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Mechanistic studies on thiophene species cracking over USY zeolite

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Abstract

Online pulse-reaction chromatography, MS transient response technique and fixed bed reaction apparatus were used to investigate the cracking of thiophene and alkyl-thiophene species. Thiophene cracks over the USY zeolite to propylene, butane, butene and H_2S. Furthermore, 2-methyl-thiophene, 3-methyl-thiophene, di-methyl-thiophene, tri-methyl-thiophene and benzothiophene are formed, but cracking desulfurization is the dominant reaction. Compared to thiophene, alkyl-thiophene species in gasoline are easier to desulfurize via cracking over the specially prepared sulfur removal catalyst with the USY zeolite as the cracking component, and the conversion increases with the alkyl carbon number of alkyl-thiophene. Cracking and hydrogen transfer are two important elementary reaction steps for thiophene and alkyl-thiophene species desulfurization via cracking. Higher temperature favors the former, while lower does the latter. The contradiction leads to about 400 °C to be the optimal temperature for thiophene and alkyl-thiophene species to desulfurize via cracking.

Keywords: Thiophene species; USY; Cracking; Desulfurization; Mechanism

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1. Introduction

Sulfur in gasoline is not only a direct contributor to SO_x emissions, it is also a poison affecting the low-temperature activity of automobile catalytic converters and, therefore, it has an effect on volatile organic compounds, NO_x and total toxic emissions [1]. About 90% sulfur in gasoline originates from FCC gasoline, so reducing sulfur content of FCC gasoline is the main target of sulfur removal. Several different routes to reduce the content of sulfur can be considered, such as hydrotreatment of FCC feed, hydrodesulfurization of FCC gasoline, and adsorbing desulfurization of FCC gasoline, etc. The great disadvantage of FCC feed hydrotreatment means high operating and capital costs. Hydrodesulfurization of FCC gasoline may lead to a significant loss of octane number [2,3]. Although adsorbing desulfurization is very effective in sulfur reduction, the processes are very complex. In some cases, even H_2 is needed during adsorbing and desorbing regeneration [4]. The additives for sulfur reduction of FCC gasoline, invented by Wormsbecher and Kim [5–7], can be added into the reaction-regeneration system of FCC expediently according to real situation to promote the cracking of sulfur compounds in the gasoline range. The maximum percentage of sulfur reduction is about 40% compared to that not adding the additive if specially developed FCC catalyst is used [8]. Anderson et al. [9] investigated many additives with different compositions and obtained four best additives, and their sulfur reduction activity order is Zn/hydrotalcite >

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Zr/alumina > Zn/titania > Mn/alumina. The USY/ZnO/Al_2O_3 additive we prepared has excellent sulfur removal effect. When adding 30% the additive in FCC catalyst, the sulfur content of gasoline produced can be reduced to less than 800 μg/g from 1230 μg/g (using pure FCC catalyst) with only a little change in product distribution [10]. Sulfur reduction additive, as a cheap and effective sulfur removal technique, has attracted more and more attentions.

Our studies [11,12] show that about 90% sulfur concentrates in the distillate of FCC gasoline higher than 100 °C. In the distillate, mercaptans, thioethers and disulfides only account for about 10% in the total sulfides, and the others are thiophene species. The cracking mechanism of thiophene species in FCC conditions, however, is still vague. So studying the cracking of thiophene is instructive for improving the additives for sulfur reduction of FCC gasoline.

There are only several papers reported on the adsorption and reaction of thiophene. Before 1980s, most of the studies focused in the adsorption of thiophene on Ni/SiO_2, HY and H-montmorillonite [13–16]. Until 1990s, reports on the cracking of thiophene over ZSM-5, HY and Beta, etc. were published [17–22].

The additive for sulfur reduction of FCC gasoline invented by Kim [5,6] is composed of materials that can adsorb sulfides selectively, and the cracking of sulfides is dependent on acid sites of the zeolites on FCC catalyst. Generally, USY is the most important component to play cracking role in FCC catalyst. In this paper, therefore, the mechanism of thiophene cracking over the USY zeolite was studied with online pulse-reaction chromatography and MS transient response technique.

2. Experimental

Zhoucun Catalyst Factory provided the USY zeolite. Thiophene and *n*-heptane are all of analytical pureness. N_2 and Ar are all of high pureness. The catalyst for gasoline desulfurization via catalytic cracking was prepared with impregnation plus co-precipitation [23].

