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The Effect of Lanthanum and Niobium on Additives for Olefins Reduction of FCC Gasoline

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Abstract To develop a novel additive that has excellent olefin reduction capability for FCC gasoline without loss in octane number, different additives based on magnesia-alumina spinel were prepared by sol–gel method. The catalytic activities of additives for reducing the olefins in the fluid catalytic cracking (FCC) gasoline were assessed in a micro fixed bed reactor and the influences of Mg/Al ratio, the modification of La and Nb on the additive performance were studied as well. Results indicated that the additive with the Mg/Al ratio of 1.0 possessed the highest reaction activity due to the formation of $MgAl_2O_4{\cdot}MgO$ spinel. The activities of additives modified by La and Nb were also improved, for example, the reaction activity of additive with 4–5 wt% La was 34%. The XRD results showed that the effect of reducing olefin was the function of both $MgAl_2O_4{\cdot}MgO$ spinel and La_mO_n or $MgAl_2O_4{\cdot}MgO$ spinel and Nb_2O_5.

Keywords Additive · Spinel · Lanthanum · Niobium · FCC gasoline · Reducing olefin · Hydrogen transfer

1 Introduction

The rapid development of automotive industry brings about the great increase of fuel consumption, and, as a consequence, the air pollution caused by exhaust gas becomes more and more serious [1–3]. In China approximately 80% of gasoline comes from FCC gasoline in which the olefins content is usually as high as 40–55 vol.% [4]. The high olefins content has brought negative influence to the sediment of engine, the emission of deleterious gas from engine and actinochemistry reaction activity of the tail gas. At the beginning of 2005, SINOPEC put forward that, because of Beijing Olympic Games in 2008 and world's fair in Shanghai in 2010, the two cities were enforced to take the lead in using the Europe III vehicle standard of unleaded gasoline. It is predicted that the Europe IV vehicle standard will be performed in all Chinese big cities in 2010.

Therefore, various measures have been taken to control the olefins content of FCC gasoline. It has been found that by means of operation optimization of FCC units and use of novel olefins reduction FCC catalysts [5–7] the olefins content can be decreased to around 35 vol.% [8], which is still much higher than the upper value 18 vol.% as regulated by Europe III vehicle standard of unleaded gasoline. Several selective hydrogenation routes have been proposed and some of them have been put into pilot-scale operations, but none of them enables satisfactory olefins control with acceptable loss in both gasoline research octane number (RON) and yield [8]. Therefore, it is urgent to develop a novel technique that can preserve the octane value while reducing the olefins content of gasoline. At this time, the function of the additive for reducing olefin doesn't allow to be ignored.

The magnesia-alumina spinel, as an important catalytic material, has catalytic activity, and can be widely used as supporting material. It not only has these two advantages, but also has some other new advantages, which makes the exploitation of spines being an important research direction in catalytic field [9]. In this paper, lanthanum and niobium were carried on magnesia-alumina spinel and it was found that the effect of the additive for reducing the olefin had been improved greatly.

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2 Experimental

2.1 Additive Preparation

A number of additives have been prepared using sol–gel method. Initially, two solutions were prepared: one solution containing aluminum ions by dissolving 102.0 g alumina and a given amount of $H_2C_2O_4$ into 900 mL deionized water and another containing magnesium ions by dissolving 80.0 g magnesia and some $H_2C_2O_4$ into 450 mL deionized water. Then, mixed solutions were added into different mass fraction of lanthanum or niobium. Afterwards, the homogeneous mixture was maintained under reflux at 353 K with continuous stirring for 3 h until the gel was formed. Additives were activated by baked two hours in the oven at the indicated temperature after being dried at 393 K. Then, additives were prepared with 40–80 meshes for being used. The additives, S301–S305, with different amounts of Nb and S401–S406 with different amounts of La were prepared, and the S201–S205 were the additives with different ratios of Mg and Al.

2.2 Activity Testing

The proportion of <C7 fractions is about 30%, which part has the most olefin in FCC gasoline (about 70%). C5–C7 olefin fractions are the main source of being volatile organic substance, nitric oxides and the toxicant. Because of the instability of olefin, easily being oxidized and isomerized, the feed stock could easily be great different. In order to select the additive effectively, the simulative gasoline, which consists of hexene and aroma, was used. The compositions of feed stock were showed in Table 1.

