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A novel FCC catalyst synthesized via in situ overgrowth of NaY zeolite on kaolin microspheres for maximizing propylene yield

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Abstract

NaY/kaolin composite microspheres were synthesized by an in situ method using calcined kaolin microspheres as raw material. By mixing the modified NaY/kaolin composite microspheres and additive microspheres containing ZSM-5, a novel fluid catalytic cracking (FCC) catalyst for maximizing propylene yield in FCC unit was prepared. The catalyst was characterized by X-ray diffraction (XRD), temperature-programmed desorption of ammonium (NH_3-TPD), and N_2 adsorption–desorption techniques and tested in a bench FCC unit. The characterization results indicated that the catalyst has more meso- and macro-pores and more acid sites than the reference catalyst and thus can increase propylene yield by 1.27%.

Keywords: FCC catalyst; In situ synthesis; NaY/kaolin composite microspheres; Propylene

1. Introduction

The product selectivity of fluid catalytic cracking (FCC) units is one of the main topics to be understood and controlled in order to increase process benefits and comply with mandatory regulations on the compositions of transportation fuels [1]. At present, there is an increasing interest in maximizing propylene yield of FCC units. In 2000, about 34% of the worldwide propylene production was from FCC units. In fact, FCC units have become an important source of light olefins. In the next decade, it is expected that worldwide propylene supply from FCC units will continuously increase. Therefore, both process changes and new catalysts need to be considered together to improve the propylene yield of FCC processes.

For a long time, zeolite ZSM-5 has been employed as a FCC catalyst additive of great industrial importance to improve propylene yield owing to its special pore structure and acidic properties. Generally, to maximize propylene yield, the content of ZSM-5 in FCC catalysts should be increased, but the costs to be paid are the loss of catalyst activity and other desirable products.

In traditional FCC catalysts, zeolite Y provides the major surface area and active sites [2] and thus is the key component that controls catalyst activity and selectivity [3–6]. The usual way to incorporate Y into FCC catalysts is to mechanically bind it with a matrix by a binder alumina, so no chemical bonds are formed between the zeolite and the matrix. To better disperse zeolite Y on matrix and increase its thermal and hydrothermal stability, the former Engelhard Corp. (now acquired by BASF) developed an in situ synthesis method by overgrowing NaY in kaolin microspheres. By this way, Engelhard Corp. obtained a series of NaY/kaolin composites with NaY crystallinity over 30% (US Patent 4,235,753 [7]) and 70% (US Patents 4,493,902 [8] and 5,023,220 [9]). In the synthesis procedure, the kaolin microspheres used contain both kaolin and metakaolin, and the liquid to solid ratio in crystallization is over 7. Moreover, the kaolin used should be of high quantity. In this work, we report a novel in situ synthesis method for preparing FCC catalysts for maximizing propylene production.

2. Experimental

2.1. In situ synthesis of NaY/kaolin microspheres

In this work, a novel NaY/kaolin composite was prepared by a newly developed in situ synthesis method. Firstly, kaolin

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microspheres were prepared from a slurry of kaolin clay, pseudo-boehmite and sodium silicate by spray drying; the microspheres were separated into two parts that were calcined at temperatures around 830 and 950 °C respectively, to produce two kinds of kaolin microspheres with each rich in chemical active SiO_2 and Al_2O_3; secondly, the two kinds of kaolin microspheres were mixed together by one to one weight ratio and the addition of appropriate amounts of sodium hydroxide, directing agent was followed, then the resulting mixture was heated at 95–98 °C for 24–30 h, here the liquid to solid ratio of the mixture was about 5; thirdly, after crystallization, the resulting NaY/kaolin composite microspheres were collected by vacuum filtration and subsequent washing with distilled water.

2.2. Catalyst preparation

The as-synthesized NaY/kaolin composite microspheres were then subject to NH_4^+ and Re^{3+} ion exchange four times and steam stabilization at 600 °C with 100% steam for 2 h to generate the active sites and appropriate pore structures necessary for catalytic cracking.

