

## Oxidation of Thiophenes over Silica Gel in Hydrogen Peroxide/Formic Acid System\*

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**Abstract** Thiophene (C<sub>4</sub>H<sub>4</sub>S) and 3-methylthiophene(3-MC<sub>4</sub>H<sub>4</sub>S) are typical thiophenic sulfur compounds that exist in fluid catalytic cracking (FCC) gasoline. Oxidation of C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S were conducted in hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and formic acid system over a series of silica gel loaded with metal oxide. The silica gel loaded with copper and cobalt (1:1) oxide was found very active for the model compound oxidation using H<sub>2</sub>O<sub>2</sub>/formic acid, while the silica gel unloaded with metal oxide was less active. The sulfur removal rate of thiophenes was different as solvent was changed. And the conversion of C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S was improved at higher temperature, but reduced when olefin was added. The sulfur removal rate of model sulfur compounds was enhanced when the phase transfer catalyst emulsifier polyethylene glycol octyl phenyl ether or tetrabutylammonium bromide(TBAB) was added. The sulfur removal rate of simulated gasoline containing 524μg·ml<sup>-1</sup> sulfur reached 90%. Interestingly, in a H<sub>2</sub>O<sub>2</sub> and formic acid system with the addition of TBAB, a bromine substitution trend appeared in the oxidation of thiophenes, suggesting the influence of TBAB.

**Keywords** oxidative desulfurization, silica gel, thiophene, 3-methylthiophene

### 1 INTRODUCTION

Due to growing environmental concern to impact of sulfur oxides contained in engine exhaust emissions, sulfur content specifications in light oils are becoming more and more stringent worldwide<sup>[1,2]</sup>. The necessity of producing low sulfur fuels to meet new regulation mandates requires new desulfurization techniques. As for the current hydrodesulfurization (HDS) technology, higher temperature, higher pressure, larger reactor volume, and more active catalysts are unavoidable, and refiners begin to look for technology of oxidative desulfurization (ODS) under much milder conditions as an alternative or complementary technology to HDS for deep desulfurization.

The ODS process is generally consisted of two processes: the first step is oxidation of sulfur-containing compounds in fuels; the next step is removal of oxidized sulfur-containing compounds by liquid extraction. Oxidants can convert sulfur-containing compounds to much more polar oxidized species. In previous studies<sup>[3–12]</sup>, hydrogen peroxide was found to be effective in the oxidation of organic sulfur compounds normally contained in fuels and it appears as a promising oxidizing agent for the industrial desulfurization of light oils. The reactivity of sulfur compounds for oxidation is increased with electron density on sulfur atom. Otsuki *et al.*<sup>[8]</sup> reported that the thiophene and thiophene derivatives with electron densities of 5.696 to 5.716 on the sulfur atoms could not be oxidized at 50 °C, while benzothiophene with electron density equal to 5.793 and other benzothiophene and

dibenzothiophenes with higher electron densities could be oxidized.

Sulfur-containing compounds typically in FCC gasoline determined by gas chromatograph (GC) equipped with a flame photometric detector (FPD) are given in Table 1, showing that C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S are the major components. In this work, the oxidative desulfurization of C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S was studied in the hydrogen peroxide and formic acid system, particularly, the influence of the silica gel loaded with copper and/or cobalt oxide, solvent, temperature, olefin and phase transfer catalyst toward the oxidation of organic sulfur compounds.