The reactions were carried out in the fixed-bed reactor, whose outer diameter is 8 mm and inside diameter is 6 mm and length is 50 cm. About 2 g catalyst (the property, showed in Table 2) and 0.016 g additive were loaded in the middle of the reactor, and the other spaces were filled with quartz sand (40–60 meshes). In order to make sure the temperature was steady, some aluminum was wrapped around the reactor. The reaction space velocity was 20 h^{-1}. The amount of the olefin in the samples was measured by iodine value method (ASTM D-2163). The reaction activity was calculated by following equation:

$$\text{The reaction activity} = \frac{I_1 - I_2}{I_1} \times 100\%$$

I_1—iodine value of the sample before reaction; I_2—iodine value of the sample after reaction.

Table 1 The compositions of feedstock

Component	Content (wt%)	Component	Content (wt%)
Non-aromatics	<1	*M*-xylene	19.8
Toluene	<0.5	*O*-xylene	10.3
Ethyl benzene	8.6	C_9-aromatics	25.8
P-xylene	8.6	C_{10}-aromatics	12.0
Hexene	14.0		

Table 2 The property of FCC catalyst

Activity (%)	Surface area (m^2/g)	Pore volume (mL/g)	Metal content (μg/g)					
56.9	99	0.14	Fe	Ni	Cu	V	Na	Ca
			3,400	8,000	40	2,520	2,600	1,440

2.3 Additive Characterization

2.3.1 Structure Identification—X-ray Diffraction

XRD patterns of the thin films were taken on an X-ray diffractometer (RiGAKu Co. DMAX-IIIc, Japan) using CuKα radiation, 40 kV and 30 mA, for identification of the phase and structure of the thin film. The scan speed and step-size were respectively 2°/min and 0.02°.

2.3.2 Acidity Characterization—Infrared Ray

The acid amount and the acid variety were measured by Magna-IR55 infrared spectroscopy from the Nicolet Company using pyridine as the probe molecule. There are two kinds of acid variety. One is Bronsted acid (B), whose absorption peak is at 1,490 cm^{-1}, the other is Lewis acid (L), whose absorption peaks is at 1,450 cm^{-1}.

3 Results and Discussion

3.1 The Influence of Reducing Olefins of Additives with Different Ratios of Mg and Al

The reactions were carried out at 673 K, 20 h^{-1}, and the reaction activities of different Mg/Al mole ratios were showed in Fig 1.

It can be seen that the activity of magnesia-alumina additive reaches a maximum with increasing Mg/Al mole ratio, and the additives with the Mg/Al mole ratio of 1.0 showed the best reaction activity.

Figure 2 is the XRD spectra of samples with different Mg/Al mole ratio. Magnesia-alumina spinel was observed when the thin film was calcined at a certain high temperature, indicating that it was well crystallized. With the

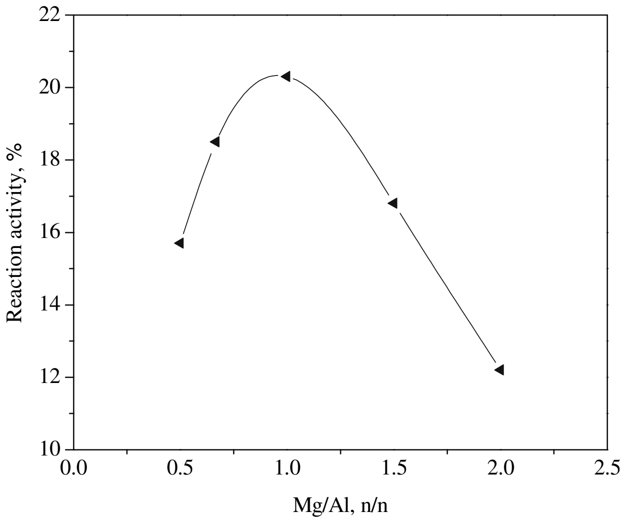

Fig. 1 The influence of additives for reducing olefins with different ratios of Mg and Al

content of Al_2O_3 increasing, the characteristic peaks of MgO and $MgAl_2O_4 \cdot MgO$ were strengthened, afterwards, the $MgAl_2O_4 \cdot MgO$ characteristic peak disappeared and $MgAl_2O_4$ characteristic peak was presented. Because the $MgAl_2O_4 \cdot MgO$ spinel had the greater lattice constant than $MgAl_2O_4$ spinel and the inflation effect of the crystal cell was also stronger than $MgAl_2O_4$ spinel, this crystal structure was conducive to cell volume increase and bulk diffusion, as a result, a deep reaction could be processed. $MgAl_2O_4 \cdot MgO$ spinel had both acid and alkaline active centers, which would be conducive to enhance oxidation absorption activity of the additive.