Fig. 1 shows the schematic diagram of online pulse-reaction chromatography (HP4890 with PONA7531 column and FID detector). Between the sampling inlet and the column, there is a mini reactor with 2 mm inner diameter. Liquid sample pulsed is gasified at the sampling inlet and is carried by carry gas to the catalyst bed to react to products that go directly into the column after distributary and are detected by FID. To ensure the sample pulsed to gasify quickly and completely, the temperature at sampling inlet is controlled at 250 °C. The flow rate of carry gas (high pureness N_2) is 30 ml/min. USY zeolite of 14 mg (0.078–0.18 mm) is used and 1 μl sample is pulsed in the experiments.

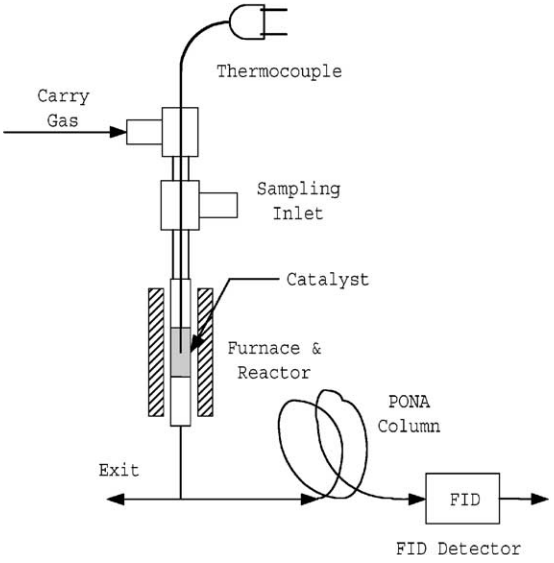


Fig. 1. Schematic diagram of online pulse-reaction chromatography.

Furthermore, thiophene/*n*-heptane (sulfur content 0.33%, Burning-Light method) and FCC gasoline distillate higher than 100 °C (sulfur content 1650 μg/g) are used as the feeds to react in a fixed bed reactor with 25 g catalyst to validate the results obtained from online pulse-reaction chromatography. Thiophene/*n*-heptane of 10 g or the gasoline distillate is pumped into the reactor within 1 min. Sulfides in the liquid product collected in the condenser are analyzed with Varian3800 chromatography combined with CB80 column and PFPD detector. Sulfur content of the liquid product is also measured with Burning-Light method.

The apparatus of MS transient response has been described somewhere [24]. USY of 30 mg is placed in the middle of the quartz reactor. To quicken response time, the other space of the reactor is filled with 0.3–0.45 mm quartz sand. The effluents are detected with a quadrupole mass spectrometer (AMTEK QuadLink 1000) with the minimum dwell time of 3 ms.

3. Results

3.1. Thiophene cracking over the USY zeolite

USY of 14 mg was placed in the reactor of online pulse-reaction chromatography and the height of the catalyst bed was 4 mm. When the temperature of the reactor increased to 490 °C in 30 ml/min N_2 gas-flow and the chromatography was stable, a pure thiophene pulse was conducted. The results were shown in Fig. 2. The conversion of thiophene is very low, not more than 4%. The main products include hydrocarbons (propane, propylene, isobutane, 1-butene, 2-butene) and sulfides (un-reacted thiophene, 2-methyl-thiophene, 3-methyl-thiophene and benzothiophene).

The reason that the conversion of thiophene is very low may be ascribed to the very short contact time (less than 10^{-2} s). The formation of butane and butene indicates that the ring of thiophene is opened and S is removed. Furthermore, hydrogen transfer must happen simultaneously, otherwise only high-unsaturated hydrocarbon can be produced. If a thiophene cracks to a butene and a H_2S, it must obtain six hydrogen atoms. Under the experimental conditions, no H_2 participates in the reaction. So hydrogen can only be obtained via hydrogen transfer among thiophene molecules or thiophene and hydrocarbon fragments. In addition, after several thiophene pulses, significant coke deposits on the USY zeolite, which illustrates that dehydrogenation of hydrocarbons or hydrocarbon fragments or sulfides must take place during the reaction. That no H_2S peak is detected does not mean that there is no H_2S produced during the reaction. The following MS transient response experiments prove that H_2S is surely produced along with the cracking of thiophene. The reason that no H_2S peak is detected here may be the strong adsorption between H_2S and the PONA column.

