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## ARTICLE

## Alkylation desulfurization of C<sub>9</sub> fraction over Amberlyst 36 resin

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C<sub>9</sub> fraction is the by-products of catalytic reforming and ethylene cracker, it is usually considered as a kind of petroleum resin raw material. Recently, it was studied for use as a gasoline additive to enhance the economic benefits. However, C<sub>9</sub> fractions are getting higher in sulfur contents. According to these, C<sub>9</sub> fraction alkylation desulfurization process, which consists of weighing down the sulfuric compounds by catalytic alkylation with olefins present in the feed and distillation followed by, is a rather attractive way. In this paper, 2-Ethyl-5-methylthiophene, 2,5-Dimethylthiophene and 2-n-Propylthiophene were selected as the model compounds. Firstly, the alkylation reaction of thiophenic compounds with vinyltoluene was researched over macroporous sulfonic resin Amberlyst 36. Then the octane number of C<sub>9</sub> fraction was measured. It was found that the conversions of the thiophenic compounds could reach to above 99%, and the octane number of C<sub>9</sub> fraction was increased. Moreover, the alkylation of thiophenic sulfurs could be described as pseudo first order reaction, as well as the reaction rate constant and the activation energy of alkylation reactions were calculated.

### Introduction

To meet the standard of new environmental legislation and to avoid SO<sub>x</sub> pollution during fuel combustion, sulfur-containing compounds have to be largely eliminated from the fuel<sup>[1]</sup>. Then the removal of organosulfur compounds is receiving attention worldwide due to the environmental protection purpose. Therefore, it forced Chinese and others to find more environment friendly method to make refined oil, new and more economic additives are needed for producing affordable ultra-clean (ultra-low-sulfur and low-aromatics) transportation fuels and non-road fuels.

C<sub>9</sub> fraction is most commonly considered as a kind of petroleum resin raw material, while it has low economic benefits. Recently, C<sub>9</sub> fraction was studied as a gasoline additive, which could enhance the

economic benefits of enterprises, and it has good potential for use as a gasoline additive to increase the octane number of gasoline<sup>[2]</sup>. As the by-products of catalytic reforming and ethylene cracker, a large number of C<sub>9</sub> fractions have been produced every year<sup>[3]</sup>. However, C<sub>9</sub> fraction as a gasoline additive, which usually has a sulfur content of 250mg.L<sup>-1</sup>, is getting higher in sulfur contents. According to these situations, C<sub>9</sub> fraction desulfurization is receiving attention for the increasing stringent regulations on sulfur content.

As the conventional hydrotreating technology results in a significant reduction of octane number due to saturation of olefins in naphtha from fluid catalytic cracking, which also causes higher hydrogen consumption<sup>[4]</sup>. Consequently, many approaches to deep desulfurization have been proposed<sup>[5-10]</sup>. Among the non-hydrodesulfurization technologies, the alkylation desulfurization is a

rather attractive way. This approach consists in increasing the molecular weight of sulfur compounds using a catalytic alkylation reaction and hence in elevating their boiling point, thus allowing sulfur compounds to be easily separated by distillation<sup>[11]</sup>. As is well known that the alkylation of thiophenic compounds occur through the formation of carbocation<sup>[1]</sup>, macroporous acid catalysts are needed to use as the catalyst. Many acidic catalysts either with Brønsted or Lewis acidity were proposed, including various zeolites ( $\beta$ -zeolite, MCM22, USY)<sup>[12-15]</sup>, resin (Amberlyst 35)<sup>[16]</sup>, phosphoric acid on kieselguhr (also called solid phosphoric acid)<sup>[11]</sup>, etc.