**Table 1 Sulfur-containing compounds in FCC gasoline**  
(sample supplied by Shijiazhuang Refinery, China)

Sulfur-containing compound	Volume ratio, %
thiophene	10.77
methylthiophene	45.93
dimethylthiophene	25.17
trimethylthiophene	4.63
tetramethylthiophene	0.25
tetrahydro-thiophene	3.18
mercaptan	0.79
sulfide	1.18
benzothiophene	7.98

### 2 EXPERIMENTAL

#### 2.1 Materials

The silica gel loaded with metal oxide of

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1.25mmol·g<sup>-1</sup> prepared using dipping of 0.1—0.5mol·L<sup>-1</sup> acetic salt and baking at 200—600°C. The granularity and ratio surface area of loading silica gel were influenced by baking temperature and time. The organic solvents used in this study were formic acid, *N,N*-dimethylformamide (DMF), xylene(isomers) and hexane. The phase transfer catalysts (PTC) used were polyethylene glycol octyl phenyl ether [(CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>C—(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(O CH<sub>2</sub>CH<sub>2</sub>)<sub>10</sub>OH, *M*=646.86, emulsifier OP], sodium dodecyl benzene sulfonate (SDBS), tetrabutyl ammonium bromide(TBAB), polyglycol-400.

The chosen sulfur compounds were C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S, which were among those found more frequently in the light distillates from which commercial gasoline pools are produced. Hydrogen peroxide (30%), silica gel (SG-11, 45—75μm), Cu(Ac)<sub>2</sub>, Co(Ac)<sub>2</sub> and BaCl<sub>2</sub> were supplied by Tianjin Reagent Company. All the products were commercial reagent grade.

## 2.2 Procedure

The reaction mixtures were prepared adding a weighted amount of the selected sulfur compound into *n*-hexane. The elemental sulfur concentration was managed to be 524μg·ml<sup>-1</sup> for all the samples tested.

A sample of 50ml of reaction mixture and 2.5ml of formic acid and 0.1g of silica gel or silica gel loaded with metal were put in a 100ml three-necked flask equipped with a magnetic stirrer and a reflux condenser. The system was heated in a thermostatic bath under stirring at about 1500r·min<sup>-1</sup>. When the mixture reached the selected reaction temperature (40°C), 5ml of H<sub>2</sub>O<sub>2</sub> was then added and the reaction was started. Since the mixture was a heterogeneous system of three phases (an organic phase, an aqueous phase and solid phase), efficient mixing was necessary to ensure homogeneous dispersion of the phases.

To determine the initial and residual concentration of the selected sulfur compound in the organic phase, approximately 0.5ml aliquots of liquid samples were withdrawn from the reactor at fixed time intervals and after phase separation the organic phase was analyzed by HP 6890 GC equipped with FPD, using a SE-30 column of φ 0.32mm×30m. The main parameters were the following: carrier gas nitrogen at the flow rate of 2ml·min<sup>-1</sup>, oven temperature, 180°C, injector temperature at 200°C, detector temperature at 230°C and split ratio being 1/100.

## 3 RESULTS AND DISCUSSION

### 3.1 Evaluation of silica gel loaded with copper and/or cobalt oxide for oxidation of thiophenes

A series of experiments were performed to compare the activity of silica gel catalysts loaded with copper oxide and/or cobalt oxide for oxidation of C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S. The mixture of hexane solution of sulfur compounds and H<sub>2</sub>O<sub>2</sub>/formic acid settled

into three layers after oxidation: oil layer (top), aqueous layer (middle), solid layer (bottom). The conversion of C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S in oil layer is shown as the function of reaction time in Figs.1 and 2.

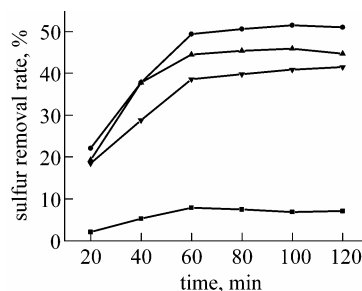


Figure 1 Oxidation of thiophene over silica gels loaded with metal oxide

■ unloaded with metal oxide; ● loaded with CuO and Co<sub>2</sub>O<sub>3</sub> (1 : 1); ▲ loaded with CuO; ▼ loaded with Co<sub>2</sub>O<sub>3</sub>