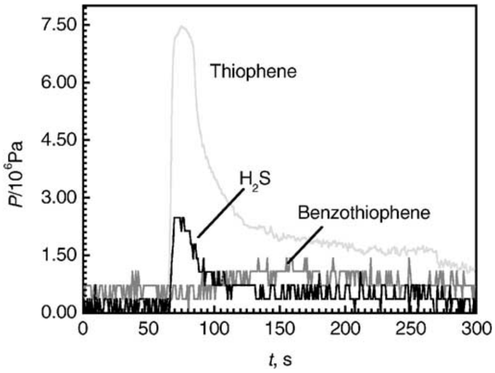


Fig. 3. Transient responses of pure thiophene pulse over the USY zeolite catalyst at 490 °C.

USY zeolite of 30 mg was used in the experiments of MS transient response. The flow rate of the carry gas Ar was also 30 ml/min. At 490 °C, 2 μl thiophene was pulsed and the results were shown in Fig. 3. The characteristic peak of H_2S ($m/e = 34$) was detected

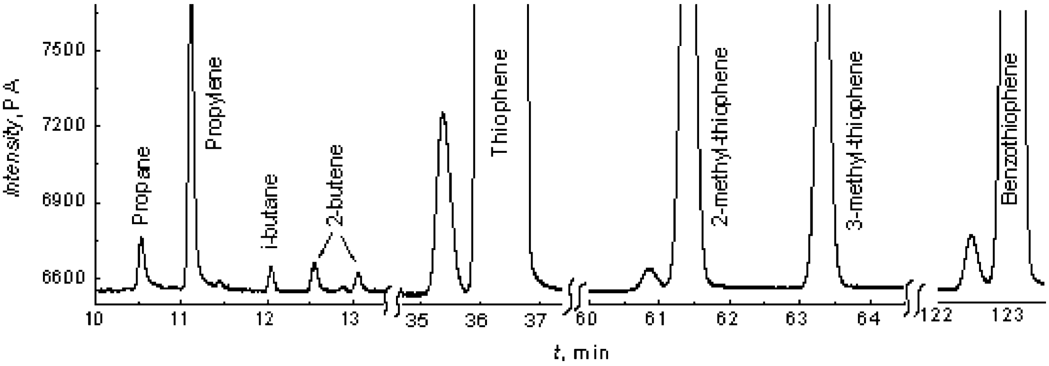


Fig. 2. Chromatograph of pure thiophene reacting over the USY zeolite at 490 °C.

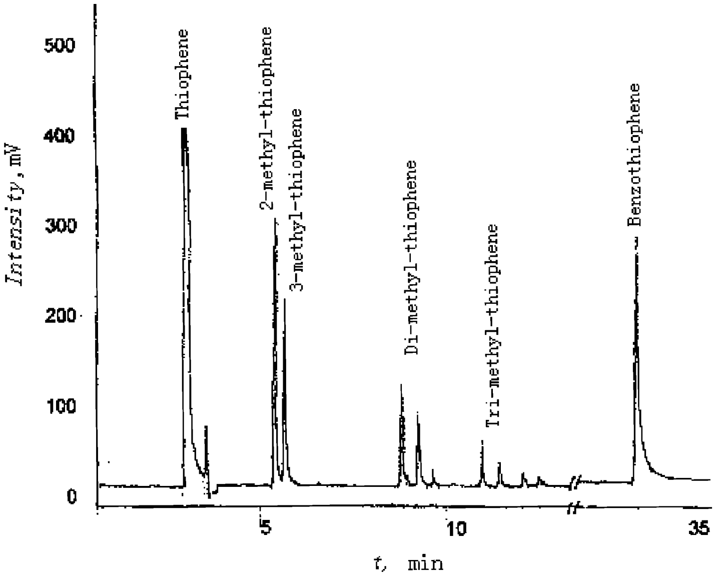


Fig. 4. Products of thiophene reacting over the USY zeolite catalyst at 490 °C analyzed with PFPD detector.

and almost appeared with that of thiophene simultaneously. This supports effectively our opinion that thiophene can crack over the USY zeolite to produce H_2S. Furthermore, benzothiophene ($m/e = 134$) was also detected and it appeared a little later than thiophene and H_2S.