Since the major sulfur species present in C<sub>9</sub> fraction being thiophenic derivatives (C<sub>2</sub> and C<sub>3</sub> thiophenes)<sup>[17]</sup>, we selected the 2-Ethyl-5-methylthiophene, 2,5-Dimethylthiophene and 2-n-Propylthiophene as the model compounds. Concerning the alkanes, its dimerisation product should not remain in the C<sub>9</sub> fraction, but it would not reduce the octane number, which is the case of its far less content. In this paper, the alkylation of thiophenic compounds in C<sub>9</sub> fraction using Amberlyst 36 resin as catalysts was carried out in a batch stirred tank reactor. Isoamylene as the conventional olefin additive has a good effect on the alkylation desulfurization<sup>[16]</sup>, in order to compare the effect of vinyltoluene and isoamylene on the alkylation desulfurization, the alkylation reactions with isoamylene were researched. Furthermore, kinetics of thiophenic sulfurs alkylation with olefins present in C<sub>9</sub> fraction was investigated, including the determination of reaction rate constant and activation energy.

## Experimental

### Materials and catalysts

The C<sub>9</sub> fraction used in this paper has a sulfur content of 250mg·L<sup>-1</sup>, with its compositions: vinyltoluene (5wt%), a-vinyltoluene (2wt%), polyene (C<sub>n</sub>H<sub>n</sub>, 10wt%), aromatics (65 wt.%), and other compositions (15wt%). The model feed was self-made with its composition: n-Decane (95wt.%) - thiophenic compound (250ug·g<sup>-1</sup>) - vinyltoluene (5wt.%), which were representative of non-active C<sub>9</sub> components, sulfur compounds and olefin in real C<sub>9</sub> fraction. Isoamylene (+99wt.%, contained 7.2wt.% 2-methyl-1-butene and

92.8wt.% 2-methyl-2-butene) and n-Decane (+99.5wt.%) were purchased from Tianjin Guangfu Company without any further purification. Vinyltoluene (+99wt.%) , 2-Ethyl-5-methylthiophene(+99wt.%), 2,5-Dimethylthiophene(+99wt.%), and 2-n-Propylthiophene(+99wt.%) were purchased from J&K Scientific company without any further purification. Amberlyst 36 (Rohm and Hass) was used as the catalyst. According to the supplier, the resin had the following characteristics (see Table.1).

**Table.1** the characteristics of Amberlyst 36 resin

Exchange capacity (mmol·g <sup>-1</sup> [H <sup>+</sup> ])	Particle size (mm)	Density (g ml <sup>-1</sup> )	Average Pore size (nm)	Specific area (m <sup>2</sup> /g)	Max temperature (K)
>5.4	0.425-1.180	1-1.2	24	33	423

Before the experiments, the catalyst was dried at 353 K for 4 h to remove the water from the catalyst structure.

### Catalyst evaluation

Reactions were carried out in a batch stirred tank reactor (100mL), with a stirring rate 320 rpm. In a typical catalytic experiment for catalyst evaluation, the reactor was charged with 3g freshly dried catalyst and 60mL C<sub>9</sub> fraction, then it was heated up to the setting temperature. The starting reaction time was taken arbitrarily when the setting temperature was reached. After 1 h of reaction, the autoclave was cooled down to room temperature and samples were withdrawn to be analyzed.

### Reaction kinetics analysis

In the experiment for reaction process investigation and reaction kinetics analysis, firstly the batch reactor was charged with 3g freshly dried Amberlyst 36 resin. After the reactor was heated up to the setting temperature, 100mL model C<sub>9</sub> fraction was introduced to the reactor. Meanwhile, the stirrer was adjusted to 320 rpm, in order to ensure the stirrer had no influence of the conversions of the sulfur compounds. The starting reaction time was taken arbitrary when this temperature was reached. In order to ensure the accuracy of the experiment, ten samples (0.4–0.5mL) were withdrawn every 25 min during the reaction course of the reaction, and the volume of the samples was negligible.

