

Gasoline Desulfurization by Catalytic Alkylation over Methanesulfonic Acid

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Methanesulfonic acid (MSA) was used as catalyst to remove trace organic sulfur (thiophene) from Fluid Catalytic Cracking gasoline (FCC) *via* alkylation with olefins. The reactions were conducted in Erlenmeyer flask equipped with a water-bath under atmospheric pressure. The influence of the temperature, the reaction time, and the mass ration of MSA were investigated. After a 60 min reaction time at 343 K, the thiophene conversion of 98.7% was obtained with a mass ration of MSA to oil of 10%. The catalyst was reused without a reactivation treatment, and the thiophene conversion reached 92.9% at the third time. The method represents an environmentally benign route to desulfur, because MSA could easily be separated from the reaction mixture *via* decantation and it could be reused.

Key Words : Methanesulfonic acid, Alkylation, Thiophene

Introduction

In the past several decades, clean fuels research including desulfurization has become a more important subject of environmental catalysis studies worldwide. Sulfur in gasoline remains a major source of air pollution. Moreover, sulfur is a well-known poison for catalytic converters. As a result the sulfur-limit for transportation fuels has been gradually decreased, *e.g.* in US for gasoline from 350 to 30 ppm by January 2005, the limit is tightened in 2009 in Europe and Japan down to 10 ppm.^{1,2} Another reason for deep desulfurization is for applications in fuel cells. Gasoline is the ideal fuel for fuel cell because of its high energy, ready availability, and ease of storage. However, trace sulfur could inactivate the catalysts for the fuel process.³

At present, hydrodesulfurization (HDS) is the most commonly used method of sulfur reduction of gasoline in refineries, which is highly efficient in removing sulfides and disulfides, but is less effective for aromatic thiophene and thiophene derivatives.⁴ The conventional hydrotreating technology results in a significant reduction of octane number due to saturation of olefins in naphtha from FCC, which also causes higher hydrogen consumption.⁵ Moreover, HDS is limited or at least expensive for deep desulfurization, and ultra-low sulfur specifications for diesel can only be met by severe conditions with respect to pressure and residence time.⁶

Therefore, the recent gasoline desulfurization studies have considered the non-hydrodesulfurization, which includes alkylation, extraction, oxidation, adsorption, *etc.*⁷ In principle, S-species in FCC gasoline are mainly thiophene derivatives. So, among all these non-hydrodesulfurization technologies, OATS (olefinic alkylation of thiophenic sulfur) seems to be the most promising which proposed to separate sulfur compounds by distillation after being weighted down by alkylation with olefins.⁸ As is well known that the alkyl-

ation of thiophenic compounds occur through the formation of carbocation,⁹ acid catalysts are needed to achieve the reactions. Many commercial plants use HF or AlCl₃ as acid catalysts.¹⁰ These processes feature serious drawbacks: for example, HF and AlCl₃ is highly toxic and corrosive. In order to overcome these drawbacks, Methanesulfonic acid could be an alternative. MSA is a strong Brønsted acid with no oxidizing properties.¹¹ Because of its excellent solubility in water, MSA can be extracted from the organic phase with only a small amount of water. Unlike other acids, it does not generate toxic fumes even at high concentration which makes it much more convenient to handle. In this paper, the influence of various reaction parameters, such as the mass ratio of MSA to oil, the reaction temperature and the reusability of MSA, were investigated. Furthermore, Fourier transform infrared spectrometer (FT-IR) was employed to characterize the structure of MSA, and gas chromatography-mass spectroscopy (GC-MS) was used to analyze the reaction products, the reaction mechanism was discussed.

Experimental Section

Materials. Methanesulfonic acid (AR) was provided by BASF-The Chemical Company. 1-hexene (AR) was purchased from Aladdin Chemistry Co., Ltd. *n*-octane (CP) was purchased from the Shanghai Ling Feng Chemical Reagent Company. Thiophene (AR) was purchased from Sinopharm Chemical Reagent Company.

The model oil, which was used to discuss the reaction mechanism, was prepared by adding a certain amount of thiophene and 1-hexene to *n*-octane resulting in a mass fraction of thiophene of 1% and that of 1-hexene of 5%.

Experiments for Conversion of Thiophene. The reactions were carried out in a 50 mL Erlenmeyer-flask, and with the help of magnetic stirrer. The temperature was kept stable by a water-bath equipped with a thermostat. The stirring

speed was 600 rpm in all of the experiments. The model oil and a certain amount of the catalyst were added to the flask, and the mixture reacted for a period of time (0–120 min) at a certain temperature (323–363 K). After the reaction, the mixture was put aside for 1 h at room temperature to gravity separate, and then the upper oil phase can be simply separated from the catalyst by decantation.