Besides butane, butene and H_2S, propylene, methyl-thiophene and benzothiophene are also produced in the cracking of thiophene. As indicates that the cracking of thiophene is very complex. To validate these results, thiophene/*n*-heptane (sulfur content 0.33%) were used as the feed to react in a fixed bed reactor with 25 g USY zeolite at 490 °C. After reaction the sulfur content of the liquid product is reduced to 0.13 and 61% sulfur has been removed. Obviously, the cracking desulfurization of thiophene is the dominant reaction. Sulfide analysis shows that in the liquid product there are thiophene, 2-methyl-thiophene, 3-methyl-thiophene, benzothiophene and a little di-methyl-thiophene and tri-methyl-thiophene, where thiophene unconverted, benzothiophene, 2-methyl-thiophene and 3-methyl-thiophene account for 67, 20, 5 and 3%, respectively (Fig. 4). That indicates that, except for cracking, thiophene can form other sulfides, and benzothiophene and 2-methyl-thiophene are easy to be produced.

3.2. Effect of temperature on thiophene cracking

The other conditions were the same as that of Fig. 2, and pure thiophene pulses were carried out in the apparatus of online pulse-reaction chromatography at different temperature. The conversion of thiophene and the yield of benzothiophene with temperature were depicted in Fig. 5. The conversion of thiophene does not increase with temperature monotonously, but has

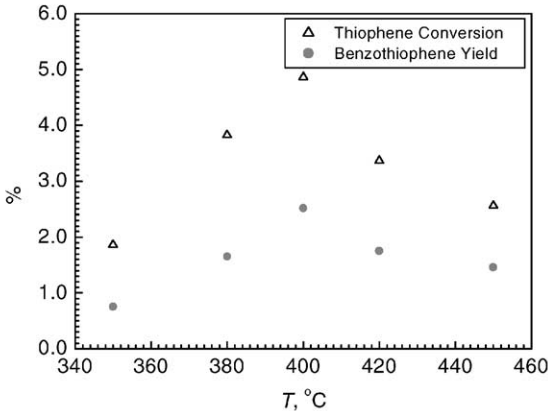


Fig. 5. Trends of thiophene conversion and the yield of benzothiophene with temperature.

Table 1
The type and distribution of sulfides in the gasoline before and after desulfurization via catalytic cracking. (Catalyst/oil = 2.5, temperature is 410 °C. All the following values represent the amount of sulfur, not sulfide.)

	Before desulfur (%)	After desulfur (%)	Before desulfur (μg/g)	After desulfur (μg/g)	Sulfur removal percent (%)
Thiophene	0.69	8.02	11.5	23.1	−102
Mercaptans	0.32	0.08	5.35	0.243	95.5
2-, 3-Methyl-thiophene	14.4	43.6	238	126	47.5
Thioethers and disulfides	11.1	3.72	184	10.7	94.2
C_2-substituted thiophene	34.5	30.6	569	88.1	84.5
C_3-substituted thiophene	26.5	10.3	438	29.6	93.3
C_4-substituted thiophene	12.5	3.68	201	10.6	94.8
Total	100	100	1650	288	82.5

a maximum at about 400 °C. Luo et al. [19] also reported that there is a maximum conversion of thiophene at 400 °C when thiophene/ethanol crack over HZSM-5. In Fig. 5, the yield of benzothiophene with temperature has the same trend as that of the conversion of thiophene, which implies that the formation of benzothiophene has some direct relations with thiophene cracking.

Hydrogen transfer plays very important role in thiophene cracking [25]. Hydrogen transfer is an exothermic reaction, and high temperature restrains the reaction. Cracking, however, is an endothermic reaction, and high temperature promotes the reaction. That 400 °C is the optimal temperature for thiophene cracking indicates that hydrogen transfer is an important elementary step and not to only saturate those products from thiophene cracking. Otherwise, the conversion of thiophene should increase with temperature. Furthermore, the conversion of thiophene and the yield of benzothiophene have the same trend with temperature may mean that the cracking of thiophene is the precondition of the formation of benzothiophene.

3.3. Gasoline desulfurization via catalytic cracking

USY zeolite has excellent cracking activity for sulfides but bad selectivity. When the FCC gasoline distillate higher than 100 °C, whose sulfur content is 1650 μg/g, reacted over it under 410 °C and the catalyst/oil ratio of 2.5, the sulfur content was reduced to less than 100 μg/g, however, the yield of gasoline was only about 40% and about 60% the gasoline distillate cracked to gas. Obviously, the USY zeolite cannot crack sulfides selectively.