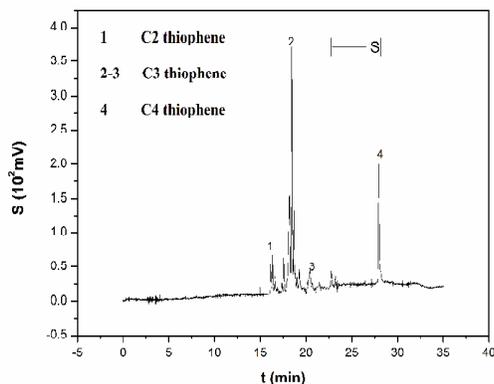
## Analysis

Samples were analyzed by a gas chromatograph (FULI 9790, Zhejiang Wenling Company) with a flame ionization detector (FID) and a flame photometric detector (FPD). The FID with a nonpolar capillary column (model OV-101, 30 m×0.25 mm×0.50μm) was employed to quantify the hydrocarbons, while the FPD with a capillary column (model OV-101, 60 m×0.25 mm×0.50μm) was utilized for the selective detection of sulfur compounds at parts-per-million levels in hydrocarbon mixtures. Total sulfur of samples were analyzed by a general coulomb meter (model: DL-2B-EE, Jiangyan Huadong company), GC-MS (7890A-5975C, Agilent), and Octane number detector (LAB131, Beijing Hightech Lab). For the analysis of model C<sub>9</sub> fraction, the temperature program started at 333 K with a hold time of 5 min, followed by a temperature ramp of 10 K/min to 553 K and then held a time of 10 min.

## Results and discussions

### Results of experiments with model sulfur compounds

C<sub>9</sub> fraction was firstly analyzed by GC-FPD and GC-MS. As can be seen from Fig. 1, the sulfur compounds in C<sub>9</sub> fraction were mostly C<sub>2</sub>–C<sub>4</sub> thiophene, and the boiling point of the sulfur compounds was in the temperature range from 413K to 443K, which was measured by the distillation methods. According to the results, 2,5-Dimethylthiophene, 2-Ethyl-5-methylthiophene, and 2-n-Propylthiophene were selected as the sulfur compounds.

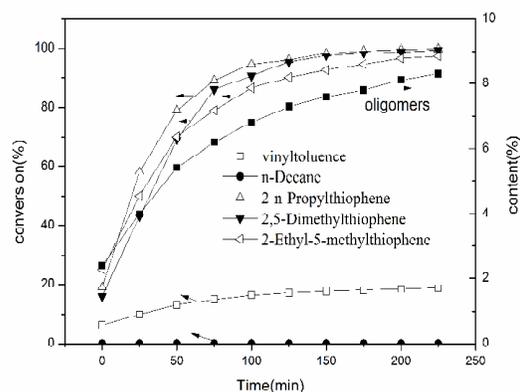


**Fig.1.** Sulfur compounds observed by GC-FPD in the real C<sub>9</sub> fraction  
**Alkylation desulfurization of real C<sub>9</sub> fraction over Amberlyst 36**

As is well known that the alkylation of thiophenic compounds occur through the formation of carbocation, macroporous acid catalysts are needed to use as the catalyst. And Amberlyst 36 is a kind of macroporous sulfonic resin, so Amberlyst 36 can be used as the catalyst. The experiments were carried out at 363K using C<sub>9</sub> fraction as a feed stock with the mass ratio of catalyst to C<sub>9</sub> fraction 1/30. It was found that sulfur content of product was 10.21 mg L<sup>-1</sup> after one hour. The conversion of thiophenic compounds was 96%, and the octane number of product was 126RON, while the octane number of C<sub>9</sub> fraction feed was 117RON.

### The feasibility of alkylation desulfurization over Amberlyst 36 in model C<sub>9</sub> fraction

To research the feasibility of reaction process in model C<sub>9</sub> fraction, reaction was carried out in model C<sub>9</sub> fraction with the mass ratio of Amberlyst 36 to vinyltoluence 3:1.95 at 363 K. Results of the experiment are presented in Fig. 2.