Methods for Analysis. The oil separated was analyzed with a Hewlett-Packard Model HP5890 gas chromatograph that was equipped for flame ionization detection (FID):

$$\text{Thiophene Conversion (\%)} = [(M_0 - M) / M_0] \times 100 \quad (1)$$

M_0 represents the initial mass ratio of thiophene (g/g), M represents the final mass ratio of thiophene (g/g).

The Magna-IR550 was employed to characterize fresh MSA and MSA after the reaction. The gas chromatography-mass spectroscopy (GC-MS) (Agilent, Model GC 6890-MS 5973 N) was used to analyze the model oil separated after reaction.

Results and Discussions

Effect of the Mass Ratio of MAS/Oil. Figure 1 shows the catalytic activity in the alkylation of thiophene with 1-hexene at 343 K over different amounts of MSA. As illustrated in Figure 1, the thiophene conversion increased with an increasing mass ratio of MSA/oil under the same reaction time. The reason for this was that as the amount of MSA in the reaction increased, the molecule of MSA might collide and aggregate with 1-hexene more often.^{12,13} Only a slight change in the thiophene conversion was observed when the reaction time was 120 min, the lowest thiophene conversion was 98.7%. The conversion increased from 80% to 98.6% when the MSA/oil ratio increased from 7% to 10% within 60 min. But when the MSA/oil ratio increased from 10% to 15%, the reaction equilibrium was approached almost at same time. Therefore, considering the cost of MSA and the reaction rate, the optimum mass ratio of MSA to oil

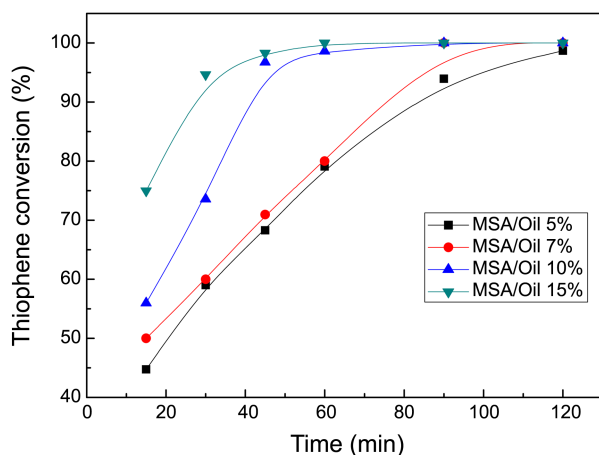


Figure 1. Effect of the mass ratio of MAS/Oil on thiophene conversion. Reaction conditions: oil = 10 g, $T = 343$ K, $P =$ atmospheric pressure.

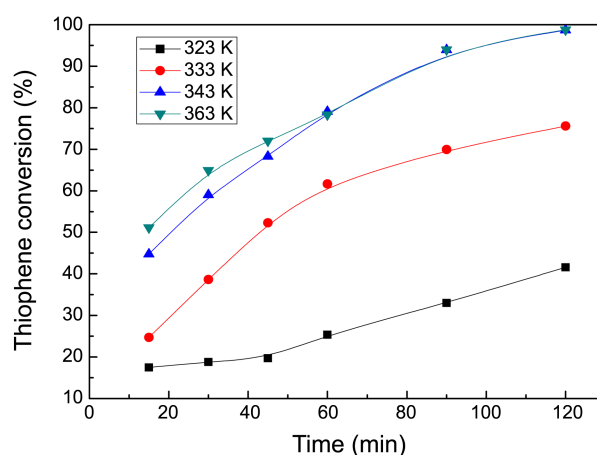


Figure 2. Effect of the reaction temperature on thiophene conversion. Reaction conditions: oil = 10 g, MSA = 0.5 g, $P =$ atmospheric pressure.

was found to be 10%.

Effect of the Reaction Temperature. Figure 2 displays the effect of reaction temperature on thiophene conversion over 5% mass ratio of MSA/oil as the temperature range from 323 to 363 K. It could be observed that the reaction activity increased with increasing temperature under the same reaction time, and this was attributed to the enhancement of the molecular thermal motion and raised the possibility effective collision.¹³ When the mass ratio of MAS/oil was 5%, the thiophene conversion was strongly influenced as the temperature increased from 323 to 343 K, and then it became almost constant. At the temperature of 323 K, the final conversion after 120 min reaction was 41.6%, and the final conversion came to 97.8% when the temperature increased to 343 K. However, the further increase in temperature from 343 to 363 K showed no significant change. Thus, considering the cost of energy, the optimal reaction temperature was 343 K.