In the gasoline distillate, more than 88% sulfur exists in thiophene species with different alkyls or alkyl number (Table 1). In Wormsbecher's opinion, thiophene species are Lewis base and can adsorb on Lewis acid sites [5,6]. So we choose ZnO/Al_2O_3, which can form Lewis acid sites, as the support to adsorb sulfides selectively from the gasoline distillate and the USY zeolite as the cracking sites for sulfides to form the catalyst that can crack sulfides in gasoline selectively (Fig. 6). After the gasoline distillate reacted over the catalyst at the same conditions (400 °C and catalyst/oil = 2.5), the sulfur content was reduced to 288 μg/g with the gasoline yield higher than 94%. Obviously, the catalyst has excellent selectivity to sulfides cracking.

In Table 1, more than 84% mercaptans (indicating the percent of sulfur; the following is the same),

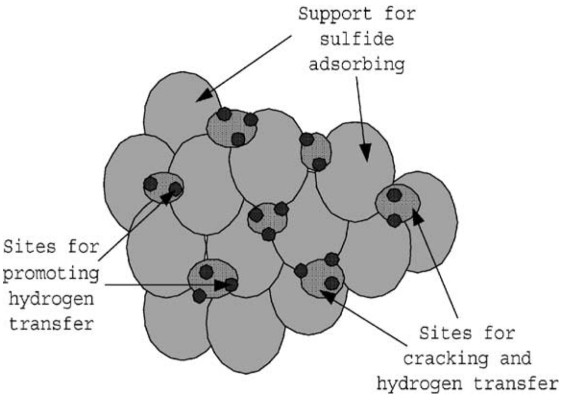


Fig. 6. Schematic diagram of the catalyst for gasoline desulfurization via catalytic cracking.

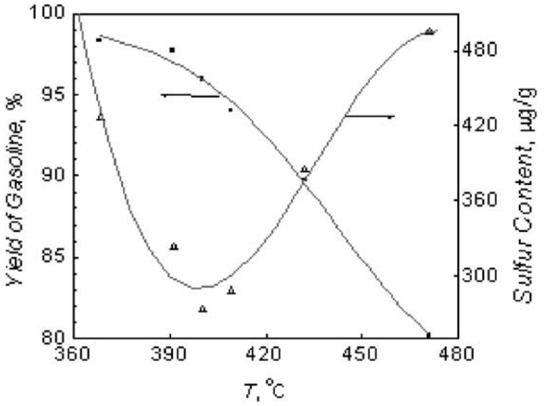


Fig. 7. Trends of yield and sulfur content of gasoline with temperature over the catalyst for gasoline desulfurization via catalytic cracking (catalyst/oil = 2.5).

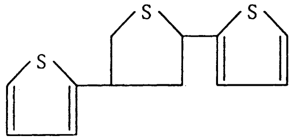
thioethers, disulfides, C_2-substituted thiophene, C_3-substituted thiophene and C_4-substituted thiophene (including only minimum benzothiophene) has been removed. They are all higher than the total sulfur removal percent 82.5%. 2-Methyl-thiophene and 3-methyl-thiophene are difficult to be removed relatively and the sulfur removal percent is only 47%. However, the amount of thiophene, although only small, has increased more than 100%. In our opinion, this does not mean thiophene cannot or is difficult to desulfurize via cracking, but it may mean that alkyl-thiophene can form thiophene via de-alkyl reaction.

We also investigated the effect of temperature on sulfur removal. In Fig. 7, we can see that the yield of gasoline after desulfurizaton via cracking decreases monotonously with temperature under catalyst/oil ratio of 2.5 for cracking reaction of hydrocarbons is expedited. However, sulfur content has a minimum value between 390 and 420 °C. It seems that high temperature is not favorable for sulfide cracking.

4. Discussion

4.1. Cracking of thiophene

For thiophene desulfurization via cracking, Luo et al. [19] thought that the following species similar to thioether in property is formed firstly.



Then it decomposes to produce H_2S via pyrogenation or catalysis. Wang's [20] viewpoint is completely different. He thought that thiophene firstly obtains hydrogen to form tetra-hydrogen-thiophene, and then tetra-hydrogen-thiophene decomposes to produce H_2S. In the experiments, however, we did not find tetra-hydrogen-thiophene and larger molecules than benzothiophene. Saintigny et al. [21] studied the mechanism of thiophene cracking over acid catalyst in theory and suggested that one of the C–S bonds breaks firstly on acid sites to form surface HC≡C–CH=CH–SH, whose C–S bond then breaks to HC≡C–C≡CH and H_2S. In the mechanism, hydrogen transfer does not happen. If so, cracking will be the dominant reaction and high temperature will favor thiophene cracking. However, our experimental results show that about 400 °C is the optimum temperature for thiophene desulfurization via cracking (Fig. 5). This is consistent to Luo's [19] report. Therefore, the cracking desulfurization of thiophene must be limited by other reactions. Based on our experimental results, we suggested that thiophene cracks by the mechanisms described in Figs. 8–10.

