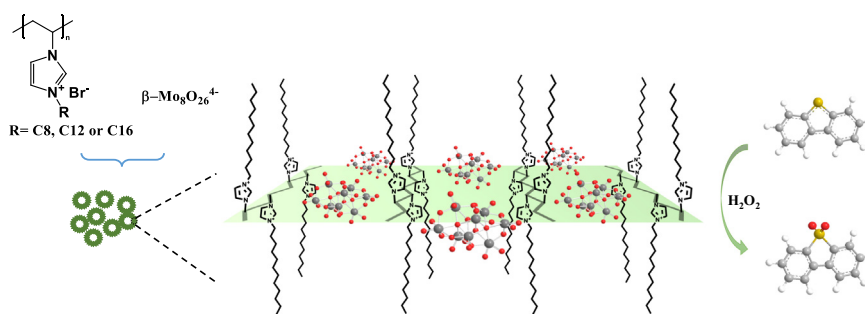
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## HIGHLIGHTS

- PIL were synthesized and assembled with  $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$  into mesoporous catalyst.
- The PIL/POM hybrid was used as catalysts for oxidative desulfurization of fuel.
- Real diesel was used for the exact evaluation of oxidative performance.
- The catalyst showed high efficiency and durability in real diesel treatment.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this work, poly(ionic liquid)s (PIL), namely poly-[1-vinyl,3-alkylimidazolium] bromine (PVABr) with different length of monomer carbon chain have been synthesized and assembled with  $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$  into novel interlinked thin-layer nano-wire mesoporous material. The resulting POM/PIL hybrids were characterized by different techniques and utilized to catalyze the oxidative desulfurization (ODS) of thiophenic compounds with  $\text{H}_2\text{O}_2$  as oxidant. Detailed experiments for ODS of synthesized diesel were carried out to investigate the influence of some important factors, including reaction temperature, molar ratio of  $\text{H}_2\text{O}_2/\text{S}$ , catalyst dosage and sulfide species. As for the desulfurization of hydrogenated diesel, it was observed that almost all of the original sulfur compounds in diesel could be completely converted and a further solvent extraction with methanol as extractant led to the deep sulfur removal. The catalyst could at least be reused for six times without noticeable changes in catalytic performance. The results demonstrate that the mesoporous isopolyanion-based polymeric hybrid is an efficient, durable and sustainable catalyst for ODS of diesel fuel.

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## 1. Introduction

Sulfur compounds in diesel fuel are converted into  $\text{SO}_x$  when combusted and further reduce combustion efficiency and increase emission of particulates. In the recent years, the deep desulfurization of fuel oils has attracted worldwide interests due to the

growing environmental concern [1]. Stringent regulations have been established in many countries to cut the S-content of diesel fuel down to 10 ppm which put forward a challenge to the refine industry [2]. Though the traditional hydrodesulfurization (HDS) can remove various sulfur compounds, it is extremely costly and difficult to achieve deep sulfur removal due to its ineffective removal of refractory thiophenic compounds [3]. Currently, alternative or supplementary desulfurization approaches based on oxidation [4–6], extraction [7,8], adsorption [9,10], etc., are wildly researched and oxidative desulfurization (ODS) is regarded as

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one of the most promising [11]. The refractory heterocyclic sulfur compounds are readily oxidized into their corresponding sulfones [12], and in subsequent operation, the oxidized compounds can be removed by extraction, adsorption, distillation or decomposition [2,13,14].

Various oxidants have been explored for ODS, including  $H_2O_2$ , molecular oxygen, organic peroxide, etc. Among them,  $H_2O_2$  with the advantages of relatively higher activity, high percentage of active oxygen, no toxic by-product and cheap price is considered as a suitable oxidant [15,16]. However, the utilization of  $H_2O_2$  aqueous solution as oxidant with heterogeneous catalysts makes the process a liquid-liquid-solid three-phase reaction [4]. Thus, the additions of co-solvent will inevitably enhance the reaction efficiency by extracting sulfur compounds and  $H_2O_2$  in polar solvent phase to make a better contact with catalysts [17,18]. But the use of solvent in reaction is environmentally unfriendly and may lead to the loss of catalysts.

In the recent years, the use of ionic liquids (ILs) as solvents as well as catalysts and extractants which lead to a biphasic liquid system can largely enhance the ODS efficiency and avoid the use of organic solvent in reaction system [15,19–21]. However, the utilization of ILs is still limited by the high cost and difficulty of recovery. On the contrary, the heterogeneous catalysts are more suitable for industrial process [22]. Among them, polyoxometalates (POMs) are probably the most common used catalysts for oxidation with  $H_2O_2$  due to their unique redox feature [23,24]. Without addition of reaction media, the POMs should firstly activate the  $H_2O_2$  in water phase before the oxidation of sulfur compounds in oil phase [25]. Thus, traditional POMs always suffer from inferior activity without reaction media due to their inherent hydrophilicity [23]. More recently, amphiphilicity POMs as phase-transfer catalysts were widely explored by introduce of functionalized organic cations [26]. The organic cations, commonly with long carbon chain, may act as phase-transfer agent to improve the affinity to oil phase [27]. Good results were led to by employing different kinds of cations including quaternary amine [27–29], quaternary phosphonium [30,31] and imidazolium [32,33], etc.

