Oxidative Desulfurization of Simulated Gasoline over Metal Oxide-loaded Molecular Sieve[*]

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Abstract   A simulated gasoline consisting of model sulfur compounds of thiophene (C_4H_4S) and 3-methythiophene (3-MC_4H_4S) dissolved in *n*-heptane was tested for the oxidative desulfurization in the hydrogen peroxide (H_2O_2) and formic acid oxidative system over metal oxide-loaded molecular sieve. The effects of the oxidative system, loaded metal oxides, phase transfer catalyst, the addition of olefin and aromatics on sulfur removal were investigated in details. The results showed that the sulfur removal rate of simulated gasoline in the H_2O_2/ formic acid system was higher than in other oxidative systems. The cerium oxide-loaded molecular sieve was found very active catalyst for oxidation of simulated gasoline in this system. The sulfur removal rates of C_4H_4S and 3-MC_4H_4S were enhanced when phase transfer catalyst (PTC) was added. However, the sulfur removal rate of simulated gasoline was reduced with the addition of olefin and aromatics.
Keywords   oxidative desulfurization, simulated gasoline, thiophene, 3-methythiophene, molecular sieve

1   INTRODUCTION

Due to increasing environmental concern, special interest has been paid to reduction of organic sulfur-containing compounds in light fuels. Therefore, sulfur content in light fuels is limited by increasingly severe regulations and its permitted level is reduced from year to year. Faced such challenges, the conventional method of catalytic hydrodesulfurization (HDS) under severe conditions for reducing sulfur content in light fuel demands further development, and many researchers are developing highly effective desulfurization technique. Much attention has been paid to oxidative desulfurization (ODS) process under low reaction temperature and pressure.

The ODS process consists generally of two stages: the first stage is oxidation of organic sulfur-containing compounds in fuels, and the following step is removal of oxidized sulfur-containing compounds by extraction. In previous papers[1—13], ODS process for sulfur-containing compounds in fuels employing oxidants and liquid-liquid extraction have been proposed. The extraction of oxidized sulfur-containing compounds is considered to be a useful method for removal of sulfur compounds[3,4,7,8]. Otsuki *et al.*[7] reported the thiophene and thiophene derivatives with lower electron densities on the sulfur atoms could not be oxidized in the H_2O_2/ formic acid system at 50℃, while dibenzothiophenes with higher electron densities were oxidized. This is in accordance with the conventional concept that thiophene cannot be oxidized by H_2O_2 under mild conditions owing to its aromaticity. Kong *et al.*[13] reported the thiophene could be oxidized over TS-1 catalyst slowly by H_2O_2 in water or *t*-butanol, but it could not be oxidized in methanol or acetonitrile solvent.

In the present work, the oxidative desulfurization of simulated gasoline was studied in the H_2O_2/ formic acid system, particularly, the influence of the oxidative system, metal-loaded molecular sieve, phase transfer catalyst and the addition of olefin and aromatics to the oxidation of C_4H_4S and 3-MC_4H_4S. The research was conducted on simulated gasoline consisted of model sulfur compounds of C_4H_4S and 3-MC_4H_4S as representative sulfur-containing compounds in commercial gasoline, and *n*-heptane as solvent.

2   EXPERIMENTAL

2.1   Materials

n-Heptane, cyclohexene and mixed xylene isomers were chosen as representatives of the most important hydrocarbon compounds consisting of the matrixes of commercial gasoline. The organic solvents used in this study were formic acid, acetic acid, oxalic acid，benzoic acid, *N,N*-dimethylformamide (DMF). The phase transfer catalysts (PTC) used were polyethylene glycol octyl phenyl ether (emulsifier OP), sodium dodecyl benzene sulfonate (SDBS), tetrabutyl ammonium bromide (TBAB), polyglycol-400.

The sulfur compounds selected were C_4H_4S and 3-MC_4H_4S that were among those found more frequently in the light distillates. Hydrogen peroxide (30%), H_2SO_4, $Cu(Ac)_2$, $Co(Ac)_2$, $Ni(NO)_3$, $Ce(NO)_3$ and $BaCl_2$ were supplied by Tianjin Reagent Company, Tianjin. Molecular sieve 5A [Si：Al＝2 (molar ratio), pore size: 0.5mm, specific area: $0.35m^2 \cdot g^{-1}$, granularity: 2.0—3.0mm] was prepared by Standard Science and Technology Company, Tianjin. Molecular sieve 5A was dipped with $0.1mol \cdot L^{-1}$ $Ce(NO)_3$ solution, and baked 2—6h at 400℃. The load of cerium oxide on molecular sieve 5A was $0.016g \cdot g^{-1}$. All the products were commercial reagent grade.

