

Surface modification of zeolite Y and mechanism for reducing naphtha olefin formation in catalytic cracking reaction

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Abstract

After modifications of rare earth and phosphorus, the acidity density and the strength in the pores of zeolite Y (PREUSY) are improved effectively; the surface acidity is suitably reduced and weakened owing to the interaction of rare earth cation and phosphate anion. NH₃-TPD analysis showed that the acid distribution of the modified zeolite is more concentrated on the range of intermediate and strong acidity. This kind of modification can direct more hydrocarbons to enter into the pores to be converted and remarkably reduces the possibility of naphtha olefins forming through a surface cracking reaction. In addition, because naphtha olefin reduction does not completely depend on olefin saturation through secondary hydrogen transfer reaction, this kind of reaction mode can decrease the excessive cracking of mediate distillate and can improve the diesel oil yield (LCO) effectively. Some reaction pathways were proposed.

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1. Introduction

A great deal of attention has been paid to developing novel olefin reducing fluid catalytic cracking (FCC) catalysts due to the legislation which places limits on the olefin content of gasoline in China. However, the application of this kind of catalyst has resulted in poorer coke selectivity and a dramatic decrease in diesel yield (LCO) [1,2]. As we know, there is always a lack of diesel oil in the Chinese oil market. So, it is very urgent to develop a novel FCC catalyst for producing lower naphtha olefin and higher diesel yield.

According to β -scission mechanism [3], a considerable concentration of olefins will always generate in a cracking reaction. Such olefins are protonated to form carbenium and then follow a secondary hydrogen transfer reaction to be saturated; the process accompanies the coke formation and diesel reduction. Recently, we prepared PREUSY on which the formation of olefins and coke was obviously suppressed

in cracking reaction by directing the reaction pathway; some reaction pathways were proposed.

2. Experimental

PREUSY was prepared as follows: zeolite Y was mixed with an aqueous solution of a rare earth compound, adjusting the pH to 3.5–4.0 with dilute hydrochloric acid; the mixture was reacted at 92 °C for 2 h. A specified amount of ammonium phosphate was added into the reaction mixture, and this combination continued to react for 1.5 h. The final reaction mixtures were filtered, washed, and calcined at 600 °C in air for 2.5 h. The contrastive zeolite sample (REUSY) was prepared from a zeolite Y and an aqueous solution of a rare earth compound, as described elsewhere [4,5]. Catalyst samples were prepared as follows [6]: zeolite sample, kaolin and Al₂O₃ binder were mixed thoroughly. The mixture was sprayed at 500–600 °C, acquiring microspheres whose average particles are about 50–70 μ m in diameter. The formed microspheres were washed, filtered, and dried.

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The composition of the samples was determined by elemental chemical analysis. The unit cell parameter (a_0) and relative crystallinity (RC) of the zeolite Y were determined by X-ray diffractometry (XRD) using a Rigaku (D/Max-3C) with Cu radiation and a Ni filter. The a_0 was obtained from the diffraction data using the strongest peak in the area $2\theta = 31\text{--}32^\circ$, using pure silicon powder as the internal standard sample. The RC was determined using the ratio of diffraction peak intensity in the area of Miller indices 5 3 3 (h k l).

The acidity properties of the samples were determined using the NH_3 -TPD method, which was performed using an ordinary flow-type apparatus with a closed circulation system for gas adsorption and a thermo-conductivity cell in a He flow for the determination of desorbed gas. The sample, 0.5 g, was evacuated at 550°C for 1 h and then was cooled to ambient temperature in vacuum. NH_3 gas was then introduced for 30 min; then the temperature of the sample was raised to 700°C in a He stream of $30\text{ cm}^3/\text{min}$ at a rate of $20^\circ\text{C}/\text{min}$.

The catalytic performance was carried out in a confined fluidized bed apparatus (CFBA) at 500°C with a mixture of Xinjiang vacuum gasoline oil (VGO) and vacuum tower bottom (VTB) as the feed. The catalyst was initially steam-deactivated at $800^\circ\text{C}/100\%$ steam for 10 h. The quantity of catalyst was 180 g, and the catalyst/oil ratio was 4.0. After distillation of the liquid product, hydrocarbon composition and octane number were analyzed with a VarianCP-3380. The gas product was determined with a HP6890.

3. Results and discussion

Table 1 shows that the rare earth modification results in REUSY with larger steamed unit cell size and better crystallinity retention. The good stability of REUSY has been attributed to the presence of poly-nuclear cations in the sodalite cages of the zeolite, containing oxygen-bridged rare earth ions [7]. After modification of rare earth and phosphorus, PREUSY has the largest steamed unit cell size and the best crystallinity retention.