The novel FCC catalyst developed in this study consists of two parts. The main part is the above modified Y/kaolin composite microspheres, the other is additive microspheres made from a slurry of HZSM-5, kaolin clay, water glass, pseudo-boehmite and alumina sol by spray drying. The two kinds of microspheres were mixed by 7:3 weight ratio and steamed at 800 °C with 100% steam for 10 h to obtain the final catalyst. The contents of HZSM-5 in the novel catalyst and a commercial catalyst used as reference catalyst are both 8 wt.%.

2.3. Physicochemical characterizations

The X-ray diffraction (XRD) patterns of the as-made catalyst and the commercial propylene maximizing FCC catalyst used as reference catalyst were obtained on a Rigaku D/Max-3C diffractometer using Cu Kα radiation with a Ni filter. Because the strongest reflections of zeolite Y and ZSM-5 overlap, the intensity of the strongest reflection in the angle region of $31 < 2\theta < 32^\circ$ was used to evaluate the relative crystallinity of the Y zeolite. The relative crystallinity of the ZSM-5 zeolite was determined by the strongest reflections in the angle region of $22 < 2\theta < 25^\circ$ after the structure of the Y zeolite was destroyed by HCl. Specific surface areas, pore volumes, and pore size distributions were measured using the standard nitrogen adsorption–desorption methods on an ASAP-2010 instrument (Micromeritics, USA). Prior to measurement, the samples were degassed at 573 K for 12 h. Micropore volumes and external surfaces areas were calculated from the *t-plot method*. Temperature programmed desorption of ammonium (NH_3-TPD) experiments were carried out in a flowing apparatus with helium as carrier gas. The sample was firstly flushed with helium at room temperature for 1 h, then heated to 100 °C in 15 min and maintained at 100 °C for 10 min, and finally heated to 600 °C in 50 min and stabilized at this temperature for 30 min. After that, the sample was cooled to room temperature, exchanged with ammonia, then heated to 100 °C in 15 min. When the desorption intensity became stable, the sample was continuously heated to 600 °C in 50 min.

Table 1
Properties of Xinjiang VGO and Xinjiang VGO

Items	Xinjiang VGO	Xinjiang VGO
Density, ρ_{20} (kg/m^3)	944.2	883.9
Residual coke (wt.%)	9.87	0.07
Average molecular weight	828	319
Simulated distillation (°C)		
Initial boiling point	420	286
10%	435	347
30%	465	392
50%	–	453
70%	–	500
90%	–	–

2.4. Catalytic cracking tests

The catalytic performances of the novel FCC catalysts and the commercial propylene maximizing FCC catalyst were tested on an advanced catalyst evaluation (ACE, Kayser Corp.) bench unit. The tests were carried out under the conditions typical for FCC units: cracking temperature 535 °C, catalyst to oil mass ratio 5.00, contact time 90 s. The chemical composition of the product FCC gasoline was determined by an on-line GC–MS. The feedstock was a mixture of 70% Xingjiang vacuum gas oil (VGO) and 30% Xinjiang vacuum tower bottom (VTB) and their properties are listed in Table 1.

3. Results and discussion

3.1. Physicochemical characterizations

As shown in Fig. 1, the XRD pattern of the NaY/kaolin composite microspheres shows the crystalline structure of faujasite-type zeolite and is identical to a normal NaY zeolite

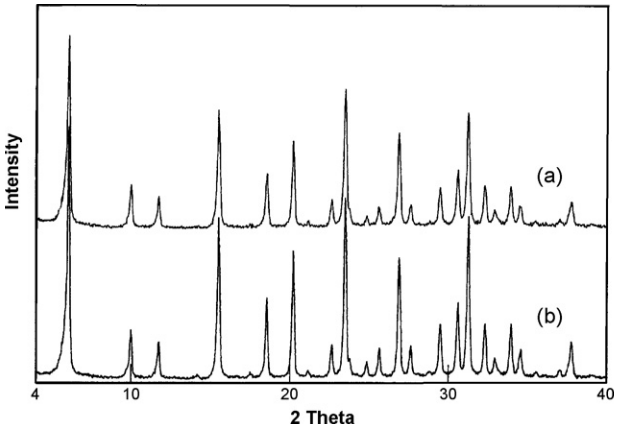


Fig. 1. XRD patterns of (a) NaY/kaolin composite microspheres and (b) NaY obtained by the conventional gel synthesis method.

