Catal Lett (2009) 127:70–74
DOI 10.1007/s10562-008-9625-z

Study on Olefin Alkylation of Thiophenic Sulfur in FCC Gasoline Using La_2O_3-Modified HY Zeolite

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Received: 9 July 2008 / Accepted: 20 August 2008 /

Abstract HY zeolite modified by La_2O_3 on olefin alkylation of thiophenic sulfur in fluid catalytic cracking (FCC) gasoline was studied in the micro fixed-bed reactor. Reaction pressure 1.5 MPa, reaction temperature 180 °C, WHSV 3.5 h^{-1}, using HY zeolite modified by 2% La_2O_3, the conversion of thiophene sulfur promoted nearly 10% with good selectivity, comparing with no-modified by La_2O_3. Acidity of modification of HY zeolite with La_2O_3 was tested in Pyridine–IR, it showed that increasing the amount of weak Bronsted (B) acid and the ratio of total B acid with total Lewis (L) acid could strengthen the hydrogen transfer activity of the catalyst, which leaded to improving the capacity of thiophene alkylation. The X-ray diffraction (XRD) results showed that the structure of catalysts could be optimized by loaded proper amount of La_2O_3 for promoting the acidic properties of HY zeolite.

Keywords Thiophenic sulfur · HY zeolite · La_2O_3 · Alkylation · FCC gasoline

1 Introduction

In recent years, air pollution due to exhaust gas from commercial gasoline and diesel has been a major concern of the public. Increasing attention has been focused on the desulfurization of transportation fuels for environmental protection. Therefore, the Environmental Protection Agency of the United States and the European Commission have recently issued regulations that will require the refineries to reduce the sulfur content of gasoline less than 10 ppm by weight in 2011 [1, 2]. Because of Beijing Olympic Games in 2008 and world's fair in Shanghai in 2010, the two cities were enforced to take relevant regulations to decrease sulfur content of transportation gasoline in our country.

Since the facing work of gasoline desulfurization is mainly to remove sulfur from fluid catalytic cracking (FCC) process that contributes about a third to the gasoline pools in USA and Europe and more than 80% gasoline in China. Many researchers and refineries have focused their efforts on the sulfur reduction of the FCC gasoline [3, 4].

At present, most refineries of the gasoline desulfurization processes are through the catalytic hydrodesulfurization (HDS) route [5, 6]. Conventional HDS can reduce the sulfur content of naphtha to low levels, but this requires substantial hydrogen consumption and can be accompanied by significant octane number loss due to olefin saturation. Consequently, many processes to deep desulfurization for FCC gasoline have been investigated. Some refiners pay attention to an attractive technology to desulfurize gasoline called olefinic alkylation of thiophenic sulfur (OATS) patented and developed by British Petroleum [7–10], the invention relates to a process for selectively removing sulfur from a naphtha feed with no octane loss by adding olefins having from carbon atoms to a sulfur-containing naphtha feed to form olefin-enriched feed, under this catalytic alkylation reaction it increases the sulfur compounds molecular weight of sulfur compounds and at the same time elevates their boiling point, then the alkylized heavy thiophenes are separated from gasoline by distillation. By this process, they reported to reach a desulfurization level of

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99.5% with a minimal octane loss (less than two points), compared to a classical HDS with the same level of desulfurization an octane loss of 6–10 points has usually been investigated. In addition, since the alkylation of thiophenes is easy to take place, the OATS process can be operated under mild conditions without hydrogen consumption.

Several works had been investigated about the OATS zeolites catalysts, such as the Hβ, MCM-41, MCM-22 [11–13]. However, the activity of the acid catalyst and the alkylation conditions are hardly to be chosen which will lead to the other competitive reactions, the aromatics alkylation, since they could decrease the selectivity of the OATS and increase the losses in gasoline yield.

2 Experimental

2.1 The Preparation of Catalysts and Feedstock

The zeolite Y used in this study was obtained by Nanjing Catalyst Company. γ-Al_2O_3 was from Catalyst Plant of Hunan Changling refinery. Thiophene (99%) and 1-hexene (99%) were purchase from Shanghai Chemical Reagent Company. Aromatics fuels were from Sinopec Zhenhai Refining and Chemical Company Limited.

Because of the instability of olefin, easily being oxidated and isomerized, the feed stock could easily be greatly changed. In order to select the catalyst effectively, in this study it used the simulative high sulfuric content FCC gasoline, which consist of 1-hexene, thiophene and aromatics. The compositions of feedstock was showed in Table 1.