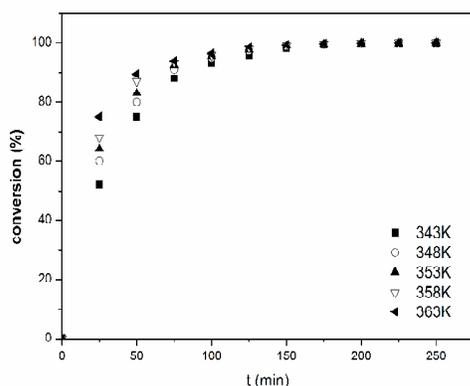
**Fig. 2.** Diagram of reactants conversion and products formation as a function of time in model reaction using Amberlyst 36 at 363 K

It was shown that vinyltoluence oligomerization took place preferable over thiophene alkylation, the reaction rate of thiophene alkylation was higher than vinyltoluence oligomerization, and the content of the oligomers were far less. Moreover, n-Decane conversion was close to 0 under all conditions. In this study, side reactions such as the reaction of oligomers with sulfur compounds were not detected. Therefore, the alkylation reaction of thiophene

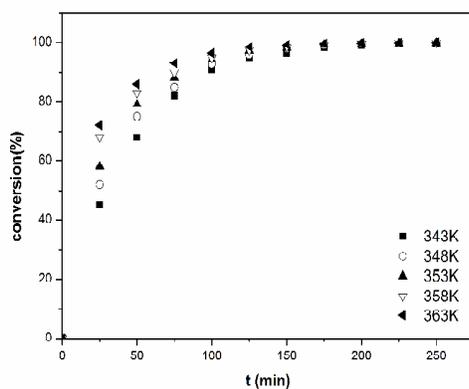
compounds with vinyltoluene was the main reactions. This suggests that the alkylation desulfurization over Amberlyst 36 in model C<sub>9</sub> fraction is feasibility.

### Kinetic of alkylation desulfurization of model C<sub>9</sub> fraction over Amberlyst 36

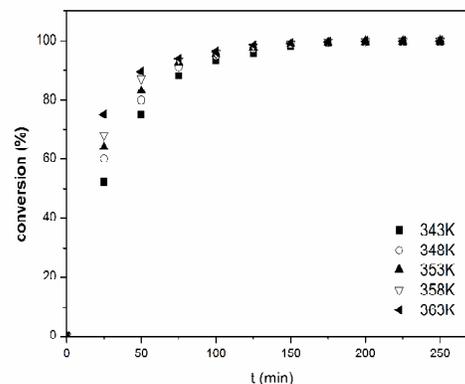
As mentioned above, 2-Ethyl-5-methylthiophene, 2,5-Dimethylthiophene and 2-n-Propylthiophene were chosen to study the kinetics of alkylation reactions of C<sub>9</sub> fraction in this paper. The experiments were carried out in model C<sub>9</sub> fraction with the mass ratio of catalyst to vinyltoluene 1/1 in the temperature range from 343K to 363K. Conversions of thiophenic compounds as a function of reaction time are presented in Fig. 3 to Fig.5.



**Fig.3.** Conversions of 2,5-Dimethylthiophene as a function of reaction time at different temperatures.



**Fig.4.** Conversions of 2-Ethyl-5-methylthiophene as a function of reaction time at different temperatures.



**Fig.5.** Conversions of 2-n-Propylthiophene as a function of reaction time at different temperatures.

As seen from these Figures, 2-Ethyl-5-methylthiophene, 2,5-Dimethylthiophene and 2-n-Propylthiophene all had very good alkylation reactivity with vinyltoluene. It was found that conversions of three sulfur compounds all reached about 99%, but increased slightly with the raise of temperature, in addition, the changing trends of the thiophenic compounds with reaction time were in a similar pattern. Before 75 min of reactions, the conversions of the sulfur compounds were changed dramatically with increase of temperature. After 100 min, the conversions of sulfur compounds were more than 99%, and the reactions reached the equilibrium quickly. Meanwhile, it could be seen that the conversions of 2-n-Propylthiophene were higher than 2-Ethyl-5-methylthiophene and 2,5-Dimethylthiophene. This indicated that C<sub>3</sub>-thiophene was more active than C<sub>2</sub>-thiophene in model reaction using Amberlyst 36 with vinyltoluene present.

