

## Selective removal of organic sulfur in fuels

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### **Abstract:**

*In a series of studies on precleaning technology based on sulfur forms, an advanced desulfurization process that can be carried out under mild conditions has been developed for the production of clean sulfur-free fuel. The selectivity of adsorption of various metal compounds to thiols, sulfides, and thiophenes in a model fuel at room temperature was investigated. Among the studies metal compounds, lead oxide showed the highest selectivity to aliphatic and aromatic thiols. For the extraction of thiophenic sulfur selectively from the fuel, halogen-free ionic liquids with different alkyl chain lengths were prepared. The extraction yield of dibenzothiophene increased linearly with an increase in the length of alkyl chains and mass ratio of the ionic liquid to the model fuel.*

**Keywords:** Organic sulfur, Extraction, Adsorption, Coal extract, Desulfurization

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### **1. Introduction**

Hydrodesulfurization is widely used in oil refining. It is carried out at high temperature with high-pressure hydrogen along with catalysis. Oxydesulfurization, in which organic sulfur is converted into sulfone using acetic acid and hydroperoxide by acid catalysis, causes the oxidation of organic compounds. Alkylation-precipitation and photo-oxidation have been reported to be used for desulfurization, despite disadvantages, such as the use of expensive alkylation reagents and slow reaction rates.

The objective of this study is to develop an advanced desulfurization process that can be carried out under mild conditions, such as atmospheric pressure and room temperature without the need for pressurized hydrogen and a catalyst. The authors have been investigating the selective removal of organic sulfur, taking into consideration the different forms of sulfur present in fuels. In the first, the selectivity of adsorption of various metal compounds to thiols, sulfides, and thiophenes in a model fuel was investigated. Secondly, halogen-free ionic liquids were prepared from alkylimidazoles and dialkylsulfates. The extraction behavior of organic sulfur from a model fuel using the ionic liquids is investigated. Coal extract prepared by using 1-methyl naphthalene was also used as the model fuel.

### **2. Experimental**

#### **2.1 Adsorption experiment**

Six kinds of reagents-PbO, CuO, BaO, CoO, ZnO and CdO were used to investigate the effect of different metals on adsorption. As organic sulfur reagents, 1-octanthiol, 1-butanethiol, benzothiol, diphenylsulfide, diphenylsulfide, diphenyldisulfide, and dibenzothiophene was used. n-Dodecane was selected as the baseline model fuel. The model fuels were prepared by dissolving the organic sulfur compounds in n-dodecane. The sulfur concentration was varied from 500 to 8800 ppm. The metal compounds were added to the model fuel in a sulfur/metal mole ratio ranging from 0.06 to 2.05. The model fuel containing organic sulfur and metal compound in a sealed glass flask was stirred by a magnetic stirrer. After a certain reaction time, the model fuel was filtered and separated into solid and liquid phases by aspiration. The recovered solid was repeatedly washed by toluene and then dried under vacuum conditions.

#### **2.2 Extraction experiment**

Ionic liquids were prepared by adding dialkyl sulfates to alkyl imidazoles according to the

method devised by Holbrey et al (2002). Dialkyl sulfates were added to alkyimidazoles in toluene and placed in an ice bath under a nitrogen atmosphere for 1 h. After the reaction, the solution was found to have separated into two phases. The upper phase, consisting of organic solvents, was recovered by decantation, and the lower phase, consisting of the ionic liquid, was washed several times with toluene. The ionic liquid phase was heated at 75°C, and aspiration was carried out to remove unreacted organic solvents.

The ionic liquids were mixed with the model fuel in a certain ratio and stirred for a certain time interval at room temperature. A gas chromatograph-mass spectrometer was used to determine the sulfur content in the fuel.

### 3. Results and Discussion

#### 3.1 Adsorption of sulfur by metal oxide

Fig. 1 shows the variation in the removal extent of organic sulfur with the different metal oxides and sulfur species. The concentrations of organic sulfur and metal oxide were 1000 ppm-S and  $2.2 \times 10^{-3}$  mol, respectively. Although every metal oxide failed to show appreciable adsorption of sulfide, disulfide, and thiophene, two metal oxides, PbO and CuO, showed a remarkable adsorption of thiol in the model fuel with removal extents of 100 and 20%, respectively. The effect of different lead compounds on thiol adsorption was investigated. Metallic lead and  $\text{Pb}(\text{CH}_3\text{COO})_2$  showed the removal extents of 40 and 15%, respectively.  $\text{PbCl}_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{PbSO}_4$ , and  $\text{PbS}$  showed no appreciable extent of sulfur removal.

The rate of adsorption of thiols on lead oxide depended on the length of alkyl chain and initial concentration of thiols (Mochizuki et al., 2008).

