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Polymer-supported ionic liquids: Synthesis, characterization and application in fuel desulfurization

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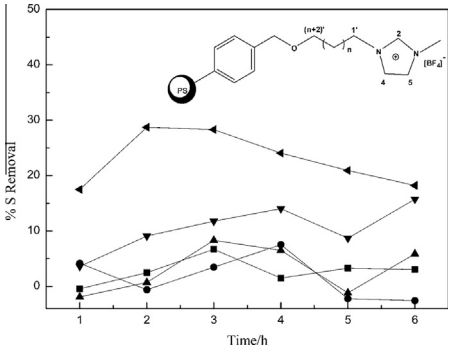
HIGHLIGHTS

- Immobilization of ILs on Merrifield resin by covalent binding.
- The morphology and surface shape of Merrifield resin were affected greatly by the immobilized ILs.
- The immobilized ILs showed better percent sulfur removal (up to ⩾30%) than Merrifield resin.

GRAPHICAL ABSTRACT



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ABSTRACT

Ionic liquids (ILs) were considered to be immobilized on solid supports to overcome the problems of the pure ILs in fuel desulfurization. Take Merrifield resin as solid support, four polymer-supported imidazole ionic liquids (PSILs) with different lengths of alkyl chain linkers were prepared by covalent binding and the structures were characterized by Fourier transform infrared (FTIR), elemental analysis, ^{13}C solid state magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectroscopy, scanning electron microscope (SEM) and energy dispersive spectrometer (EDS). The results suggested the series PSILs had been obtained. Then, the PSILs were investigated to remove thiophene (TS) or dibenzothiophene (DBT) from model gasoline (cyclohexane/TS or DBT) under certain conditions: (1) PSILs showed better sulfur removal ability than Merrifield resin, PS[unmim][BF_4] showed the best percent sulfur removal which could up to ⩾30% due to the longest alkyl chain linker and the smallest particles. (2) The sulfur removal selectivity of DBT was better than TS for its higher density aromatic π-electrons. The Sips adsorption isotherms model fitted the adsorption experimental data of PS[unmim][BF_4] for TS and DBT at 303.15 K best. Finally, the adsorption mechanism was discussed.

1. Introduction

In recent years, increasing attention has been paid to the deep desulfurization of fuels due to more stringent environmental regulations [1,2]. The emission of SOx and sulfate particulate in fuels combustion process contributes to acid rains, global warming effect, and air pollution [3,4]. So it is urgent to remove sulfides from fuels. Industrially, the removal of simple aliphatic sulfides, such as mercaptane and thioether, could be achieved by catalytic hydrodesulfurization (HDS) [5,6]. However, it is a big challenge to remove aromatic sulfides such as TS, DBT and their alkyl derivatives owing to catalyst surface interactions and stereo hindrance [4,7–11], while these aromatic sulfides take a big part of the sulfides in fuels. Ionic Liquids (ILs) become "designer solvents" and attract significant attentions owing to their unique and useful properties [1,3,12,13], especially, ILs which have aromatic structures show remarkable sulfur extracting ability attribute to the π-complexation with aromatic

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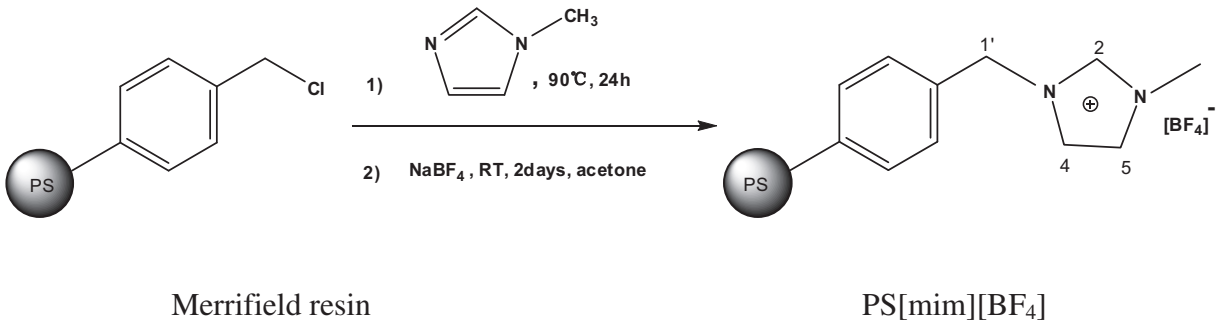
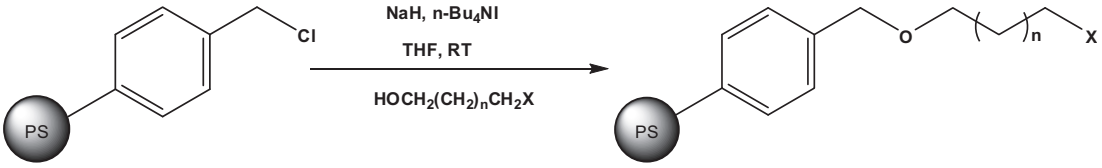


Fig. 1. Synthesis of PS[mim][BF_4].

sulfides [12,14–17]. However, the high cost, viscosity and difficulty in recycling restricted their industrial application [5,18,19]. So ILs were considered to be immobilized on solid supports, such as silica, molecular sieves, chitosan and polystyrene resin to avoid these limitations [20–24]. At present, immobilized ILs have been used for hydroformylation, hydrogenation, Friedel–Crafts alkylation and cycloaddition reactions [18,20,25,26], but few reports were about immobilized ILs on fuel desulfurization. ILs-based extractive desulfurization and immobilized ILs phase ([1-butyl-3-methylimidazole][Cl]/$ZnCl_2$ supported alumina) absorptive desulfurization



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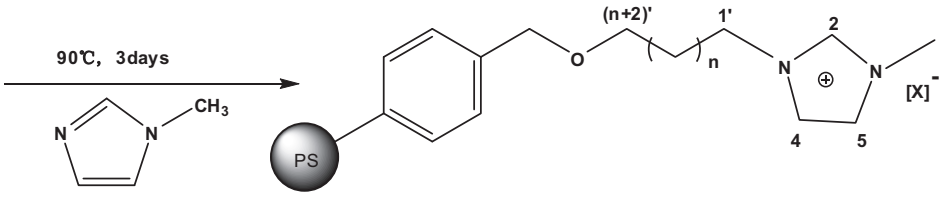
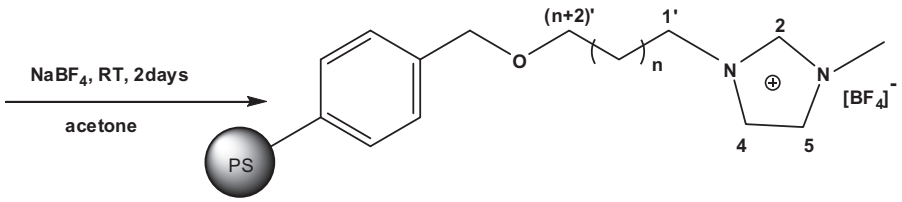
X=Cl, n=4: resins 1b
X=Br, n=9: resins 1c



X=Cl, n=1: PS[pmim][Cl]
X=Cl, n=4: PS[hmim][Cl]
X=Br, n=9: PS[unmim][Br]



n=1: PS[pmim][BF_4]
n=4: PS[hmim][BF_4]
n=9: PS[unmim][BF_4]

Fig. 2. Synthesis of the PSILs with different lengths of alkyl chain linkers.