Isoamylene is a good olefin additive for alkylation desulfurization<sup>[17]</sup>. In order to compare the effect of vinyltoluene and isoamylene on the alkylation desulfurization, the alkylation reactions with isoamylene were carried out. The results (see Table.2) showed that vinyltoluene had a better effect on the alkylation of the thiophenic compounds than isoamylene, and after 100min of the reaction, the reaction rate of carbonation formation of vinyltoluene reached the equilibrium. That can be explained that the reaction rate of carbonation formation of vinyltoluene was more rapid than

isoamylene, and after 100min of the reaction, the reaction rate of carbonation formation of vinyltoluene reached the equilibrium.

**Table.2.** Conversions of alkylation of thiophenic compounds with isoamylene and vinyltoluene after 100min at different temperatur

		Conversion (%)				
Temperature(K)		343	348	353	358	363
vinyltoluene	2,5-Dimethylthiophene	93.7	94.6	95.3	96.3	97
	2-Ethyl-5-methylthiophene	95	95.8	97.1	97.3	98.4
	2-n-Propylthiophene	95.8	97.2	97.5	98.1	98.5
isoamylene	2,5-Dimethylthiophene	68	72	79	81	88
	2-Ethyl-5-methylthiophene	70	89	90.5	94	97
	2-n-Propylthiophene	80	90.5	93.1	95.7	97.9

Besides, n-Decane conversion was close to 0 under all conditions during the reaction course. Sulfur compounds concentration decreased significantly, which could be explained by the alkylation reaction and the decrease of vinyltoluene concentration, so the method that using vinyltoluene which already present in C<sub>9</sub> fraction to reduce the sulfur compounds concentration of C<sub>9</sub> fraction had a good effect and had no influence on the reaction of n-Decane. As thiophenic compounds in C<sub>9</sub> fraction were far less than vinyltoluene, the amount of vinyltoluene consumed in thiophene alkylation could be neglected.

#### Apparent reaction kinetics equations

As a bimolecular reaction, the reaction rate of thiophenic sulfur alkylation is theoretically decided by the concentrations of olefins and thiophenic sulfurs<sup>[16]</sup>, with the reaction rate equation shown in Eq. (4). In the experiment, olefins were in far molar excess over thiophenic sulfurs in C<sub>9</sub> fraction, the concentration of olefins can be assumed to be constant during the entire reaction process.

Therefore, the reaction rate equations of thiophenic sulfur alkylation can be simplified as Eq. (2)

$$r_i = -\frac{dc_i}{dt} = k_i c_i^n c_{olefins}^m \quad (1)$$

$$r_i = -\frac{dc_i}{dt} = k_j c_i^n \quad k_j = k_i C_{olefins}^m \quad (2)$$

As the concentration of olefins can be assumed to be constant during the entire reaction process, and a stirred batch reactor is assumed to determine the reaction rate parameters for the disappearance of thiophenic sulfurs. So, i.e.n= 1, the integration of Eq. (2) yields Eq. (3)

$$-\ln(1 - X_i) = k_i t \quad (3)$$

$$\ln k = -\frac{E_a}{RT} + \ln k_0 \quad (4)$$

r<sub>i</sub> is the reaction rate, k<sub>i</sub> is the reaction rate constant, C<sub>i</sub> and C<sub>olefins</sub> are the concentration of thiophenic sulfur and olefins respectively, t is the reaction time, n and m are the reaction order, and X<sub>i</sub> is the conversion of thiophenic sulfur, including 2-Ethyl-5-methylthiophene, 2,5-Dimethylthiophene and 2-n-Propylthiophene. In Eq. (4), E<sub>a</sub> is the apparent activation energy and k<sub>0</sub> is the preexponential factor.

It can be seen from the plots in Fig. 6, -ln(1 - X<sub>i</sub>) against time at different temperatures gave straight lines passing through the origin as illustrated. The plots show that the rates of thiophenic sulfurs conversions have first-order dependence over Amberlyst 36 resin with respect to thiophenic sulfurs which is the limiting reactant, while it is of zero-order with respect to olefins which is in large excess.