2.2   Procedure

C_4H_4S and 3-MC_4H_4S (molar ratio＝1：1) were

dissolved into *n*-heptane solvent to make a simulated gasoline solution with the sulfur content of $500\mu g\cdot ml^{-1}$. 50ml of the stock solution, 5ml of acid and 0.1g of molecular sieve 5A loaded with metal oxide 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 with a magnetic stirrer at about $1500 r\cdot min^{-1}$. When the mixture reached the selected reaction temperature (50℃), 5ml of H_2O_2 (and PTC) was then added and the reaction was started.

To determine the initial and residual concentration of C_4H_4S and $3\text{-}MC_4H_4S$ in the organic phase, approximately 0.5ml aliquots of liquid samples were withdrawn from the reactor at fixed time intervals. After phase separation the samples were analyzed by HP 6890 gas chromatograph (GC-FPD) and GC 6890N/MS 5973N.

3 RESULTS AND DISCUSSION
3.1 Influence of oxidative system to the oxidation of simulated gasoline

Standard electrode potential of H_2O_2/H_2O pair $E_a= 1.763$V suggests that H_2O_2 has intensive oxidative ability in acidic condition. Formic acid, acetic acid, oxalic acid, benzoic acid and H_2SO_4，selected to acidify the system, were added into simulated gasoline solution by volume ratio of $1:1$ with 30% H_2O_2 at 50℃. The molecular sieve loaded with cerium oxide was used as the catalyst in the oxidation reaction. After the oxidative reaction was carried out for 60min, the effect of oxidative system to oxidation of C_4H_4S and $3\text{-}MC_4H_4S$ in different acid environment was shown in Table 1.

**Table 1   Influence of oxidative system to oxidation of C_4H_4S and $3\text{-}MC_4H_4S$**

Acid used	C_4H_4S removal, %	$3\text{-}MC_4H_4S$ removal, %
formic acid	78.4	82.3
acetic acid	69.7	72.5
oxalic acid	56.9	65.8
benzoic acid	66.2	73.9
H_2SO_4	32.3	36.8

The results in Table 1 showed that the sulfur removal rate of C_4H_4S and $3\text{-}MC_4H_4S$ in H_2O_2/ formic acid system was higher than the other oxidative system. The high sulfur remove rate could be caused by small formic acid molecules, which can dissolve in both simulated gasoline and H_2O_2, and its K_a was higher than acetic acid. Due to inorganic acids H_2SO_4 cannot dissolve in simulated gasoline solution, the sulfur removal rate of simulated gasoline in H_2O_2/inorganic acid was lower than in H_2O_2/organic acid system.

## 3.2 Effect of molecular sieves loaded with metal oxides

A series of experiments were performed to compare the activity of copper oxide-, cobalt oxide-, nickel oxide- and cerium oxide-loaded molecular sieve as a catalyst for oxidation of C_4H_4S and $3\text{-}MC_4H_4S$. The mixture of *n*-heptane solution of sulfur-containing compounds and H_2O_2/formic acid became two layers after oxidation: oil layer (top) and aqueous layer (bottom). The sulfur removal rates of C_4H_4S and $3\text{-}MC_4H_4S$ in oil layer are shown as functions of reaction time in Figs.1 and 2.
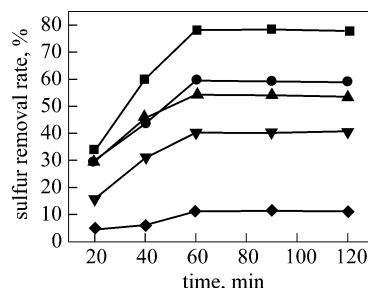
Figure 1   Oxidation of C_4H_4S over metal oxide-loaded molecular sieve
■ Ce_2O_3; ● CuO; ▲ NiO; ▼ CoO; ◆ unloaded
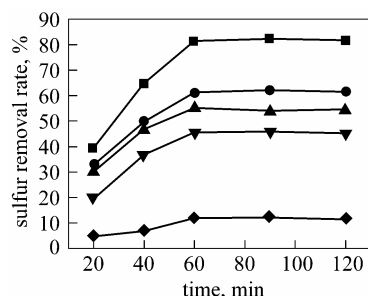
Figure 2   Oxidation of $3\text{-}MC_4H_4S$ over metal oxide-loaded molecular sieve
■ Ce_2O_3; ● CuO; ▲ NiO; ▼ CoO; ◆ unloaded