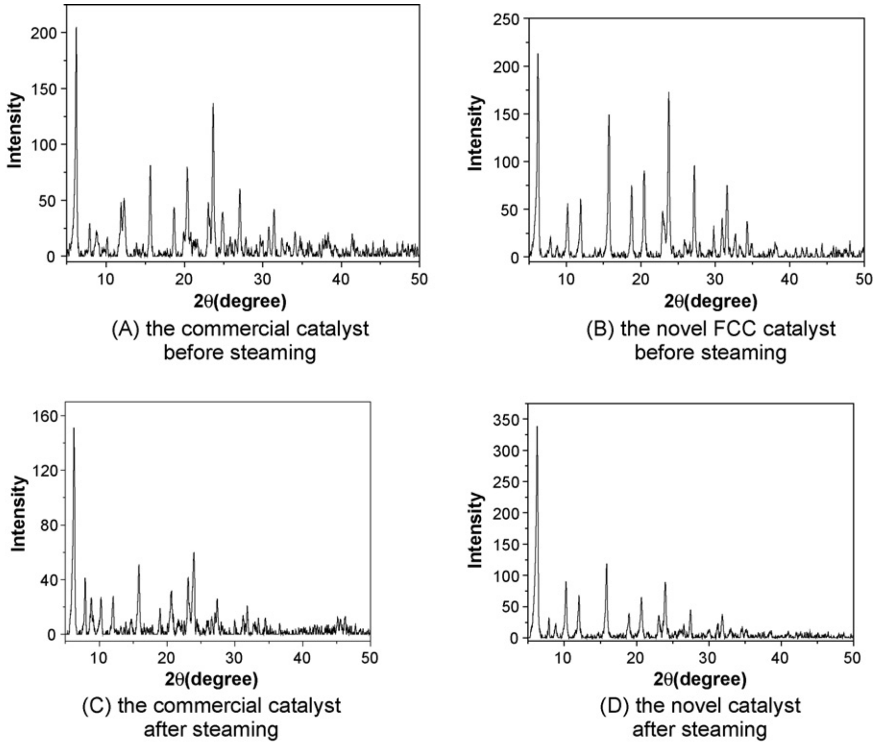


Fig. 2. XRD patterns of the catalysts before and after steaming treatment.

obtained by the conventional gel synthesis method. Fig. 1 also indicates that the NaY/kaolin composite microspheres have a relative crystallinity higher than 40% with a framework SiO_2/Al_2O_3 molar ratio of 4.83.

Fig. 2 shows the XRD patterns of the novel FCC catalyst and the commercial one. It can be seen that both of the two catalysts show the crystalline features of zeolite Y and ZSM-5. Despite of the identical H-ZSM-5 content in both of the two catalysts, the