From the plots in Fig. 6, k<sub>i</sub> (the reaction rate constant) could be evaluated, with the results list in Table 4. The representative Arrhenius plots for the reaction rate constant employing Arrhenius Equation is shown in Fig. 7. It can be seen from Table 3 that the fit of the experimental values to the Arrhenius equation is rather perfect, and the values of E<sub>a</sub> and k<sub>0</sub> derived from these plots are :17.03 kJ.mol<sup>-1</sup> and 1.25×10<sup>4</sup>h<sup>-1</sup> for 2,5-Dimethylthiophene, 16.55 kJ.mol<sup>-1</sup> and 1.19×10<sup>4</sup>h<sup>-1</sup> for 2-Ethyl-5-methylthiophene, 12.93 kJ.mol<sup>-1</sup> and 2.93×10<sup>3</sup>h<sup>-1</sup> for 2-n-Propylthiophene.

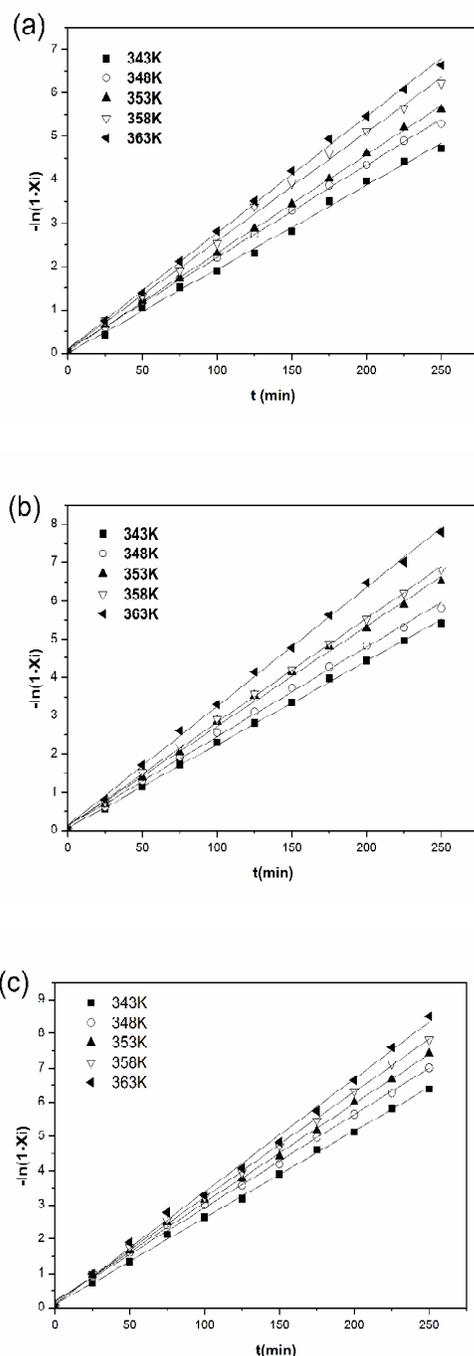


Fig.6. Pseudo first-order kinetic plots with vinyltoluene present:

(a) 2,5-Dimethylthiophene; (b) 2-Ethyl-5-methylthiophene;

(c) 2-n-Propylthiophene

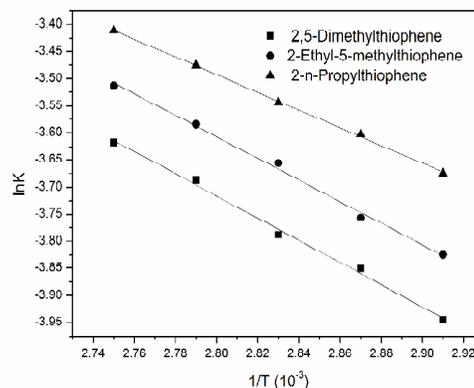


Fig.7. Arrhenius plots of alkylation desulfurization over Amberlyst 36 resin

Table 3. Kinetics parameters of different thiophenic compounds

	$E_a$ (kJ.mol <sup>-1</sup> )	$k_0$ (h <sup>-1</sup> )
2,5-Dimethylthiophene	17.03	$1.25 \times 10^3$
2-Ethyl-5-methylthiophene	16.55	$1.19 \times 10^3$
2-n-Propylthiophene	12.93	$2.93 \times 10^2$