Effect of Reusability of the Catalyst. The reusability of the MSA was also investigated (Figure 4). The MSA was

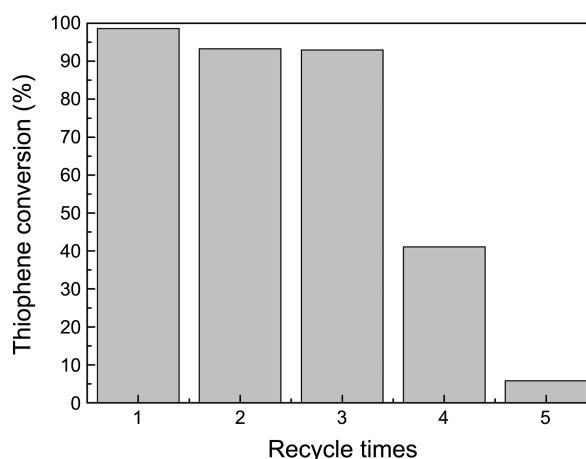


Figure 3. Effect of reusability of the catalyst. Reaction conditions: MSA/oil = 10%, $T = 343$ K, $t = 60$ min, $P =$ atmospheric pressure.

separated from the reaction mixture and reused up to 5 times directly with fresh model oil for 60 min. The mass ratio of MSA/oil was 10%, the temperature was kept at 343 K by a water-bath. The pure MSA was colorless and odorless, after the first run, the MSA phase turns brown, as the recycle times increased, the color of MSA became darker and it was totally black after the fifth run. As can be seen in Figure 3, the thiophene conversion decreased as times increased. Luong *et al.*¹⁴ have investigated the deactivation of MSA for the production of linear alkylbenzenes. They concluded that the presence of water in the reaction mixture was detrimental for the activity of MSA and if MSA contained more than 0.25 wt % of water there was a strong decrease in the activity of MSA. The experimental materials used in this study generally contained small amounts of water, for

example, the water content of n-Octane was $\leq 0.02\%$. Thus, the reason for the deactivation of MSA might be the same with the results obtained by Luong *et al.* On the other hand, the reason for the abrupt decrease of the activity at the fourth recycle might be that the water amassed in the reaction mixture was more than 0.25 wt %. However, the thiophene conversion of 92.9% could still be obtained at the third time.

Mechanism of Thiophene Conversion

The experimental data indicated that MSA was an active substance. To study the mechanism of thiophene conversion, FT-IR was used to characterize the fresh MSA and MSA after reaction. The results are shown in Figure 4. The band between 1230-1120 cm^{-1} was assigned to the S=O asymmetric stretching vibration, and the band between 1080-1010 cm^{-1} was ascribed to the S=O symmetric stretching vibration

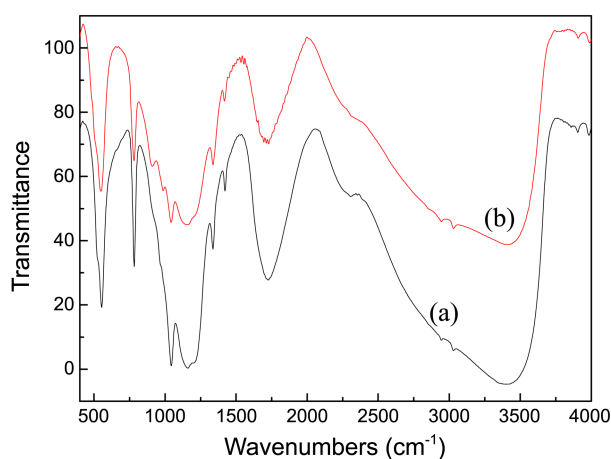


Figure 4. FT-IR of MSA: (a) fresh; (b) after the reaction. Reaction conditions: oil = 10 g, MSA/oil = 10%, $T = 343\text{ K}$, $t = 60\text{ min}$, $P = \text{atmospheric pressure}$.

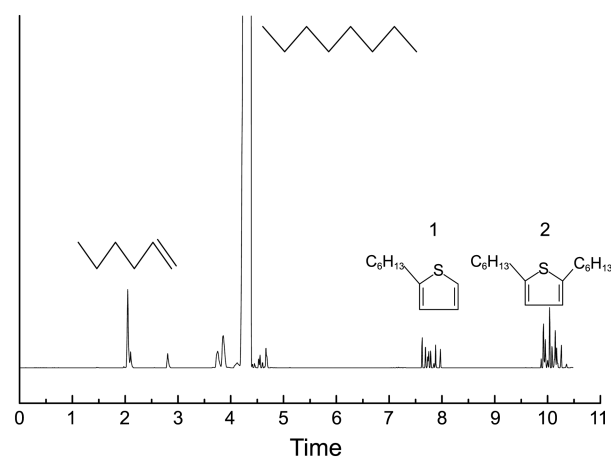


Figure 5. GC-MS of the model oil separated after the reaction.