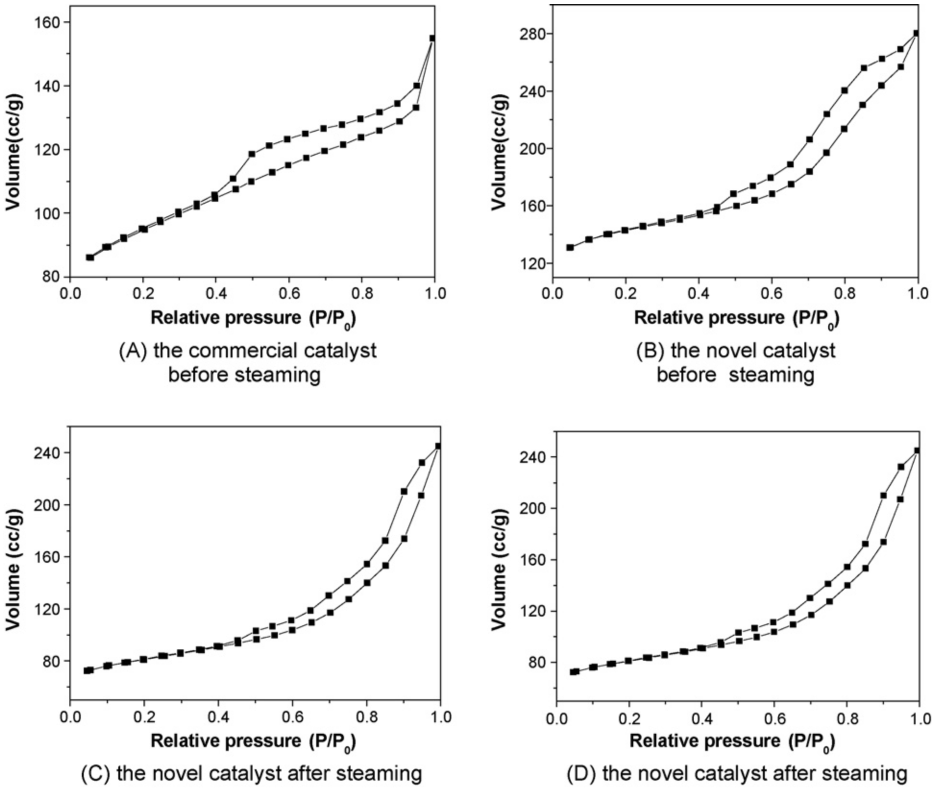


Fig. 3. N_2 adsorption–desorption isotherms of the novel and the commercial FCC catalysts before and after steaming treatment.

Table 2
Pore properties of the catalysts before and after steaming treatment

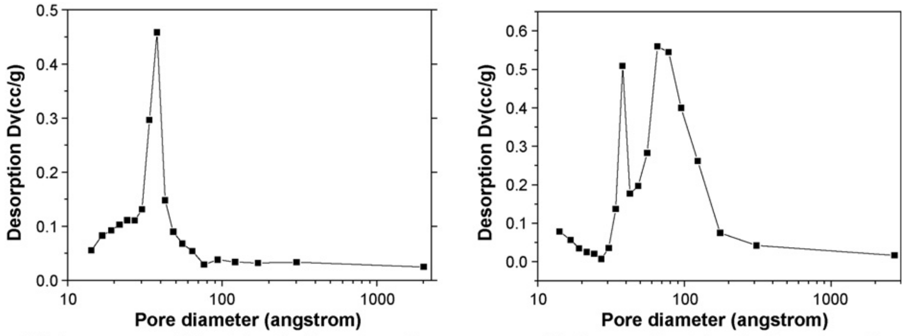
Catalyst	Before steaming		After steaming	
	The commercial catalyst	The novel catalyst	The commercial catalyst	The novel catalyst
BET surface area (m^2/g)	311.8	468.6	178.2	267.5
External surface area (m^2/g)	61.9	168.4	99.31	178.4
Micropore surface area (m^2/g)	249.9	300.1	78.9	89.2
Total pore volume (cc/g)	0.24	0.43	0.25	0.38
Micropore volume (cc/g)	0.13	0.15	0.04	0.04
Average pore diameter (Å)	30.53	36.76	55.17	56.29

intensity of the peaks assigned to ZSM-5 shows slight difference, possibly because the presence of other substances in the catalysts.