The acidity of three modified zeolite Y samples was examined by the NH_3 -TPD method. The results are shown in Fig. 1. The USY sample gives a spectrum composed of three desorption peaks with maxima at about 120, 260,

Table 1

The hydrothermal stabilities of three modified zeolite Y samples

Zeolite samples	a_0 (nm)		RC (%) ^a		RC retention (%)
	Fresh	Steamed ^b	Fresh	Steamed ^b	
USY	2.450	2.432	66	30	45.5
REUSY	2.458	2.435	57	32	56.1
PREUSY	2.460	2.436	55	34	61.8

^a RC stands for relative crystallinity determined by XRD analysis.

^b steaming condition: $800^\circ/100\%$ steaming for 3 h.

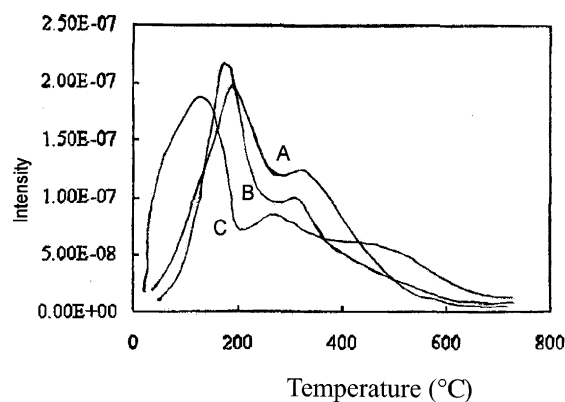


Fig. 1. The NH_3 -TPD of three modified zeolite Y samples: (A) REUSY; (B) PREUSY; (C) USY.

and 500°C , and the acidity sites are mainly weak (below 200°C). Through the rare earth modification, the spectrum of REUSY has only two desorption peaks with maxima at about 200 and 320°C ; here the property of acidic sites is mainly intermediate or strong (between 200 and 500°C). The density of acidity is more than one of the USY. The polarization effect of the rare earth ion on water combining with RE^{3+} makes each water molecule produce more B acidity in REUSY. After modification of rare earth and phosphorus, the strength of acidity in PREUSY becomes weaker, and the acidity sites concentrate at the desorption peak of 200°C . When the phosphorus reacts with zeolite Y, the hydroxyl connected with aluminum atoms on the zeolite surfaces was replaced by P-OH, and the acid strength was weakened as the phosphorus content increased because the acid strength of P-OH was weaker than that of Al-OH [8].

In comparison with C-USY, Table 2 shows that C-PREUSY and C-REUSY have much lower heavy oil, and C-PREUSY has 0.76% lower LCO yield and 0.13% more

Table 2

Effect of modified zeolite Y on catalyst performance and olefin content of naphtha in CFBA

Catalysts ^a	Dry gas (%)	LPG (%)	Naphtha (%)	LCO (%)	HCO (%)	Coke (%)	PONA of naphtha (%) ^b				RON	MON
							P	O	N	A		
C-PREUSY	1.33	13.47	50.41	22.47	2.94	7.98	48.4	14.0	10.7	26.9	93.5	81.7
C-REUSY	1.35	14.31	51.30	20.16	3.01	8.21	52.1	14.3	11.6	22.0	92.8	81.4
C-USY	1.31	12.17	49.89	23.23	3.97	7.85	47.2	20.6	11.9	20.3	93.0	81.0

^a C-PREUSY, C-REUSY, and C-USY catalyst using PREUSY, REUSY, and USY as an active component, respectively.

^b P, O, N, and A stand for paraffin, olefin, naphthene, and aromatic, respectively.

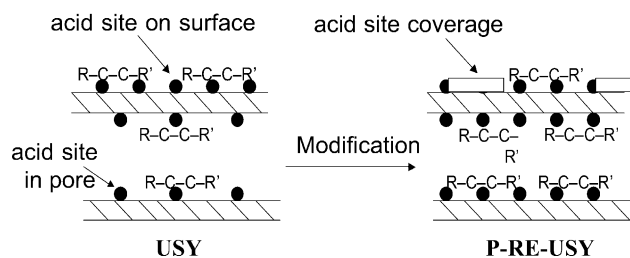


Fig. 2. Effect of acid site modification on reaction orientation.

coke yield; REUSY has 3.07% lower LCO yield and 0.36% more coke yield, indicating that C-PREUSY and C-REUSY all exhibit better heavy oil cracking capability. C-PREUSY has better coke selectivity and 2.31% higher LCO oil yield than that of C-REUSY. The good product selectivity and higher LCO yield of C-PREUSY are obviously related to its active component, through properly reducing the acidity strength of zeolite and therefore effectively controlling the ratio of hydrogen transfer activity and crackability in the catalytic reaction. From the PONA analyses of cracked naphtha, it can be seen that C-PREUSY and C-REUSY have more than 6% lower naphtha olefin content than C-USY. Due to the desirable acidity properties of the active component in C-PREUSY, reduction in naphtha olefin is not at the expense of gasoline octane; thus higher RON and MON are retained for the *iso*-paraffins and aromatics.