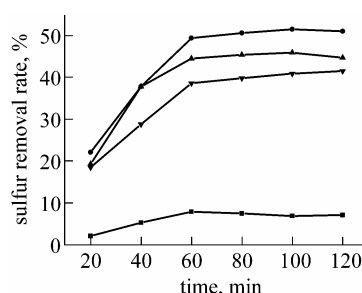


Figure 2 Oxidation of 3-methylthiophene over various silica gel loaded with metal oxide

■ unloaded with metal oxide; ● loaded with CuO and Co<sub>2</sub>O<sub>3</sub> (1 : 1); ▲ loaded with Co<sub>2</sub>O<sub>3</sub>; ▼ loaded with CuO

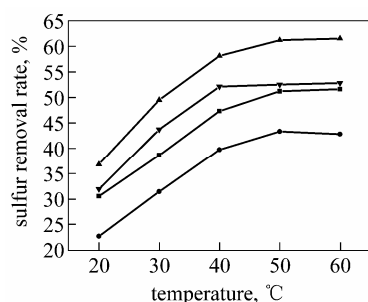
In the H<sub>2</sub>O<sub>2</sub>/formic acid system, it is clear that silica gel loaded with copper oxide and/or cobalt oxide is much better as compared to the silica gel without metal oxide loading. The sulfur removal rates are the same when *N,N*-dimethylformamide (DMF) be used as the extractant. There were no new peaks in GC-FPD analysis in the oil layer after oxidation, but precipitate occurs obviously in the aqueous layer when BaCl<sub>2</sub> is added. This phenomenon indicates that sulfur in C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S has been converted to SO<sub>4</sub><sup>2-</sup> in the oxidation.

### 3.2 Influence of solvent and temperature to oxidation of model sulfur compounds

Xylene (isomers) and hexane were the important hydrocarbon types constituting the matrixes of light distillates. Therefore, xylene and hexane were used as the organic solvents in the oxidation of C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S in H<sub>2</sub>O<sub>2</sub>/formic acid systems. The oxidation behavior in different solvents at different temperature is shown in Fig.3.

It can be seen from the Fig.3, the sulfur removal rates are improved with the temperature increasing. When the temperature exceeds 50°C, the sulfur removal rates increase rarely. The conversion of C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S are lower when xylene was used as the

solvent compared to hexane. Low sulfur removal rate of thiophenes could be resulted by the competition of solvent xylene and thiophenes on catalyst.

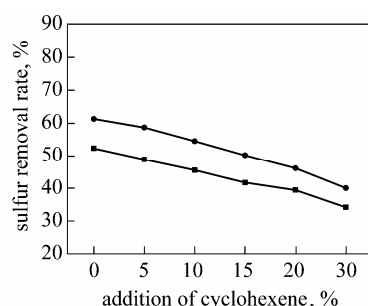


**Figure 3** Influence of solvent to oxidation of model sulfur compounds

■ C<sub>4</sub>H<sub>4</sub>S, solvent hexane; ● C<sub>4</sub>H<sub>4</sub>S, solvent xylene;  
▲ 3-MC<sub>4</sub>H<sub>4</sub>S, solvent hexane; ▼ 3-MC<sub>4</sub>H<sub>4</sub>S, solvent xylene

### 3.3 Influence of olefin to oxidation of model sulfur compounds

Cyclohexene chosen as representative olefin were added into model sulfur compounds. In H<sub>2</sub>O<sub>2</sub>/formic oxidative systems, the sulfur removal rate of C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S was reduced with the addition of cyclohexene showed in Fig.4, in which the added cyclohexene was based on the mass of hexane. Low sulfur removal rate of model sulfur compounds could be caused by reduction of H<sub>2</sub>O<sub>2</sub> induced by oxidation of cyclohexene.