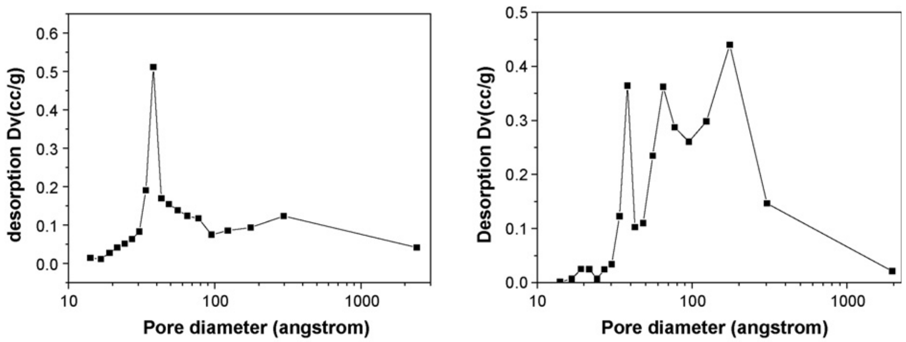
One of the most important properties for an FCC catalyst is its pore characteristics. Fig. 3 shows the nitrogen adsorption–desorption isotherms of the novel and the commercial FCC catalysts before and after steaming treatment.

In Fig. 3, the nitrogen adsorption and desorption branches of the isotherms for the novel catalyst have a steeper fall and a larger hysteresis loop than the commercial one, indicating that in the novel catalyst there exist larger pores. Fig. 3 also shows that the isotherms of the novel catalyst after steaming treatment still has a steeper fall and a bigger hysteresis loop. The pore properties of the commercial and novel FCC catalyst are summarized in Table 2. Comparably, the novel catalyst has a much larger BET surface area, external surface area and total pore volume, while its micropore surface area and micropore volume show no obvious differences from those of the commercial catalyst, further indicating that the novel catalyst is richer in meso- and macro-pores. This phenomenon is also well illustrated in Fig. 4.

Fig. 4 provides the further evidence that more meso- and macro-pores exist in the novel catalyst because of its unique synthesis route. In the in situ synthesis method, both the Al–O and Si–O species to form zeolite come from the kaolin microspheres. During the crystallizing process, the Al–O and Si–O species were leached from kaolin microspheres under the caustic conditions and thus resulted in the formation of more meso- and macro-pores in kaolin microspheres. It had been reported that the residue of the caustic leached kaolin matrix can effectively improve the acidity and stability of the resulting FCC catalyst [10,11] and endow the catalyst with higher meso- and macro-pores [12]. Furthermore, in the novel catalyst the NaY zeolite grew in the pores of the kaolin microspheres and hence the mass-transfer resistance in the reaction process was effectively reduced. After steaming treatment, more large pores



(A) the commercial catalyst before steaming (B) the novel catalyst before steaming



(C) the commercial catalyst after steaming (D) the novel catalyst after steaming

Fig. 4. Pore distributions of the two catalysts before and after steaming treatment.

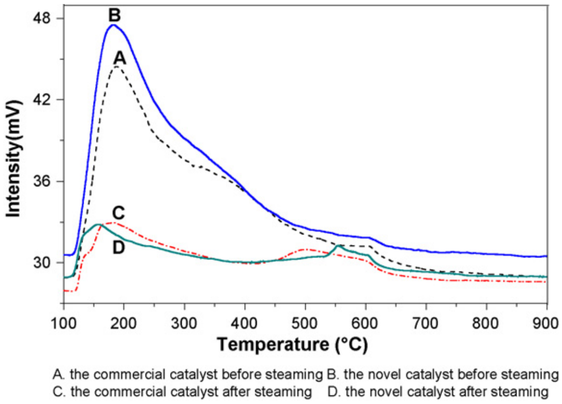


Fig. 5. NH_3-TPD spectra of the commercial and the novel catalyst before and after steaming.

are generated in the novel catalyst, which is helpful to provide better accessibility to bulky molecules and thus improve catalytic efficiency.