Zeolite Y was calcinated at 550 °C for 2 h under air to remove the organic templates, followed by an ion-exchange method, to convert it into the H-form. After ion exchange, the sample was mixed with adhesive γ-Al_2O_3 (weight ratio 0.55:0.45), added with the modification of 0–8% La_2O_3, blended with proper amount of 10% HNO_3 solution, squeezed to form strips to make a series of modified catalyst, calcined in a muffle furnace in air at 550 °C for 3 h, crushed and screened 20–40 mesh for being used.

Table 1 The compositions of feedstock

Component	Content wt (%)	Component	Content wt (%)
Benzene	1.0	Thiophene	2.0
Toluene	0.5	*m*-Xylene	19.8
Ethyl benzene	8.6	*o*-Xylene	10.3
p-Xylene	8.6	C_9-aromatics	25.8
1-Hexene	12.0	C_{10}-aromatics	12.0

2.2 Catalytic Tests

The reactions were carried out in the fixed-bed reactor, whose outer diameter is 8 mm, inside diameter is 6 mm, and length is 50 cm. Two grams catalyst were loaded in the middle of the reactor, and the other spaces were filled with quartz sand (40–60 mesh). Nitrogen was introduced into the reactor through a pressure controller to keep the pressure constant during the course of experiment. The reaction were carried out under the following conditions: reaction pressure 1.5 MPa, reaction temperature 180 °C, WHSV 3.5 h^{-1}. The products in the samples were analyzed with a HP5890 gas chromatograph equipped with FID and GC–MS (GC 6890-MS 5973 N, Agilent). The reported values of conversion $(X) = [(n_i - n_f)/n_i] \times 100$, where n_i is initial moles of reactant, n_f is final moles of reactant.

2.3 Catalyst Analysis

2.3.1 Acidity Characterization—Infrared Ray

The acid amount, acid density and the acid variety were measured by FT-IR6700 infrared spectroscopy (resolving power: 4 cm^{-1}, scan 32 times, wavenumber range 4,000–400 cm^{-1}) from the Nicolet Company using pyridine as the probe molecule. There are two kinds of acid variety. One is Bronsted acid (B), whose characteristic absorption peak is at 1,540 cm^{-1} (and other, e.g., 1,490 cm^{-1}), the other is Lewis acid (L), whose characteristic absorption peaks is at 1,450 cm^{-1} (and other, e.g., 1,490 cm^{-1}). The peaks appearing at 1,490 cm^{-1} are the results of being superposed with B acid and L acid.

2.3.2 Structure Identification—X-Ray Diffraction

X-ray diffraction (XRD) patterns of the thin films were taken on a diffractometer (RiGAKu Co. DMAX-IIIc, Japan), using Cu-Kα radiation, 40 kV, and 30 mA, for identification of the structure of the thin film. The scan speed and step/sampling were respectively 2 min^{-1} and 0.02.

3 Results and Discussion

3.1 The Effect of Reaction Temperature on Conversion of Thiophene

In order to determine the effect of activation temperature, different of seven reaction temperatures were from 140 to 260 °C, which were tested with no-modified catalyst, reaction pressure 1.5 MPa, WHSV 3.5 h^{-1}. The results were showed in Fig. 1.