#### Kinetics parameters of different model Sulfur compounds

As can be seen from Table 4, the reaction rate constant of 2-n-Propylthiophene are larger than others at the same condition. Furthermore, the ratio of reaction rate constant with the raise of temperature, which indicates that high temperatures could promote the effect of alkylation reactions of thiophenic sulfurs. That can be explained by the following two aspects. Firstly, as the reaction rate of carbonation formation grows with the increase of temperature, alkylation reactions of thiophenic sulfurs have longer reaction time at high temperatures. Secondly, as an exothermic reaction, the reaction equilibrium constant decreases with temperature increasing<sup>[16]</sup>, so more olefins are remained in the system, which would increase the reaction rate of alkylation reactions. The three thiophenic compounds show similar order on the activation energy and preexponential factor: 2,5-Dimethylthiophene > 2-Ethyl-5-methylthiophene  $\approx$  2-n-Propylthiophene, which indicates that the olefin could enfold the thiophene ring and combined with the  $\alpha$ -position of S atom.

The kinetic of the alkylation mechanism is following an Eley-Rideal law<sup>[11]</sup> and the reaction intermediate seems to be an ester of

sulfonic acid. In other words, only the olefin (vinyltoluene) is adsorbed on Amberlyst 36 resin to form a carbocation through an ester of sulfonic acid. Then the thiophenic molecule in the liquid phase reacts with this ester to form a monoalkyl, which will next be desorbed by giving back a proton to the surface.

**Table 4.** Reaction rate constant ( $h^{-1}$ ) of different model Sulfur compounds

Temperature (K)	343	348	353	358	363
2,5-Dimethylthiophene	1.16	1.28	1.36	1.50	1.61
2-Ethyl-5-methylthiophene	1.31	1.40	1.55	1.63	1.87
2-n-Propylthiophene	1.52	1.64	1.73	1.85	1.98

### Conclusions

Through the research of experiments in model C<sub>9</sub> fraction, it was found that 2-Ethyl-5-methylthiophene, 2,5-Dimethylthiophene and 2-n-Propylthiophene all had very good alkylation reactivity with vinyltoluene. Conversions of thiophenic compounds were all close to 99% after 150min of the reaction, and the octane number of C<sub>9</sub> fraction was increased by alkylation reaction, which suggests a new way to reduce the sulfur content in C<sub>9</sub> fraction. However, 2-n-Propylthiophene had higher conversions than 2-Ethyl-5-methylthiophene and 2,5-Dimethylthiophene, and the alkylation reaction rate of 2-n-Propylthiophene reached the equilibrium after 125 min of the reaction, which was more rapid than 2-Ethyl-5-methylthiophene and 2,5-Dimethylthiophene. This indicated that C<sub>3</sub>-thiophene was more active than C<sub>2</sub>-thiophene in model reaction using Amberlyst 36 with vinyltoluene present. That can be explained that the alkylation reaction is a kind of electrophilic substitution reaction which mainly occurs in the  $\alpha$ -position of thiophenic compound. As methyl, ethyl and propyl both belongs to the electron-donating groups, which can strengthen the electronegativity of the  $\alpha$ -positive of thiophenic ring, on the contrary, vinyltoluene is a kind of electrophiles. So the electronegativity can make the alkylation reaction of thiophenic compounds with vinyltoluene easier to happen. As we known, the effect of the electron-donating groups: propyl > ethyl > Methyl.

Moreover, 2,5-Dimethylthiophene and 2-Ethyl-5-methylthiophene both has two  $\alpha$ -branched-chains, so the alkylation reaction must happen in the  $\beta$ -position of thiophenic ring, it is more difficult than the reaction which happens in the  $\alpha$ -positive of thiophenic ring. So we can know that C<sub>3</sub>-thiophene was more active than C<sub>2</sub>-thiophene.