**Figure 4** Influence of cyclohexene to oxidation of C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S

■ C<sub>4</sub>H<sub>4</sub>S; ● 3-MC<sub>4</sub>H<sub>4</sub>S

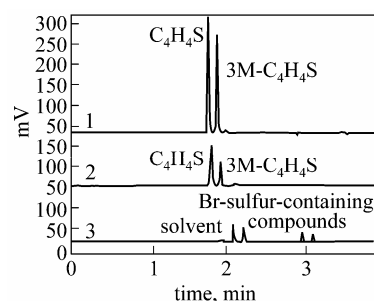
50ml FCC gasoline with 31% olefin content, 2.5ml of formic acid and 0.1g silica gel loaded with copper oxide and cobalt oxide(1:1) were heated to 40°C, then 5ml of H<sub>2</sub>O<sub>2</sub> was added. The oxidative reaction was ceased after 2h. The residual concentration

of the sulfur compound in FCC gasoline was determined in GC-FPD. In H<sub>2</sub>O<sub>2</sub>/formic acid systems, the sulfur remove rate of FCC gasoline was only 38.2%. Therefore, it is concluded that the influence of olefin on oxidation of model sulfur compounds was very significant.

### 3.4 Influence of phase transfer catalyst to the oxidation of thiophenes

Since the reaction system was heterogeneous with three phases, the oxidation reaction might be improved by PTC. Table 2 showed the sulfur content in oil phase after oxidized as PTC (1.0ml or 0.5g) was added into the oxidation system of C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S.

From Table 2, it can be seen that emulsifier OP was the most effective among four PTC for C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S. The sulfur removal rate of C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S in the oxidized oil layer was the same when DMF was used as extraction solvent. There were no new peaks in GC-FPD analysis in the oil layer after oxidation. When SDBS or Polyglycol-400 was added into the oxidative system, the sulfur removal rate of C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S was not enhanced obviously, which were compared with the case of no PTC. TBAB was the second effective PTC. The analysis of GC-FPD indicated the occurrence of bromine substitution on C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S. However, no bromine substitution on xylene or *n*-hexane was observed from the analysis of GC-FID. Fig.5 showed the influence of TBAB to oxidation of C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S.



**Figure 5** GC-FPD chromatogram of thiophenes solution 1—before oxidation; 2—after oxidation (0.02g TBAB added); 3—after oxidation (0.5g TBAB added)

The bromine substitution increases as the concentration of TBAB increases. The sulfur removal rate of C<sub>4</sub>H<sub>4</sub>S and 3-MC<sub>4</sub>H<sub>4</sub>S was nearly 100% when 0.5g

**Table 2** Sulfur content ( $\mu\text{g}\cdot\text{ml}^{-1}$ ) in oil phase and removal rate after oxidized with PTC added

Solvent	C <sub>4</sub> H <sub>4</sub> S		3-MC <sub>4</sub> H <sub>4</sub> S	
	Sulfur content	Removal rate	Sulfur content	Removal rate
emulsifier OP	81.2	84.5%	48.7	90.7%
SDBS	216.4	58.7%	169.8	67.6%
TBAB	84.8	83.8%	54.5	89.6%
polyglycol-400	252.6	51.8%	198.6	62.1%
no PTC	249.9	52.3%	202.8	61.3%

of TBAB added. This result was caused by oxidation and transformation. Part of  $C_4H_4S$  and 3-MC $_4H_4S$  was oxidized, and the other reacted to form bromine substituted  $C_4H_4S$  and 3-MC $_4H_4S$ . The extraction of sulfur compounds from the oxidized oil layer was conducted with DMF. The removal of  $C_4H_4S$  and 3-MC $_4H_4S$  was 100% in the oil layer after extraction.