The above results show that the newly developed novel FCC catalyst containing PREUSY has outstanding performance for reducing naphtha olefin content and can produce higher LCO than the conventional olefin reducing catalyst.

When adopting rare earth and phosphorus altogether to modify the zeolite Y, a part of rare earth can be exchanged with sodium into the super-cage in the zeolite, and the other part can easily react with phosphorus to form superfine complex RE–P–O oxides ($\sim 0.1 \mu\text{m}$) which obviously precipitate on the exterior surface of zeolite and unavoidably cover part of the surface acid sites [9]. In the meanwhile, the excessive phosphorus reacts with zeolite Y to form slightly weaker P–OH bonds. Therefore, the acidity density and strength in the pores of zeolite are improved effectively and the surface acidity density is reduced suitably. As shown in Fig. 2, through the above modification technique, some of the acid sites on the surface may be covered to some extent and the property of the pores becomes more acidic. Catalytic cracking is an acid-catalyzed reaction, which means that the density of the acidic active sites and their locations will affect the rates of all catalytic processes and reaction pathways. As to the PREUSY zeolite, more hydrocarbons are attracted into the pores of zeolite to be converted and the chance of a cracking reaction on the exterior surface is much reduced.

According to Wojciechowski [10,11], reaction pathways for hydrocarbons conversion could be as schemed in Fig. 3. In the catalytic cracking of paraffins, initiation involves the protolysis of a feed molecule by a Bronsted acid proton. The protolysis reactions are one type of disproportionation.

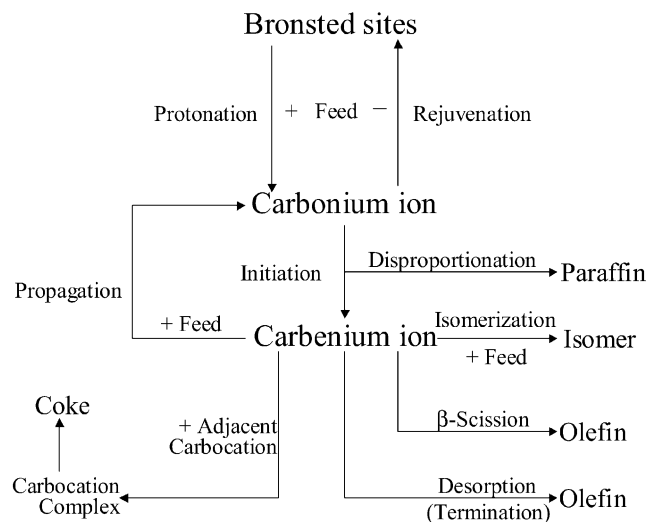


Fig. 3. Reaction pathways for hydrocarbon conversion in catalytic cracking process.

Between initiation by protolysis and termination by desorption of an olefin, there exists the possibility of a number of conversion reactions occurring on any site containing a carbenium ion. These reactions constitute a chain of self-propagating processes that result in a number of conversions of feed molecules before the surface species desorbs and terminates the chain. The interesting thing is that, in the propagation reactions, feed is converted but no olefins are formed; therefore, for each molecule converted, one molecule of paraffin is formed. Olefins can be formed when the β -scission takes place or when the carbenium ion manages to desorb before it combines with a feed molecule from the gas phase. It can be proposed that, compared with the ion formed on the exterior surface, the carbenium ion formed in the pores is hard to desorb, which will lead to less olefin formation. If acidity density and strength in the pores of zeolite are improved and the surface acidity density is reduced, the propagation reactions proceeding in the pores are enhanced, with the olefins formation being greatly reduced. Furthermore, since coke precursor prefers being produced and adsorbed on the strong acid sites [12], less coke may be formed on the surface acid sites of zeolite Y modified with rare earth and phosphorus.

It can be concluded that the compound modification of rare earth and phosphorus remarkably reduces the formation of naphtha olefins in the pores of zeolite Y and also decreases the coke formation on its surface.

4. Conclusions

After modification of rare earth and phosphorus, zeolite Y has a larger steamed unit cell parameter and good hydrothermal stability; and the acidity density and strength in the pores of zeolite Y are improved and the surface acidity density is suitably reduced. This kind of modification can

direct more hydrocarbons to enter into the pores to be converted and can remarkably reduce the possibility of naphtha olefins forming through surface cracking reactions. In addition, because naphtha olefin reduction does not completely depend on olefin saturation through secondary hydrogen transfer reaction, this kind of reaction mode can decrease the excessive cracking of mediate distillate and can improve the diesel oil yield effectively.

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