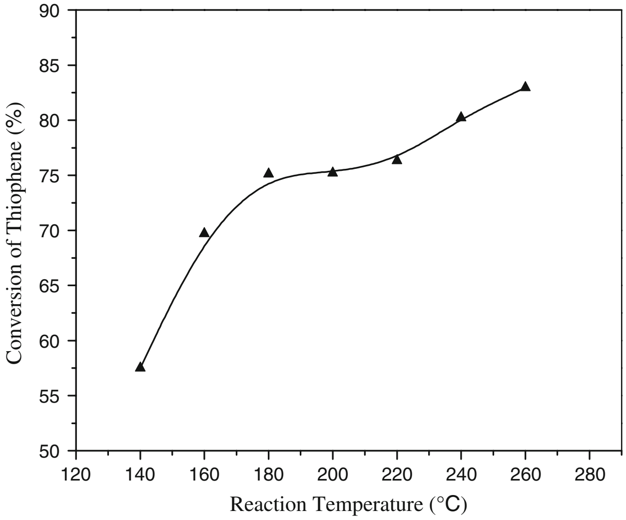


Fig. 1 Conversion of thiophene at different reaction temperatures

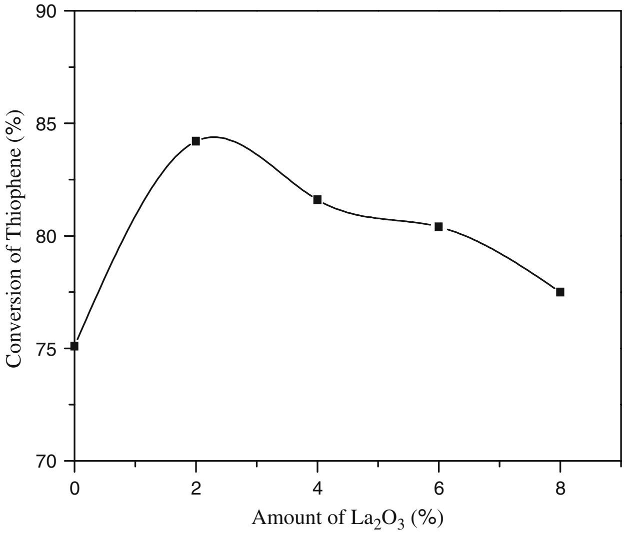
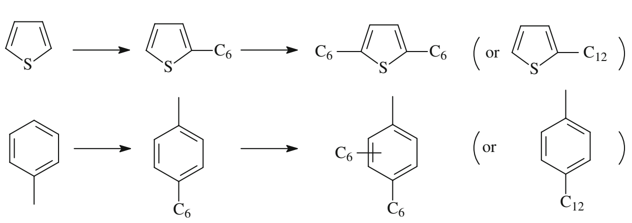


Fig. 2 Conversion of thiophene with different amounts of La_2O_3

Although the reaction of alkylation have reported at lower temperature that could be taken place, it could not act effective on high sulfuric content gasoline [13]. While the temperature below 140 °C, the conversion of thiophene is no more than 57.5%. During 180–220 °C the behaviors of catalyst activity go up slowly, which stay about 75% conversion rate level. A correlation between the alkylation reaction activity and the reaction temperature had been found, showing that with the reaction temperature growing the reaction activity increased, especially above 220 °C. However, in practice at 260 °C, it was detected that the contents of 1-hexene and aromatics declined sharply in the light parts, the alkylation products of benzene, toluene, and xylene increased obviously in the heavy parts by GC–MS. In general, the alkylation of thiophene and aromatics with 1-hexene give mono- and di-alkylated compounds by successive reactions, as are summarized in Scheme 1. That because alkylation performance of aromatics with hexene was improved, which could lead to selectivity of catalyst down. Therefore, the optimized reaction temperature is 180 °C, which was adopted in the following deep research.



Scheme 1

3.2 The Effect of the Amount of La_2O_3 on Thiophene Alkylation

The reactions were carried out at reaction pressure 1.5 MPa, temperature 180 °C, WHSV 3.5 h^{-1}. A correlation between thiophene alkylation and the different amount of La_2O_3 supported on zeolite Y had been tested, showed in Fig. 2.

The performances of La–HY catalysts are more effective comparing with no-modified by La_2O_3, the conversion of thiophene up to 84.2%, as the amount of 2% La_2O_3 loaded. The maximum is near 10% higher than no-modified by La_2O_3. However, after the maximum, with the increasing amount of La_2O_3, the conversion of thiophene declined obviously, while added 8% La_2O_3 loaded, it reduced to 77.5% closing to no modified catalyst.

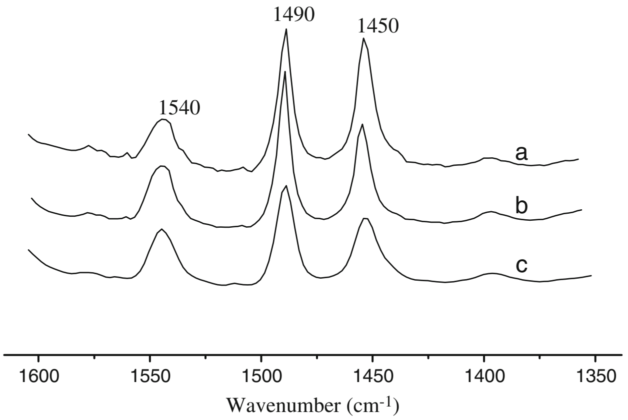


Fig. 3 The spectra of acidic properties at 200 °C desorption. (a) HY; (b) 2% La_2O_3/HY; (c) 6% La_2O_3/HY

The results of Infrared ray spectra of the acidity characterization of HY catalysts loaded by 0, 2, and 6% La_2O_3 were showed in Figs. 3, 4 and Table 2.