Thiophene firstly obtains proton on the B acid sites of USY to form carbonium ion, and then the C–S bond at β position breaks for its bond energy is 268 kJ/mol, the lowest among that of C–H, C–C and C=C. Thus, the ring of thiophene opens to form mercaptan species with two double bonds (Fig. 8). After carbonium ion isomerization and hydrogen transfer, the remaining C–S bond of the mercaptan at β position breaks, and H_2S and dibutene are produced. Through hydrogen transfer, dibutene can convert to butene and even butane.

Besides butane and butene, propylene is also produced during the cracking of thiophene. In our opinion, the formation of propylene has close relations with the formation of methyl-thiophene. In Fig. 8, the mercaptan with two double bonds from ring open of thiophene polymerizes with thiophene. If polymerization happens at α position in Fig. 8, Species A is produced. After carbonium ion isomerization and

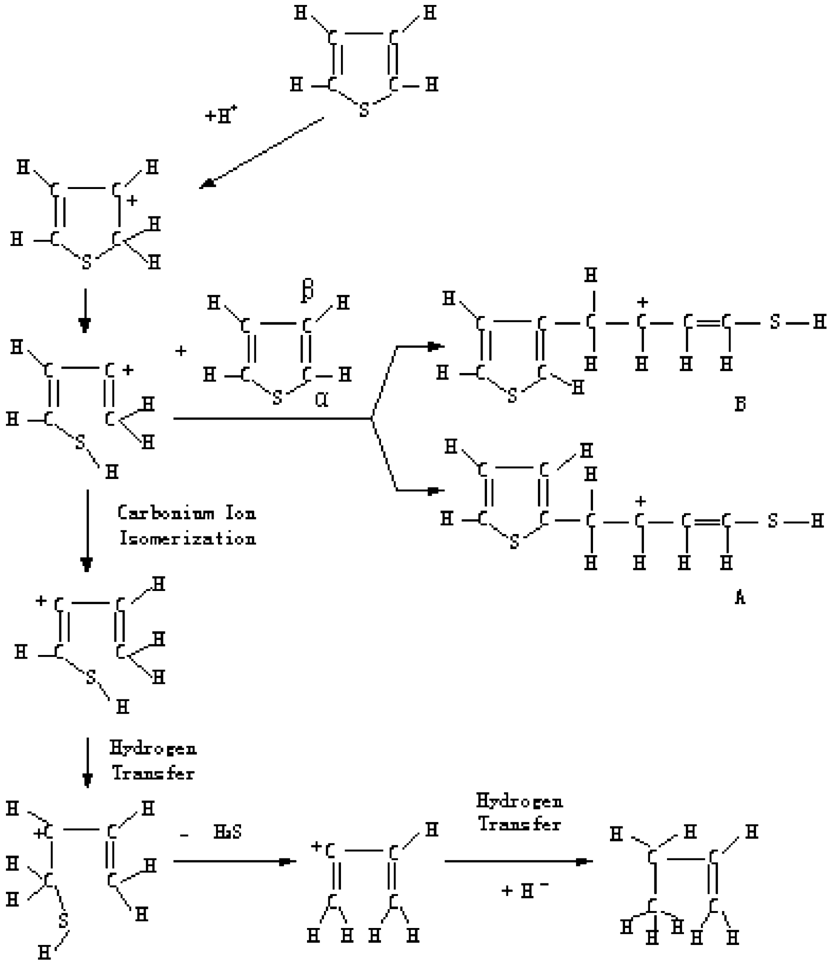


Fig. 8. The formation of butene and H_2S in the cracking of thiophene.

hydrogen transfer (Fig. 9), the C–S bond at β position of A breaks, and H_2S and 2-butenyl-thiophene are produced. 2-Butenyl-thiophene cracks at β position to 2-methyl-thiophene and propylene after hydrogen transfer.