3.2 The Influence of Reducing Olefins of Additives with Different Amount of Nb

As a new catalytic materials niobium oxide due to its unique nature of the redox has been growing concern. The

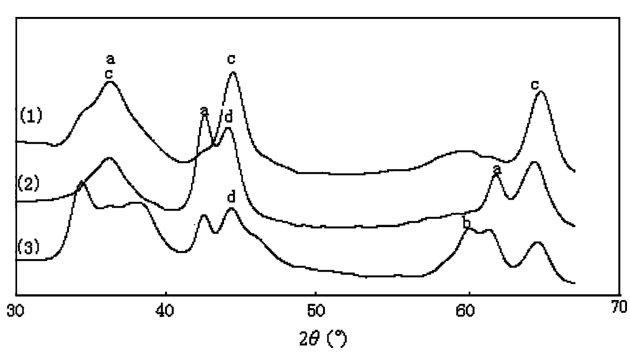

Fig. 2 XRD pattern of samples with different ratios of Mg and Al. a—MgO, b—Al_2O_3, c—$MgAl_2O_4$, d—$MgAl_2O_4 \cdot MgO$. (1) S201: Mg/Al=1:2; (2) S203: Mg/Al=1:1; (3) S205: Mg/Al=2:1

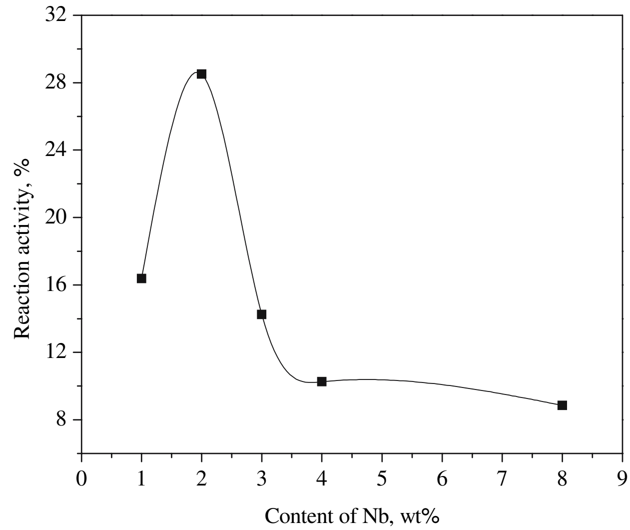

Fig. 3 The influence of reducing olefins of additives with different amount of Nb

reactions were carried out at 673 K, 20 h^{-1}. Magnesia-alumina additives with the Mg/Al mole ratio of 1.0 were added into different mass fraction of niobium.

Figure 3 presents the results of reaction activity of additives with niobium. It can readily be seen that the reaction activity is still satisfactory. When the Nb content was 2 wt%, the reaction activity reached the maximum 28.5%.

Figure 4 illustrates the XRD results of samples, we can see that there was a strong diffraction peak of Nb_2O_5 when the Nb content was 2 wt%. It has changed the structure of magnesia-alumina spinel, made the crystal particles increase, crystal trend to perfect, and easily lead to the surface

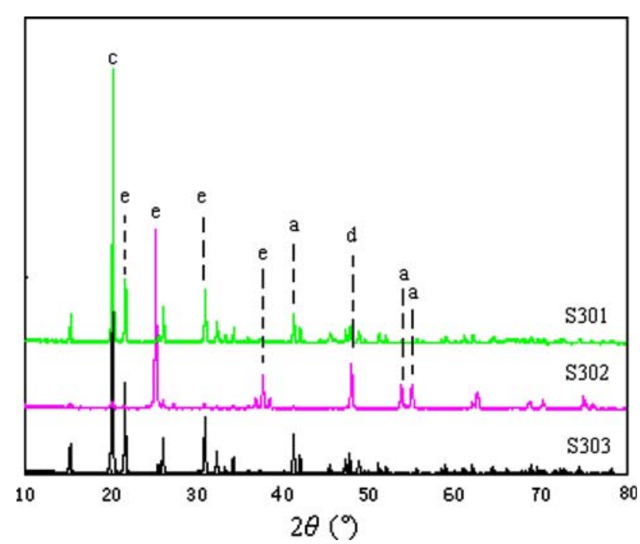

Fig. 4 XRD pattern of samples with different content of Nb. a—MgO, c—$MgAl_2O_4$, d—$MgAl_2O_4 \cdot MgO$, e—Nb_2O_5

defects of the crystal decreased. The structure of additive with 2 wt% Nb content greatly increased the hydrogen transfer activity of magnesia-alumina spinel, promoted the hydrogen transfer reaction, so the reaction result was satisfactory.