It was showed that with increasing contents of La_2O_3 the amount of total strong L acid reduced, but the total B acid firstly increased then decreased. As 2% La_2O_3 loaded, the catalyst had the most amount of total B acid. The reason is that with increasing La_2O_3 contents the changes of strong B acid were not significant, the changes of total B acid were influenced mainly by the weak B acid, while the changes of the total L acid were affected by combination of weak and strong L acid. The changes of the ratio of total B acid and total L acid were the same as the weak B acid. Therefore, increasing the amount of the weak B acid and ratio of the total B acid with the total L acid were contributed to increase the hydrogen transfer activity of the catalyst, thus, improving the capacity of thiophene alkylation.

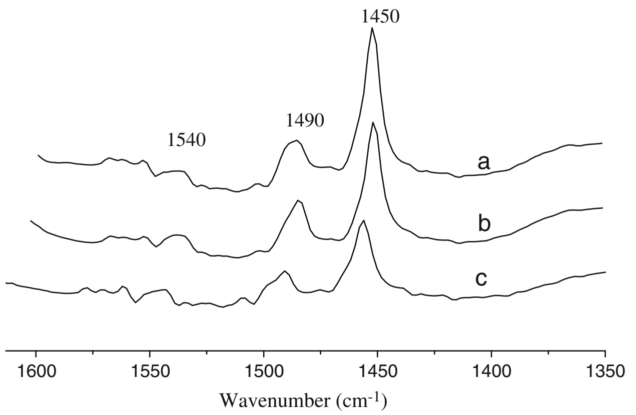


Fig. 4 The spectra of acidic properties at 450 °C desorption. (a) HY; (b) 2% La_2O_3/HY; (c) 6% La_2O_3/HY

Table 2 Acidic properties of different amounts of La_2O_3

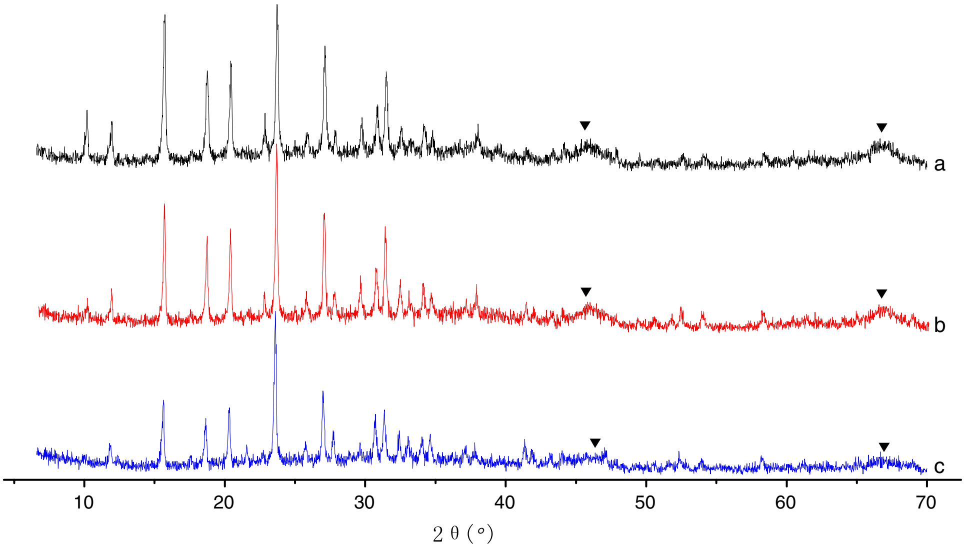
Catalysts	C/($\times10^{-4}$ mol g^{-1})							TB:TL (%)
	T	TL	TB	SL	SB	WL	WB	
0% La_2O_3	64.52	28.27	36.25	15.55	3.59	12.72	32.66	1.282
2% La_2O_3	67.27	21.06	46.21	13.23	5.23	7.83	40.98	2.193
6% La_2O_3	59.75	18.87	40.88	8.84	4.66	10.03	36.22	2.164

T—Total acid; TL—total L acid; TB—total B acid; SL—strong L acid; SB—strong B acid; WL—weak L acid; WB—weak B acid

X-ray diffraction spectra of the HY catalyst loaded by 0, 2, and 6% La_2O_3 were showed in Fig. 5.