Poly(ionic liquid) (PIL), a special class of polyelectrolytes expanding classical property profiles, have been researched for years. The unique properties of functionalized ILs can be incorporated into the polymer, giving rise to the polymeric materials [34]. PIL possesses various advantages including tunable solubility, designable structure and chemical and thermal stability which make them suitable for catalytic application [35]. High loading exchange of functionalized counterion allows for further variation of properties. Up to date, some pioneer work was reported for the PIL based catalysts. Jeon et al. synthesized linear polymer-support methylselenites for the oxidative carbonylation of aniline [36]. Pourjavadi et al. prepared functionalized PIL coated magnetic nanoparticles to form easily separable Brønsted acid catalysts [37]. In Wang's group, several kinds of mesoporous cross-linked ionic copolymer were synthesized by the direct polymerization of different kinds of IL monomer [38,39]. After that, they reported the preparation of hierarchical PIL through an ionothermal route [40]. More recently, hierarchical meso-macroporous PIL monolith was prepared derived from a single soft template [41]. In Wang's work, task-specific anion species were then introduced to the as-prepared mesoporous polymeric materials through ion exchanged to provide different catalytic effects. On the other hand, Biboum et al. synthesized several PILs and assembled with a multielectronic-process sustaining POM into novel nanomaterials [42]. Similarly, Leng et al. prepared polymeric hybrids by anion-exchange of designed water-soluble PIL with phosphotungstic acid in water phase [43]. However, the microstructures of the materials synthesized by this direct precipitation approach were not revealed. Zhao et al. reported a template-free synthetic route

towards PIL complexes via *in situ* ionic complexation of two kinds of polymer [44]. The resulting PIL complex with spontaneous mesoporosity was utilized as catalytic support of copper salts.

Inspired by these reports, we considered it interesting to test catalysts with POMs supported on PIL in the ODS of diesel fuel with  $H_2O_2$  aqueous solution as oxidant. The ionic self-assembly of the polymerized multivalent cations and polyoxoanions may offer the material quite special natures due to the formation of large ionic bond network. In this work, several PILs, namely poly-[1-vinyl, 3-alkylimidazolium] bromine (PVABr) with different length of carbon chain were synthesized and directly assembled with molybdenum isopolyacid ( $[\beta-Mo_8O_{26}]^{4-}$ ) into PIL/POM catalysts poly-[1-vinyl, 3-alkylimidazolium] $Mo_8O_{26}$  (alkyl = C8, PVOMo; alkyl = C12, PVDMo; alkyl = C16, PVHMo). The resulting mesoporous materials formed by PIL cation and isopolyanion ionic self-assembly were characterized by different techniques and utilized as catalysts for the ODS of a synthesized diesel. Significant factors including composition of PILs, reaction temperature, molar ratio of  $H_2O_2/S$  and catalyst dosage upon the ODS process were investigated in detail. The catalysts possessed excellent sulfur removal performance with low catalyst dosage. Following that, the ODS were applied to a hydrogenated diesel, the species and concentration of the S-compounds were measured, and the reusability of the catalyst was also tested.

## 2. Experimental

### 2.1. Materials and chemicals

n-Octyl bromide, n-dodecyl bromide, n-hexadecyl bromide, hydrogen peroxide (30%wt), benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethylbenzothiophene (4,6-DMDBT) were purchased from Aladdin Reagent Co. Ltd. 1-Vinylimidazole were purchased from Tianjin Heowns Biochem LLC. Ammonium heptamolybdate tetrahydrate ( $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ ), ethanol (EtOH), methanol and ethyl acetate (EA) were purchased from Tianjin Jiangtian Chemical Technology Co., Ltd. Hydrogenated diesel and low-sulfur diesel were provided by SINOPEC Tianjin Petrochemical Co., Ltd.

### 2.2. Synthesis of ionic liquid

The ILs monomers in this work were prepared according to the literature with some modification [45]. In short, 0.05 mol 1-vinylimidazole and 0.055 mol alkyl bromide were charged into a flask equipped with a reflux tube. The mixture was stirred at 60 °C for 24 h under the  $N_2$  atmosphere. After the reaction, the IL products were purified by EtOH/EA recrystallization or successive EA extraction based on the phase state of the ILs, and then dried under vacuum at 60 °C for 24 h.

### 2.3. Polymerization of IL monomer

In a typical procedure, 3.0 g 1-vinyl-3-alkylimidazolium bromide was charged into a Schlenk flask and dried under vacuum overnight. Then, AIBN (3.5% mol. eq.) and 15 ml EtOH were charged into the flask. The flask was degassed with five vacuum/nitrogen cycle, and subsequently immersed in a preheated water bath at 70 °C. The polymerization was allowed to proceed under the protection of  $N_2$  for 24 h before the reaction was cooled to room temperature. Following that, the polymer was precipitated in pure water, then filtered, washed with water and dried at 60 °C for 12 h under vacuum.

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