3.3 The Influence of Reducing Olefins of Additives with Different Amount of La

The reactions were carried out at 673 K, 20 h^{-1}. Magnesia-alumina additives with the Mg/Al mole ratio of 1.0 were added into different mass fraction of lanthanum.

As shown in Fig. 5, the reducing olefin effects of La-supported spinels were all effective and the activity reached a maximum as the amount of La loaded onto the spinel increases. This maximum, corresponding to optimum reaction activity, falls exactly in the region of monolayer La dispersion when the La content is 4–5 wt%. In this region, the maximum reaction activity is about 34%.

The samples, S401–S406, corresponding to the La content in the range 1.5–10 wt% were prepared. Figure 6 lists the results of XRD patterns of additives with different amount of La. It tells us that after added into lanthanum, different phases, $Al_xLa_yO_z$, La_mO_n were identified in the samples, and the diffraction peak intensities of MgO, $MgAl_2O_4$, $MgAl_2O_4$·MgO were obviously weakened. Compared to 2#, 3# and 4# samples, with the content of La increasing, the trend of diffraction peak intensities of magnesia-alumina spinel and La_mO_n were fully consistent with reaction activity. So the improvement of the activity is the common action of magnesia-alumina spinel and La_mO_n.

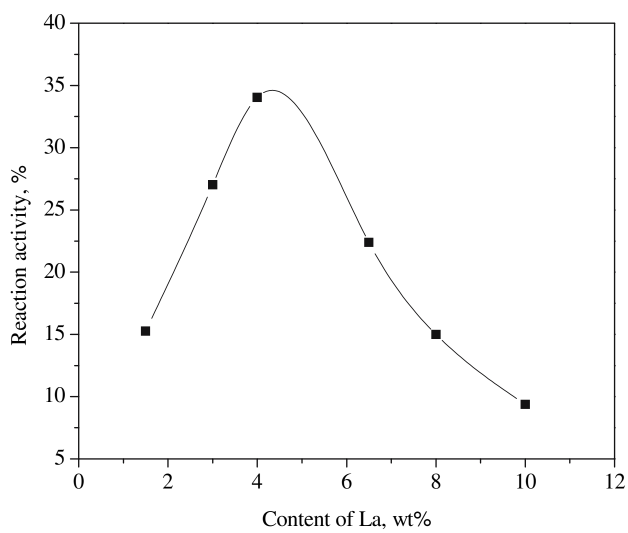

Fig. 5 The influence of reducing olefins of additives with different amount of La

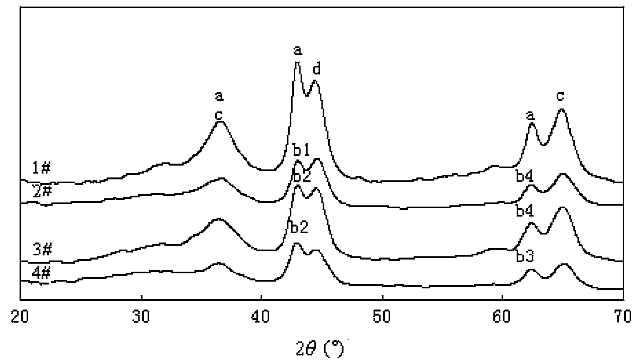

Fig. 6 XRD pattern of samples with different amount of La. a—MgO, b1—$La_2Al_{24.4}O_{39.6}$, b2—$Al_{22}La_2O_{36}$, b3—La_2O_3, b4—LaO, c—$MgAl_2O_4$, d—$MgAl_2O_4$·MgO, 1#: S203, 2#: S401, 3#: S403, 4#: S404

All the reaction results above confirm that the additive modified by La has better activity. The results of the acidity characterization of the additives were showed in Figs. 7 and 8. Compared to FCC catalyst, S203 and S403, it can be seen that the amount of total L and B acids increased at 473 K, meanwhile, the amount of strong L and B acids decreased at 723 K, as a result, the weak L and B acids increased, which was contributed to increase the hydrogen transfer activity.