Moreover, kinetics parameters of different model Sulfur compounds were calculated, and three thiophenic compounds alkylation in model C<sub>9</sub> fraction shows the kinetic characteristic of an apparent pseudo first order reaction, assuming that the concentration of olefins is constant.

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### Notes and references

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- Breyse M, Djega-Mariadassou G, Pessayre S, et al. Deep desulfurization: reactions, catalysts and technological challenges. *Catalysis Today*, 2003, 84: 129-138.
- Shapiro H, De Witt E G, Brown J E. *US* 2,839,552, June 17, 1958. CA, 52: 17286.
- Dumskii Y V, Butov G M, Cherednikova G F, et al. Synthesis of petroleum polymer resins by initiated oligomerization of the C<sub>8</sub>/C<sub>9</sub> gasoline pyrolysis fraction. *Petroleum Chemistry*, 2014, 54: 69-71.
- Shafi R, Hutchings G J. Hydrodesulfurization of hindered dibenzothiophenes: an overview. *Catalysis Today*, 2000, 59: 423-442.
- Collins N A, Trewella J C. Alkylation process for desulfurization of gasoline: *U.S. Patent* 5,599, 441. 1997-2-4.

- 6 Song C, Ma X. New design approaches to ultra-clean diesel fuels by deep desulfurization and deep dearomatization. *Applied Catalysis B: Environmental*, 2003, 41: 207-238.
- 7 Zhang J, Wang A, Li X, et al. Oxidative desulfurization of dibenzothiophene and diesel over  $H_3PMO_{12}O_{40}$ . *Journal of Catalysis*, 2011, 279: 269-275.
- 8 Yansheng C, Changping L, Qingzhu J, et al. Desulfurization by oxidation combined with extraction using acidic room-temperature ionic liquids. *Green Chemistry*, 2011, 13: 1224-1229.
- 9 Hansmeier A R, Meindersma G W, de Haan A B. Desulfurization and denitrogenation of gasoline and diesel fuels by means of ionic liquids. *Green Chemistry*, 2011, 13: 1907-1913.
- 10 Kedra-Królik K, Fabrice M, Jaubert J N. Extraction of thiophene or pyridine from n-heptane using ionic liquids. Gasoline and diesel desulfurization. *Industrial & Engineering Chemistry Research*, 2011, 50: 2296-2306.
- 11 Bellière V, Lorentz C, Geantet C, et al. Kinetics and mechanism of liquid-phase alkylation of 3-methylthiophene with 2-methyl-2-butene over a solid phosphoric acid. *Applied Catalysis B: Environmental*, 2006, 64: 254-261.
- 12 Hu L, Zhang Z, Xie S, et al. Effect of grain size of zeolite Y on its catalytic performance in olefin alkylation thiophenic sulfur process. *Catalysis Communications*, 2009, 10: 900-904.
- 13 Liu Y, Yang B, Yi C, et al. Kinetics study of 3-methylthiophene alkylation with isobutylene catalyzed by NKC-9 ion exchange resin. *Industrial & Engineering Chemistry Research*, 2011, 50: 9609-9616.
- 14 Zhang Z, Li X, Zhang L, et al. Modification of HY zeolite by fluorine and its influence on olefin alkylation thiophenic sulfur in gasoline. *Asia-Pacific Journal of Chemical Engineering*, 2008, 3: 503-508.
- 15 Isernia L F. FTIR study of the relation, between extra-framework aluminium species and the adsorbed molecular water, and its effect on the acidity in ZSM-5 steamed zeolite. *Materials Research*, 2013, 16: 792-802.
- 16 Guo B, Wang R, Li Y. Gasoline alkylation desulfurization over Amberlyst 35 resin: Influence of methanol and apparent reaction kinetics. *Fuel*, 2011, 90: 713-718.
- 17 SUN G, LIU G. Analysis of the C9 Fraction by GC-MS and GC-FTIR. *Journal of Instrumental Analysis*, 2004, 23: 289-292.