If polymerization between the mercaptan with two double bonds and thiophene happens at β position in Fig. 8, Species B is formed and 3-methyl-thiophene is produced by the above reactions. If thiophene polymerizes with two or three mercaptans with two double bonds at different position simultaneously, di- or tri-methyl-thiophene is formed. For the probability that thiophene polymerizes with two or three mercaptans simultaneously is lower than that polymerizing with one mercaptan even if we do not consider the effect of space obstruction, the quantity of di- or tri-methyl-thiophene is smaller than that of methyl-thiophene. For α position of thiophene is more active than β position [26], the quantity of 2-methyl-thiophene is larger than that of 3-methyl-thiophene in Fig. 4.

Figs. 8 and 9 also illustrate that cracking and hydrogen transfer are two important elementary steps. If any one of the two is blocked, the cracking desulfurization of thiophene will be affected. Just because hydrogen transfer is also an important reaction affecting thiophene and thiophene species to desulfurize via catalytic cracking, the optimum temperature appears in

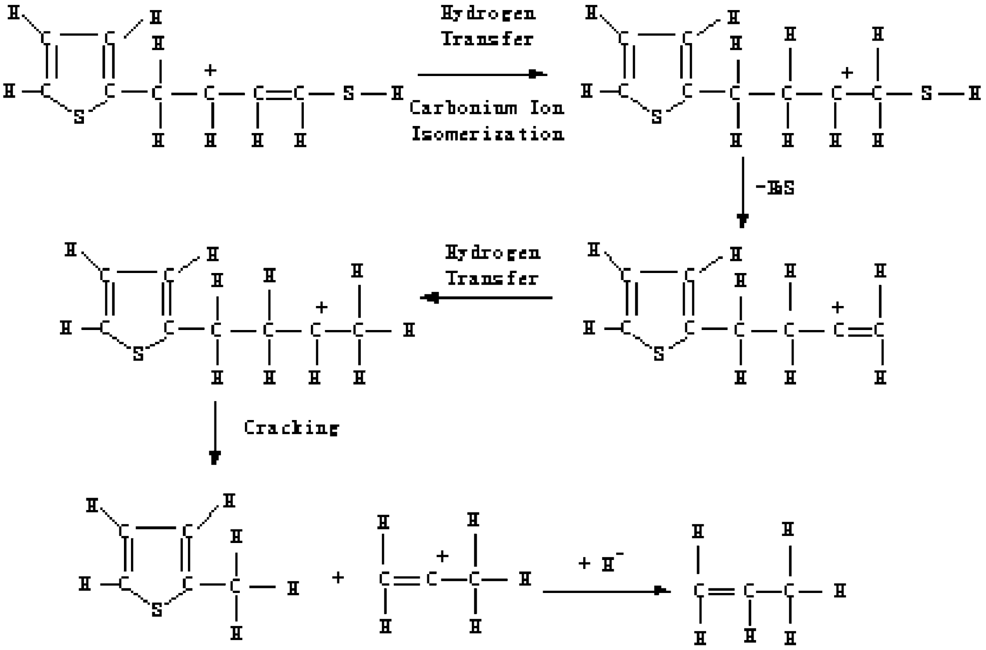


Fig. 9. The formation of propylene and 2-methyl-thiophene in the cracking of thiophene.

Fig. 5 for low temperature limits cracking reaction and high temperature is unfavorable for hydrogen transfer.

In Fig. 8, if H_2S is removed from Species A via β cracking after double bond isomerization and carbonium ion isomerization, 1,3-butenyl-thiophene will be formed. Benzothiophene can be produced through cyclization of 1,3-butenyl-thiophene (Fig. 10). Obviously, ring open of thiophene is the precondition of the formation of thiophene, and the step may be the rate-limited step, so the yield of benzothiophene and the conversion of thiophene with temperature have the same trend (Fig. 5).

4.2. Cracking of alkyl-substituted thiophene

In the gasoline distillate higher than 100 °C we used as the feed, the amounts of mercaptans, thioethers and disulfides are small and they are all easy to