La_2O_3 was not detected in the XRD spectra of La_2O_3 loaded sample, however in the samples loaded 2%, 6% La_2O_3 acidic $LaAlO_3$ was identified at 23.44° with the most intense diffraction of $LaAlO_3$ plane (0 1 2) in the reference card. With increasing the amount of La_2O_3 the main diffraction peaks of HY at 15.58°, 18.58°, 20.24°, 23.52°, 26.9°, 31.28° were corresponding weakened and reduced to about 50% in the sample added 6% La_2O_3, The reason is parts of La^{3+} inserted into framework of HY vacant sites, the structure of HY was optimized by loaded proper amount of La_2O_3, however too much La_2O_3 could greatly destroy crystallinity of catalyst. The same as peaks of HY changes, the γ-Al_2O_3 diffraction peaks were corresponding weakened with increasing the La_2O_3 content for the reaction between γ-Al_2O_3 and La_2O_3. This result could further illustrate that increasing contents of La_2O_3 the amount of total L acid reduced in the infrared ray spectra. When the La_2O_3 content was 2%, the reaction activity was the optimum.

Fig. 5 XRD spectra of the catalyst. (a) HY; (b) 2% La_2O_3/HY; (c) 6% La_2O_3/HY. The diffraction peaks ▼ for γ-Al_2O_3



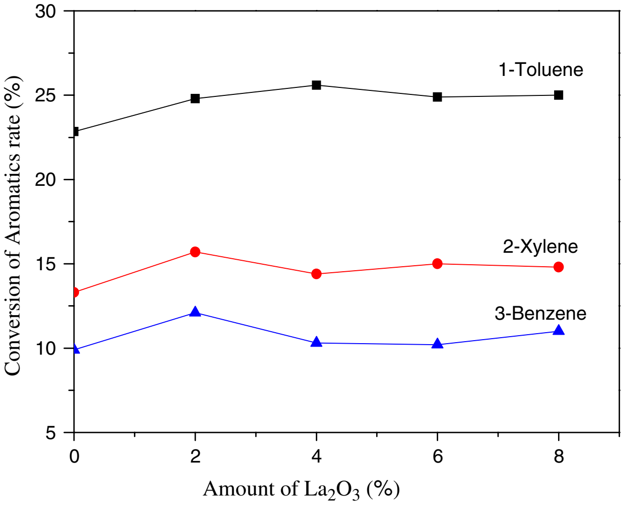


Fig. 6 Conversion of aromatics with different amounts of La_2O_3

3.3 The Effect of the Amount of La_2O_3 on Aromatics Alkylation

As seen in the Fig. 6, the reactivity of aromatics alkylation decrease in the order toluene > benzene > xylene. That because one side chain added to benzene ring could improve alkylation reactivity, however with the increases of the side chains the reaction decreased for the steric effect. Aromatics alkylation activity with the different amounts of La_2O_3 supported on zeolite Y changed not as obviously as thiophene. The first explanation for the performance is that the optimized structure of HY by loaded 2% La_2O_3 was only helpful to thiophene alkylation, The other explanation for this result could be attributed to the carbocation competition between thiophene alkylation and aromatics alkylation. While the catalyst was modified by La_2O_3, with the special electronic cloud distribution thiophene was the most reactive among the feedstock and consumed most of the carbocations.

Owing to changeless aromatics alkylation and promotional thiophene alkylation, it could be inferred that the selectivity of thiophene alkylation was improved.

4 Conclusions

With the activation temperature growing the reaction activity increased, alkylation performance of thiophene and aromatics with hexene was improved, which could lead to the yield and selectivity of the OATS catalyst decreasing. So the optimized reaction temperature is 180 °C using HY zeolite catalyst.

The structure of HY is optimized by proper amount of La^{3+} inserted into framework of HY vacant sites which are limited, however a larger amount of no acidic La_2O_3 will dilute the catalyst acidity and cause the destruction of the crystallinity of catalyst. The acidity characterization results showed that, loading 2% La_2O_3, the amount of the weak B acid and ratio of the total B acid with the total L acid enhanced, which strengthened the hydrogen transfer activity leading to the increase of thiophene alkylation capacity and almost changeless for aromatics alkylation. The effect of activity and selectivity were promotional using 2% La_2O_3-modified on the HY catalyst.

Acknowledgments The authors thank Sinopec Zhenhai Refining and Chemical Company Limited for providing aromatics and financial support.

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