### 3.5 The oxidation mechanism of model sulfur compounds

The facts that the same sulfur removal rates were obtained when DMF be used as the solvent to extract the oxidized oil phase and there were no new peaks in GC-FPD analysis in the oil layer after oxidation indicated that no new organic sulfur compounds came into being in the oxidation process. And precipitate occurs obviously in the aqueous layer when BaCl $_2$  is added. This phenomenon suggests that the model sulfur compounds have been converted to  $SO_4^{2-}$  during the oxidation. Fig.6 showed the possible pathway of oxidation of  $C_4H_4S$ .

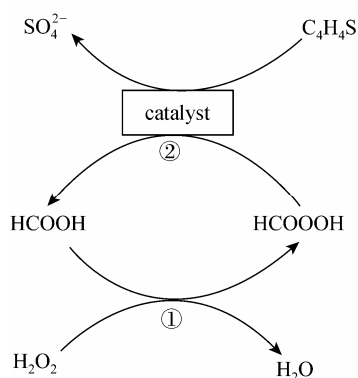


Figure 6 The oxidation process of  $C_4H_4S$

### REFERENCES

1 Avidan, A., Klein, B., Ragsdale, R., "Improved planning can optimize solutions to produce clean fuels", *Hydro-*

*carbon Process*, **80**, 47—53(2001).

- 2 Murata, S., Murata, K., Kidena, K., Nomura, M., "A novel oxidative desulfurization system for diesel fuels with molecular oxygen in the presence of cobalt catalysts and aldehydes", *Energy and Fuel*, **18**, 116—121(2004).
- 3 Te, M., Fairbridge, C., Ring, Z., "Oxidation reactivities of dibenzothiophenes in polyoxometalate/ $H_2O_2$  and formic acid/ $H_2O_2$  systems", *Appl. Catal. A: Gen.*, **219**, 267—280(2001).
- 4 Shiraishi, Y., Tachibana, K., Hirai, T., Komasaawa, I., "Desulfurization and denitrogenation process for light oils based on chemical oxidation followed by liquid-liquid extraction", *Ind. Eng. Chem. Res.*, **41**, 4362—4375(2002).
- 5 Collins, F.M., Lucy, A.R., Sharp, C.J., "Oxidation desulfurization of oils via hydrogen peroxide and heteropolyanion catalysis", *Mol. Catal. A*, **117**, 397—403(1997).
- 6 Mei, H., Mei, B.W., Yen, T.F., "A new method for obtaining ultra-low sulfur diesel fuel via ultrasound assisted oxidative desulfurization", *Fuel*, **82**, 405—414(2003).
- 7 Kong, L.Y., Li, G., Wang, X.S., Wang, Y., "Thiophene oxidation over titanium silicalite using hydrogen peroxide", *Chinese J. Catal.*, **25**(2), 89—90(2004). (in Chinses)
- 8 Otsuki, S., Nonaka, T., Takashima, N., Qian, W., Ishihara, A., Imai, T., Kabe, T., "Oxidative desulfurization of light gas oil and vaccum gas oil by oxidation and solvent extraction", *Energy Fuels*, **14**, 1232—1239(2000).
- 9 Shiraishi, Y., Hirai, T., "Desulfurization of vacuum gas oil based on chemical oxidation followed by liquid-liquid extraction", *Energy Fuels*, **18**(1), 37—40(2004).
- 10 Hirai, T., Shiraishi, Y., Komasaawa, I., "Desulfurization process for benzothiophenes from light oil by photochemical reaction and liquid-liquid extraction", *Ind. Eng. Chem. Res.*, **35**(2), 586—589(1996).
- 11 Wang, H., Tang, X.D., Zhou, J.J., Liu, L., "Progress of oxidative desulfurization on diesel oil", *Chemical Engineering of Oil and Gas*, **32**(1), 38—41(2003). (in Chinses)
- 12 Hirai, T., Shiraishi, Y., Ogawa, K., Komasaawa, I., "Effect of photosensitizer and hydrogen peroxide on desulfurization of light oil by photochemical reaction and liquid-liquid extraction", *Ind. Eng. Chem. Res.*, **36**(3), 530—533(1997).