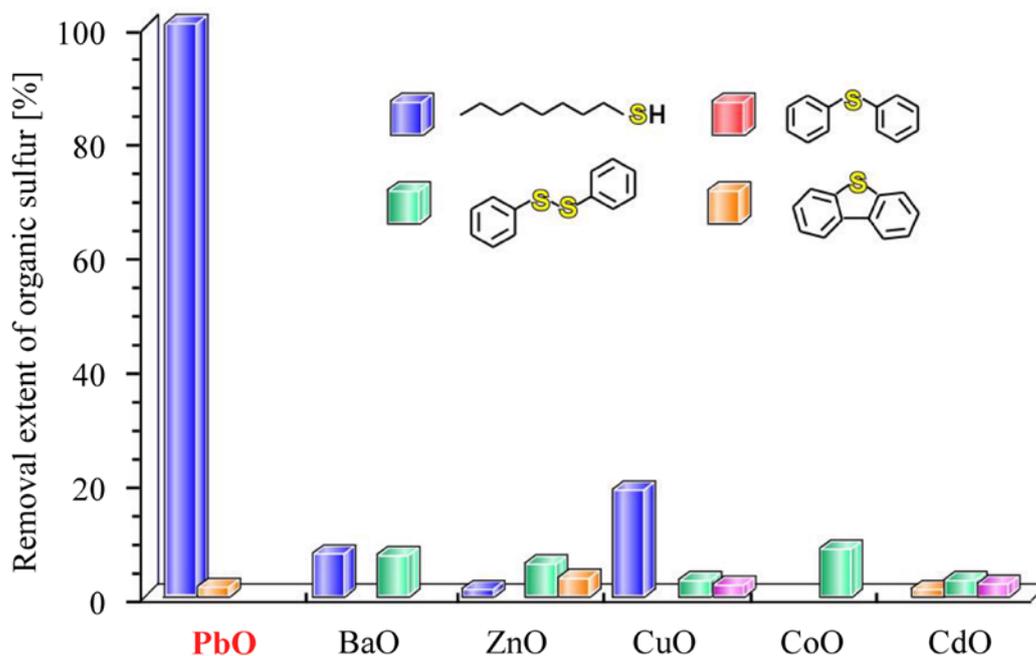


Fig. 1 Adsorption of sulfur by metal oxides

#### 3.2 Extraction of sulfur by ionic liquid

The selectivity to organic sulfur exhibited by the ionic liquids was investigated using dibenzothiophene, diphenylsulfide, and diphenyldisulfide and three types of ionic liquids, BEIMeEtSO<sub>4</sub> (1-butyl -3-ethylimidazorium ethyl sulfate), EEIMeEtSO<sub>4</sub> (1-ethyl -3-ethylimidazorium methyl sulfate), and BMIMeSO<sub>4</sub> (1-butyl -3-methylimidazorium methyl sulfate). While the extraction yield of

dibenzothiophene exceeded 15%, that of diphenyl sulfide and diphenyldisulfide remained in the range of 3–6%, as shown in Fig.2. Strong selective extraction of dibenzothiophene results from the  $\pi$ - $\pi$  interaction between the imidazolium and thiophene rings. The ionic liquids show significant  $\pi$ - $\pi$  interaction with the aromatic ring. The small extraction yield of diphenylsulfide and diphenyldisulfide may be due to the interaction of the ionic liquids with the phenyl groups.

The extraction yield of dibenzothiophene increased linearly with an increase in the alkyl chains and the mass ratio of the ionic liquid to the fuel. The effect of the change in the type of solvent was not appreciable, and dibenzothiophene was efficiently removed regardless of whether tetralin, benzene, or n-dodecane was used as the solvent (Mochizuki et al., 2008). Removal behavior of sulfur from the coal extract was also investigated by using the ionic liquids and metal compounds.

#### 4. Conclusions

It was demonstrated that PbO selectively adsorbed thiols in a model fuel at atmospheric pressure and room temperature. Although both aliphatic and aromatic thiols were completely adsorbed by PbO, the adsorption behavior depended on the structure and initial concentration of thiols. Dibenzothiophene was extracted from a model fuel at room temperature using the halogen-free ionic liquids. The extraction yield of dibenzothiophene increased linearly with the number of carbons of the alkyl group in the ionic liquids. When the mass ratio of the ionic liquid/model fuel was 1.0, dibenzothiophene was successfully extracted using MMIMeSO<sub>4</sub> with the yields of 70% after one round extraction.

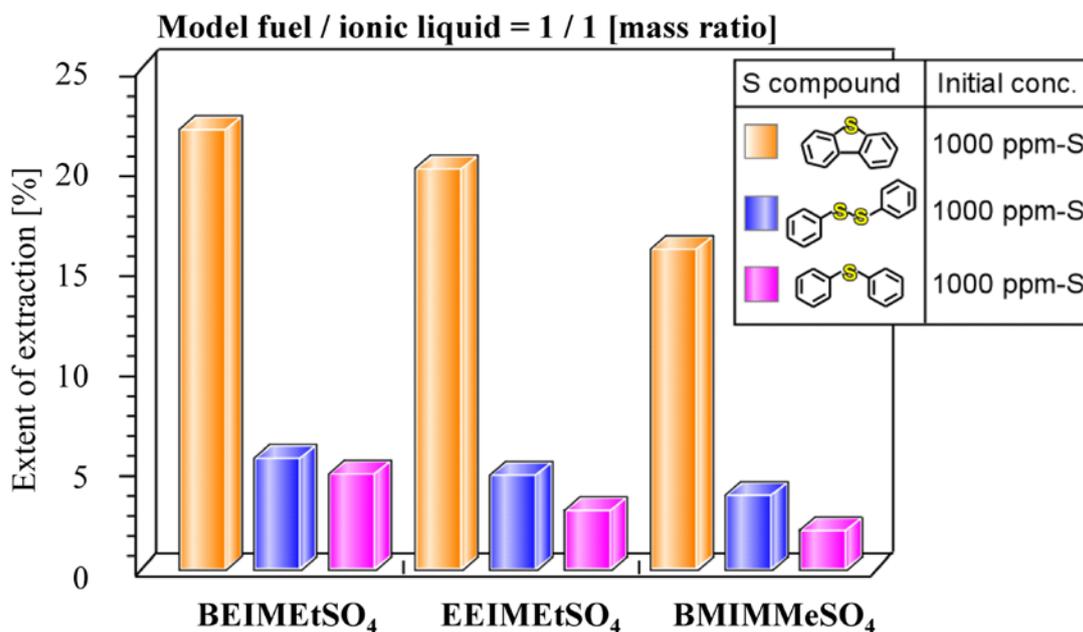


Fig. 2 Change in extraction yield with the sulfur forms and ionic liquids.

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