The NH_3-TPD spectra of the commercial and the novel catalyst before and after steaming treatment are shown in Fig. 5. The spectra of the both catalysts before steaming treatment show a low temperature peak of different intensity at 180 °C. In literature, the low temperature peak is usually ascribed to the desorption of ammonia bound to weak Brönsted or Lewis acid sites or to silanol groups, and the high temperature peak is attributed to decomposition of NH_4^+ formed over strong acid Brönsted sites and some Lewis sites related to the presence of specific extra-framework Al-species [13,14]. As shown in Fig. 5, before steaming treatment, the spectrum intensity of the novel catalyst is higher in the whole desorption temperature range, signifying that it has more weak and strong acid sites than the reference catalyst. After the steaming treatment, the low temperature peak of the novel catalyst shifts to lower temperature, but that of the commercial one is not affected at all, while the high temperature peaks of the both catalysts shift to lower temperatures, especially for the commercial one. From these results, we can conclude that after the steaming treatment more strong acid sites are mostly retained in the novel catalyst.

3.2. Catalytic cracking tests

The catalytic cracking results were shown in Table 3. In these tests, the cut point of gasoline is 211 °C and that of diesel is 343 °C. The propylene selectivity is defined as: propylene selectivity = (propylene yield)/(liquefied petroleum gas (LPG) yield).

Table 3
Product distributions of the two propylene maximizing FCC catalysts

Product	The commercial catalyst	The novel catalyst	Δ
Dry gas (wt.%)	2.91	2.83	−0.08
LPG (wt.%)	26.44	27.90	1.46
C_5^+ gasoline (wt.%)	48.39	47.49	−0.90
Diesel (wt.%)	10.13	10.53	0.40
Heavy oil (wt.%)	4.96	5.53	0.57
Coke (wt.%)	7.71	5.72	−1.99
Liquid yield (wt.%)	84.96	85.92	0.96
Propylene yield (wt.%)	8.08	9.35	1.27
Propylene selectivity (wt.%)	30.56	33.49	2.93

Table 4
LPG composition

	The commercial catalyst	The novel catalyst	Δ
Propane	1.68	1.41	−0.27
Propylene	8.08	9.35	1.27
n-Butane	1.35	1.07	−0.28
Isobutane	6.54	5.52	−1.02
C_4 olefins	8.79	10.57	1.78
1-Butene	1.64	1.88	0.24
Isobutylene	2.53	3.53	1.00
c-2-Butene	2.32	2.60	0.28
t-2-butene	2.31	2.56	0.25

From Table 3, it can be seen that compared with the commercial propylene maximizing FCC catalyst, the novel FCC catalyst developed can increase propylene yield by 1.27% points and propylene selectivity by 2.93% points. At the same time, coke yield is decreased by 1.99 wt.%. Table 4 shows the LPG compositions over the two catalysts. It is noted that the yield of C_4 olefins of the novel FCC catalyst is outstandingly higher than that of the commercial catalyst. These excellent catalytic performances can be attributed to the novel synthesis route of the NaY/kaolin composite microspheres.

4. Conclusions

NaY/kaolin composite microspheres were synthesized by an in situ method. In the method, all the Al–O species and part of the Si–O species to form Y zeolite come from calcined kaolin microspheres, which is the most prominent feature of the in situ synthesis method compared to the tradition gel synthesis method. The as-made NaY/kaolin composite microspheres had Y crystallinity of 40% and molar SiO_2/Al_2O_3 ratio of 4.83. After the modification and steaming stabilization process, the composite microspheres were mixed with additive microspheres containing HZSM-5 and then a novel catalyst for maximizing propylene production was obtained. The results of N_2 adsorption–desorption isotherm measurements showed that the novel catalyst has more meso- and macro-pores due to the unique synthesis route. The results of acidity characterization exhibited that the novel catalyst has more acid sites than the commercial one. The catalytic cracking results showed that compared to the commercial catalyst, the propylene yield of the novel catalyst was increased by 1.27% points and the coke yield was decreased by 1.99% points.

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