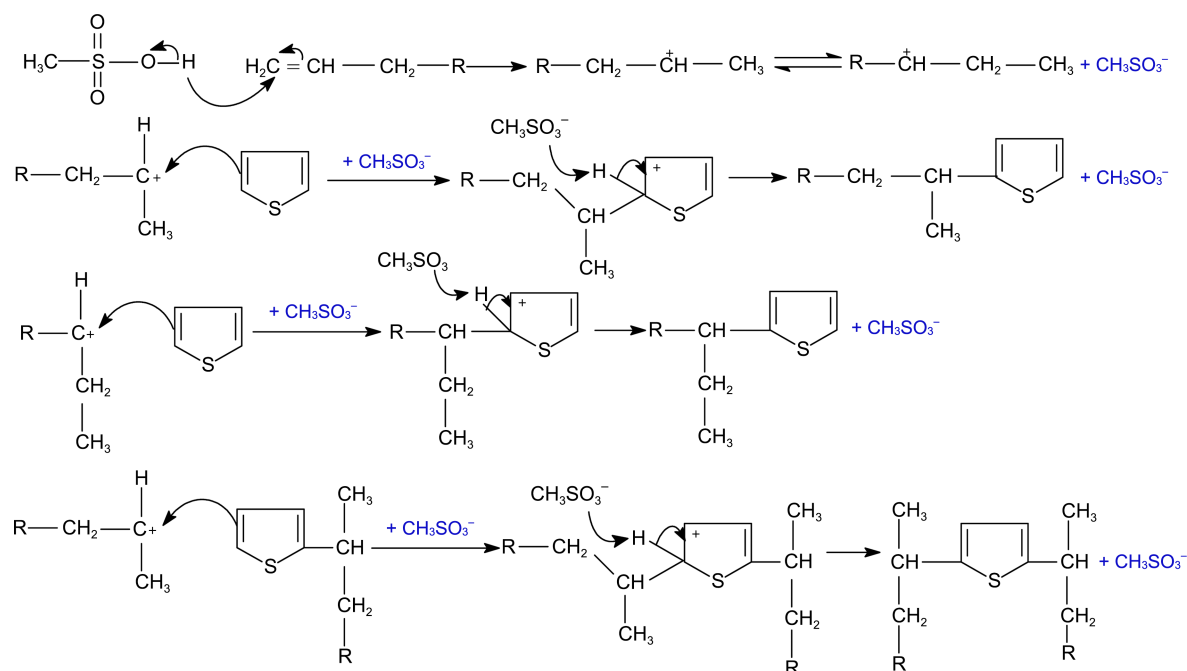


Figure 6. Mechanism of the catalytic reaction.

of the $-\text{SO}_3\text{H}$ group. In addition, from Figure 4, it is worth noting that there was no significant change in main peaks, thus we judged that there are little differences in structure of MSA before and after reactions.

For further exploring, the GC-MS was employed to analyze the model oil after reaction. The results are shown in Figure 5. Thiophene was converted completely, the peaks from 7.5 to 8 min were confirmed to be alkylates which are isomeric with the product 1 (shown in Figure 5), and peaks from 9.8 to 10.5 min were confirmed to be alkylates which are isomeric with the product 2 (shown in Figure 5). Combine the figure of FT-IR with the results of GC-MS, it can be concluded that the alkylation of thiophene with 1-hexene was under the catalysis of Methanesulfonic acid. On the other hand, Ying Tian *et al.*¹³ used MSA as catalyst for the alkylation of olefins with aromatics and Maria Arias *et al.*¹⁵ used silica-supported heteropolyacids to catalyze alkylation of 3-methylthiophene with 2-methyl-2-butene, the similar conclusion was obtained. Consequently, the mechanism for alkylation of 1-hexene with thiophene in the presence of MSA is illustrated in Figure 6.

Thiophene is considered to be aromatic, and the “electron pairs” on sulfur are significantly delocalized in the pi electron system. As a consequence of its aromaticity, thiophene exhibits the similar properties with benzene, such as alkylation. As shown in Figure 6, MSA is a pure proton acid, it firstly involves the interaction with 1-hexene to form reactive intermediates called carbocation, the carbocation undergo a rapid rearrangement in varying degrees, and result in the formation of isomeric carbocations. Finally, the isomeric carbocations attack the thiophene to form the isomeric alkylation products.

Conclusions

(1) Thiophene could be converted to alkylation products using methanesulfonic acid as the catalyst. The alkylation products can be separated as the high-boiling sulfur compounds from the main gasoline stream by distillation. Thus the sulfur contents in gasoline could be reduced.

(2) Under the optimal conditions, the thiophene conver-

sion could reach 98.6% in 60 min. The catalyst could be reused without reactivation treatments and the thiophene conversion rate could achieve 92.9% the third time.

(3) Methanesulfonic acid is a strong Brønsted acid with high catalytic activity, which has high thermal stability and low vapor pressure. Moreover, the advantages of recyclable and biodegradable make it an alternative to catalyze the alkylation.

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