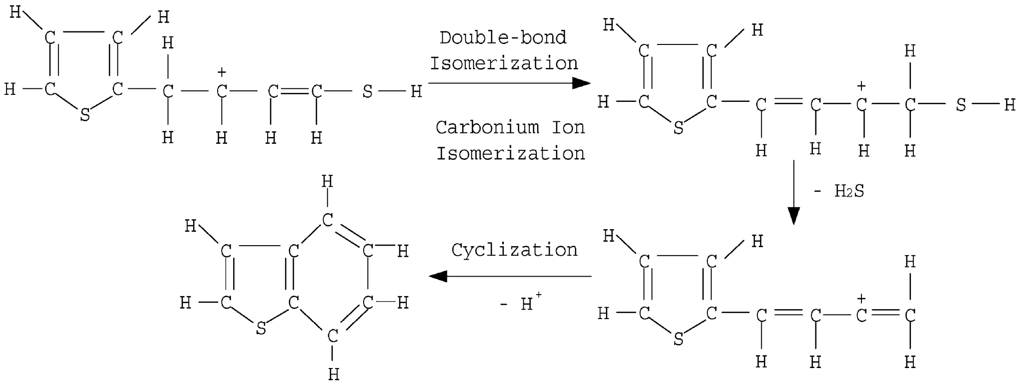


Fig. 10. The formation of benzothiophene in the cracking of thiophene.

desulfurize via catalytic cracking. After the reaction, more than 94% are removed. The amount of thiophene is also very small, whose sulfur is 11.5 μg/g, only accounts for 0.69% of total sulfur. After desulfurization, it does not decrease, but increases to 23.1 μg/g. According to the experimental results with pure thiophene, here it is impossible for thiophene not to crack, and the reasonable explanation, in our opinion, is that alkyl-substituted thiophene species, which is large amount, can form thiophene via de-alkyl reaction.

In the gasoline distillate there are many thiophene species with different alkyl substitutions. Obviously, the environment is different from what we use pure thiophene or high concentration thiophene in heptane as the reactant. Here the amount of thiophene is very small and that its conversion may be restrained by its low concentration. However, this looks incredible. According to the results listed in Table 1, with the increase of carbon number of substituted alkyl, the conversion of alkyl-substituted thiophene species rises, and it seems that the conversion is independent on the concentration, for the concentration of C_4-substituted thiophene is lower than that of C_2- or C_3-substituted thiophene but the conversion is higher than theirs. So the conclusion that ‘multi-alkyl’ may favor the cracking desulfurization of thiophene species can be made. It is well known that iso-alkane is easier to crack than *n*-alkane. If the alkyl exists at α position, then the tetra-carbonium shown in Fig. 11 is more stable. If β-scission takes place at bond 1, then a mercaptan species is formed; if β-scission takes place at bond 2, then a thioether species is formed. No matter which one is produced, they are all easier to desulfurize via cracking. If the alkyl exists at β position, then through β-scission of the carbonium two kinds of mercaptan species are produced. They are also easier to desulfurize via cracking. Perhaps the more the alkyls (in FCC gasoline, the thiophene species with long alkyl is impossible to exist in large amount), the easier the thiophene cycle is to crack. So the conversion of alkylthiophene increases with the carbon number of alkyl.

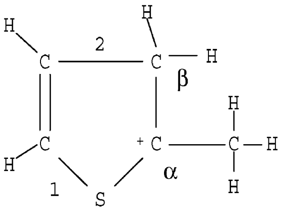


Fig. 11. Carbonium of alkyl thiophene.

Furthermore, the conversion of alkyl-substituted species is also the result of the synergism of cracking and hydrogen transfer. This is the same as that of thiophene. Otherwise, we will not be able to explain why the optimum temperature for sulfur removal appears in Fig. 7.

5. Conclusions

Thiophene can crack over the USY zeolite to propylene, butane, butene and H_2S. Accompanying by cracking reaction, 2-methyl-thiophene, 3-methylthiophene, di-methyl-thiophene, tri-methyl-thiophene and benzothiophene are also formed, but cracking desulfurization is the dominant reaction.

Compared to thiophene, alkyl-thiophene species in gasoline are easier to desulfurize via cracking over the specially prepared sulfur removal catalyst with the USY zeolite as the cracking component, and the conversion increases with the alkyl carbon number of alkyl-thiophene. The conversion sequence is thiophene $<$ 2 or 3-methyl-thiophene $<$ C_2-substituted thiophene $<$ C_3-substituted thiophene $<$ C_4-substituted thiophene (not including benzothiophene).

Cracking and hydrogen transfer are two important elementary reaction steps for thiophene and alkyl-thiophene species to desulfurize via cracking. Higher temperature favors the former, while lower is favorable for the latter. The synergism of cracking and hydrogen transfer makes about 400 °C the optimum for thiophene and alkyl-thiophene species to desulfurize via cracking.

Acknowledgements

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