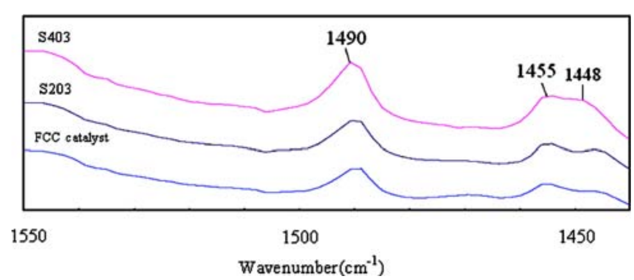

Fig. 7 The spectra of acidic properties of different samples treated at 473 K

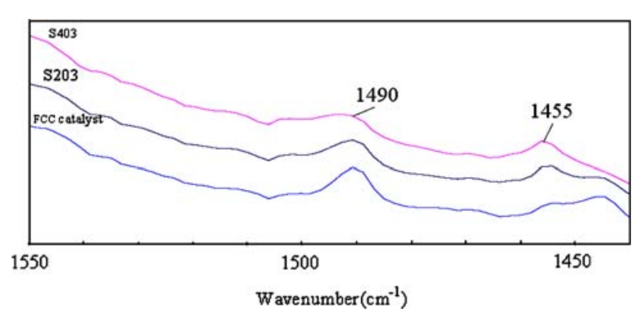

Fig. 8 The spectra of acidic properties of different samples treated at 723 K

4 Reaction Mechanism

In the fluid catalytic cracking system, there are many catalytic reactions, such as, cracking, hydrogen transfer, aromatization, isomerization, alkylation, transalkylation, dismutation, condensation, polyreaction, et al. Some reactions are conducive to olefins reduction in the FCC gasoline, e.g., aromatization, hydrogen transfer, isomerization, alkylation, and hydrogen transfer plays a decisive role in reducing olefins. It is known that hydrogen transfer can be divided into two types according to whether the desorption of arenes occurs [10, 11], i.e.,

Type I:

$$3C_nH_{2n}(\text{Olefin}) + C_mH_{2m}(\text{Cycloalkane or Olefin}) \xrightarrow{\text{Hydrogen tranfer}} 3C_nH_{2n+2}(\text{Alkane}) + C_mH_{2m-6}(\text{Arene})$$

Type II:

$$C_nH_{2n}(\text{Cycloalkene}) + C_mH_{2m-6}(\text{Arene}) \xrightarrow[\text{Condensation}]{\text{Hydrogen transfer}} \text{Precursor of coke}$$

We should choose the additive that increases the hydrogen transfer activity and promotes the Type I hydrogen transfer reaction in order to reduce the olefins and not to increase the amount of coke.

Table 3 illustrates the evaluation results of the distribution of hydrocarbon in FCC gasoline. It can be seen that by this measurement the additive not only has stronger olefins reduction ability but also has better stability in olefins reduction in FCC gasoline. Its RON is preserved while the olefins content is reduced greatly. And from the value of Alkane/olefin, we can see that additives effectively promote the Type I hydrogen transfer reaction.

Table 3 The distribution of hydrocarbon in FCC gasoline after treatment by different additive

Catalyst	Aromatics (wt%)	Olefins (wt%)	Alkanes (wt%)	Alkane/olefin (wt%)	RON
FCC catalyst	24.5	33.1	42.4	1.28	90.4
Mg–Al	31.7	19.6	48.7	2.48	90.5
Nb/Mg–Al	32.0	18.2	49.8	2.74	90.6
La/Mg–Al	33.2	16.7	50.1	3.00	90.9

Note: Reaction conditions: Catalysts/oil ratio = 4.5, Space velocity = 10 h^{-1}, Temperature = 773 K

5 Conclusions

In order to develop a novel additive to reduce the olefins content in FCC gasoline, different additives based on magnesia-alumina spinel carriers were prepared and their catalytic performances for reducing olefins in FCC gasoline were studied. The result showed that the additives with the Mg/Al mole ratio of 1.0 possessed the highest reaction activity due to the formation of $MgAl_2O_4{\cdot}MgO$ spinel. The activities of additives modified by La and Nb were also improved. When the La content was 4–5 wt%, the reaction activity reached the maximum about 34%. When the Nb content was 2 wt%, the optimum reaction activity was about 28.5%. It was found that the effect of reducing olefin was the function of both $MgAl_2O_4{\cdot}MgO$ spinel and La_mO_n or $MgAl_2O_4{\cdot}MgO$ spinel and Nb_2O_5. When the proportion of the two was up to the optimum one, the effect was optimum. The additive strengthened the hydrogen transfer activity, so the effect of reducing olefin was improved. The most outstanding characteristic of this additive is that olefins content is greatly reduced avoiding the loss of the RON of FCC gasoline.

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