In the H_2O_2/fomic acid systems, it is clear that metal oxide-loaded molecular sieves are much better catalyst compared to unloaded molecular sieve. The cerium-loaded molecular sieve was very active catalyst for the oxidation of C_4H_4S and $3\text{-}MC_4H_4S$ with 78.4% and 82.3% sulfur removal rate, while the copper oxide- and nickel oxide-loaded molecular sieves were less active, the sulfur removal rate were 59.5%, 62.2% and 54.3%, 55.2% respectively. The sulfur removal rate was only 40.3% and 45.9% when cobalt oxide-loaded molecular sieve was used as catalyst for the oxidation. As H_2O_2 became used up and the activity of catalyst reduced, the sulfur removal percentage does not increase after 60min. If more H_2O_2 was added into the reaction system, the sulfur removal would increase further at this time. The sulfur removal would increase obviously if fresh catalyst was also added.

3.3 The oxidation mechanism of thiophenes

The sulfur removal rate of the oxidized oil layer was the same while it was extracted with *N,N*-dimethylformamide. There were no new peaks in

GC-FPD and GC-MS analysis in oil layer after oxidation. This indicated that new organic sulfur compounds did not come into being in the organic phase. There were plentiful CO_2 and CH_3COOH in aqueous layer after oxidation in GC-MS analysis. And deposition occurred obviously in aqueous layer when $BaCl_2$ was added. This phenomenon indicted that the sulfur of C_4H_4S and $3-MC_4H_4S$ have been converted to SO_4^{2-} in the process of oxidation. The oxidation process of the model sulfur compounds C_4H_4S and $3-MC_4H_4S$ were showed in Fig.3.

$$\text{(thiophene ring with R)} + H_2O_2 \longrightarrow SO_4^{2-} + CH_3COOH + CO_2$$

R=H (or CH_3)
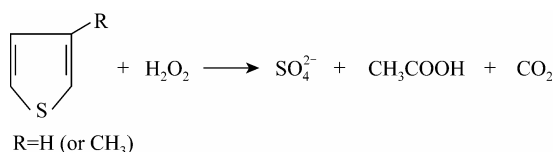
Figure 3   Oxidation process of C_4H_4S and $3-MC_4H_4S$

3.4   Influence of phase transfer catalyst

Since the reaction system was heterogeneous with three phases, the oxidation reaction could be improved by phase transfer catalyst (PTC). The oxidation of n-heptane solution of C_4H_4S and $3-MC_4H_4S$ was studied over molecular sieve loaded with cerium oxide in the H_2O_2/fomic systems when PTC was added. Table 2 shows the influence of PTC to oxidation of C_4H_4S and $3-MC_4H_4S$.

Table 2   Influence of PTC to oxidation of C_4H_4S and $3-MC_4H_4S$

PTC	C_4H_4S removal, %	$3-MC_4H_4S$ removal, %
emulsifier OP (0.5ml)	94.5	96.2
TBAB (0.5 g)	91.3	93.6
no PTC	78.4	82.3

From Table 2, it can be seen that emulsifier OP was the more effective than TBAB with 94.5% and 96.2% sulfur removal rate. The sulfur removal rate of C_4H_4S and $3-MC_4H_4S$ in the oxidized oil layer was the same as N,N-dimethylformamide was used as the extraction solvent. There were no new peaks in GC-FPD analysis in oil layer after oxidation. TBAB was the less effective PTC with 91.3% and 93.6%. The analysis of GC-FPD indicated bromine substitution reactions on C_4H_4S and $3-MC_4H_4S$. However, there was no bromine substitution on n-heptane from the analysis of GC-FID. After emulsifier OP was added into the reaction system, foams appeared under the same conditions but the operation was not disturbed. However, there was no obvious foaming if TBAB was added into the oxidative system.

Figure 4 shows the influence of PTC to oxidation of C_4H_4S and $3-MC_4H_4S$, suggesting that there was no new sulfur-containing compound after oxidation with emulsifier OP as PTC. However, there were Br-sulfur-containing compounds after oxidation when TBAB was added as PTC. From curve 3 in Fig.4, part of C_4H_4S

and $3-MC_4H_4S$ was oxidized, and the others reacted to form bromine substituted C_4H_4S and $3-MC_4H_4S$. If sulfur-containing compounds in the oil layer after oxidation was extracted with N,N-dimethylformamide, the sulfur removal rate was 100% in the oil layer after extraction.
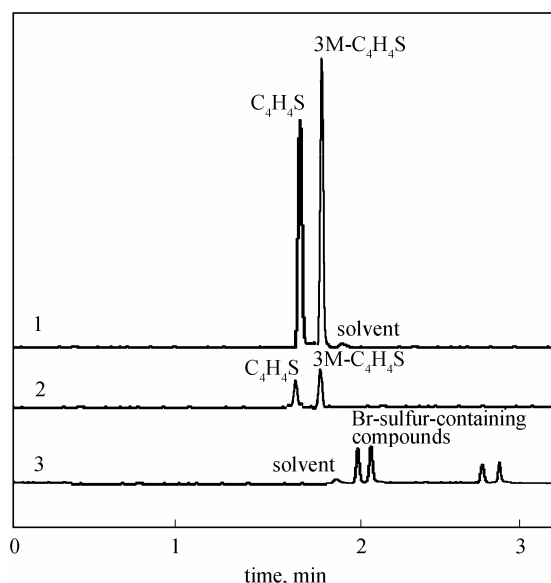

Figure 4   GC-FPD chromatogram of simulated gasoline
1—before oxidation; 2—after oxidation with addition of emulsifier OP; 3—after oxidation with addition of TBAB

3.5   Influence of olefin and aromatics to oxidation

Cyclohexene and xylene chosen as representative olefin and aromatics were added separately into the simulated gasoline. In the H_2O_2/fomic oxidative systems, the sulfur removal rate of C_4H_4S and $3-MC_4H_4S$ with addition of cyclohexene and xylene was showed in Figs.5 and 6.
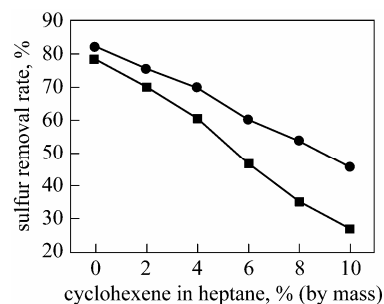
Figure 5   Influence of cyclohexene to oxidation of C_4H_4S and $3-MC_4H_4S$
■ C_4H_4S; ● $3-MC_4H_4S$

Figure 5 indicated that the sulfur removal rate of C_4H_4S and $3-MC_4H_4S$ was reduced with the addition of cyclohexene. Low sulfur removal rate of simulated gasoline could be caused the reduction of H_2O_2 possibly by oxidation of cyclohexene. Fig.6 indicated that the sulfur removal rate was reduced with the addition of xylene possibly due to the competition of solvent xylene and sulfur-containing compounds on catalyst. In the H_2O_2/formic acid system, the sulfur removal
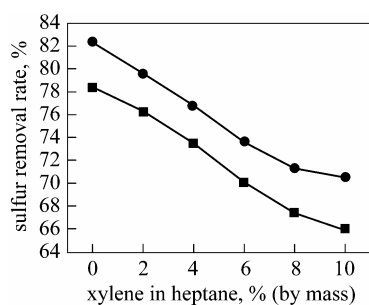
Figure 6　Influence of xylene to oxidation of
C_4H_4S and $3\text{-}MC_4H_4S$
■ C_4H_4S;　● $3\text{-}MC_4H_4S$

percentages of C_4H_4S and $3\text{-}MC_4H_4S$ were 78.4% and 82.3% over 0.1g cerium-loaded molecular sieve 5A in 60min, which were higher than that in Ref.[13] in the same reaction time.

4　CONCLUSIONS

The sulfur removal rate of simulated gasoline was higher in H_2O_2/organic acid systems than in H_2O_2/inorganic acid systems. In the H_2O_2/formic acid system, the cerium oxide-loaded molecular sieve 5A was very active catalyst for the oxidation of C_4H_4S and $3\text{-}MC_4H_4S$, with 78.4% and 82.3% sulfur removal rate respectively. Phase transfer catalyst improved the sulfur removal rate of C_4H_4S and $3\text{-}MC_4H_4S$ in the oxidation reaction system. However, the sulfur removal rate of C_4H_4S and $3\text{-}MC_4H_4S$ was reduced with the addition of cyclohexene and xylene into the solvent *n*-heptane.

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