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Synthesis, characterization and evaluation of a novel resid FCC catalyst based on *in situ* synthesis on kaolin microspheres

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A new way was provided for *in situ* synthesized FCC catalyst. Characterization and evaluation results indicated the catalyst is more suitable for cracking resid feed because of its unique manufacturing process which makes this catalyst has appropriate pore structures in which large resid molecules are more accessible to the active sites. The high zeolite content (above 40%) keeps the catalyst having higher activity and selectivity. These advantages ensure the *in situ* catalyst developed more adaptable for cracking resid and resid-containing feedstocks, particularly the feed containing large amounts of contaminant metals.

KEY WORDS: catalytic cracking; FCC catalyst; *in situ* synthesis; zeolite modified.

1. Introduction

Fluid catalytic cracking (FCC) is a central technology in modern refining [1]. The FCC unit is used to upgrade heavy gas oils and resid fuels to gasoline, diesel fuel, and light gases [2]. With the ever increasing cost and difficulty of obtaining high-quality crude for FCC operations, many refiners have been processing at least a portion of resid as a feedstock in the units or even use 100% of resid as the feedstock. As for resid FCC catalyst, it must have commercially acceptable activity, selectivity, bottoms upgrading ability, and hydrothermal stability characteristics for resid cracking and thus can be to maximize the profitability of a refinery.

FCC catalysts are microspheres composed of zeolite Y as the main active component and the non-zeolite component as matrix materials which also perform many important functions related to both catalytic and physical properties of the catalyst. Catalytic cracking activities of FCC catalysts are attributed to both the zeolites and non-zeolite components. Zeolite cracking tends to be selectively cracking, producing valuable products such as gasoline. Non-zeolite (matrix) cracking tends to be non-selectively cracking, producing undesirable products such as coke and dry gas. So, to increase the ability of zeolite cracking is always the target of FCC catalyst research [3].

The active zeolitic components are generally incorporated into the microspheres of the catalyst by one of two general techniques. In one technique, the zeolitic components are crystallized firstly and then incorporated into kaolin containing microspheres by a separate step. In the second technique, the *in situ* technique, microspheres are firstly formed and the zeolitic components are then crystallized into/on the microspheres themselves to provide the composites containing both zeolitic and non-zeolitic components [3].

As Y-faujasite content in the FCC catalysts is increased, the activity and selectivity of catalyst tend to be improved greatly. Generally speaking, it is difficult to increase zeolite content in microspheres of incorporation catalyst. When zeolite content of incorporation catalyst is increased, the attrition resistance is turned to be worse and usage life reduced. To the best of our knowledge, the commercial FCC catalysts containing about 40% (wt) Y-faujasite is very rare. While *in situ* catalysts have attractive attrition resistance effect even if the zeolite content is above 40% because of its unique structure inherited from the *in situ* crystallization synthesis process based on thermal activating reaction technology of kaolin clay [3].

In present work, the high zeolite content resid catalysts have been prepared by *in situ* synthesis from precursor microspheres by spray dying. The catalysts have excellent activity, selectivity, bottoms upgrading ability, hydrothermal stability, and anti-contamination ability of heavy metals. It is expected to be utilized widely in the field of heavy crude processing. Here in this paper we would like to report the synthesis, characterization and evaluation of this novel *in situ* FCC catalyst.

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2. Experimental

2.1. Raw materials

The kaolin from the China Kaolin Corporation was selected for the present study. The main characterization data of the kaolin clay were showed in the following table 1. XRD profiles of the kaolin are shown in figure 1. Evidently, its dominant component is kaolinite with form $2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$ and a small quantity of other phases.

2.2. Catalyst preparation

The hydrous kaolin slurry was mixed with sodium silicate which acts as fluidizing agent for the slurry. The mixture is then turned into microspheres by spray drying and the as-made microspheres are separated into two parts. One part is calcined into metakaolin microspheres which undergo a strong endothermic reaction associated with dehydroxylation for 2 h in a muffle furnace at 700–850 °C. Another part is calcined into fully clay microspheres which undergo the characteristic kaolin exothermic reaction at 950–1050 °C for 2 h in a muffle furnace, sometime referred to as the spinel form of calcined kaolin.

Y-faujasite is allowed to crystallize by fully calcined kaolin microspheres and metakaolin microspheres with the appropriate amounts of other constituents such as sodium silicate, sodium hydroxide, water and zeolite initiator, and then the resulting slurry was warmed to 90–92 °C for 24–28 h to crystallize at least about 40% by weight Y-faujasite into/on the microspheres. The crystallization recipe utilized in this process has a gel oxide molar ratio of: $SiO_2/Al_2O_3 = 9$; $Na_2O/SiO_2 = 0.48$; $H_2O/Na_2O = 30$. When the crystallization was finished, the mother liquor was removed from the reaction mixture, and the microspheres containing crystalline sodium form of Y-faujasite (the as-synthesized composites) were collected and washed with distillation water.

Table 1
Properties and composition data of the kaolin

Index	Value
XRD phase determine	
Kaolin (wt%)	88
Quartz (wt%)	0.5
Other phase (alunite, mica)	Few
Size distributions	
D(v,0.1) (μm)	0.34
D(v,0.5) (μm)	1.68
D(v,0.9) (μm)	7.75
Chemical composition(dry base)	
Na_2O (wt%)	0.19
K_2O (wt%)	0.28
Fe_2O_3 (wt%)	0.43
Al_2O_3 (wt%)	40.94
SiO_2 (wt%)	57.17

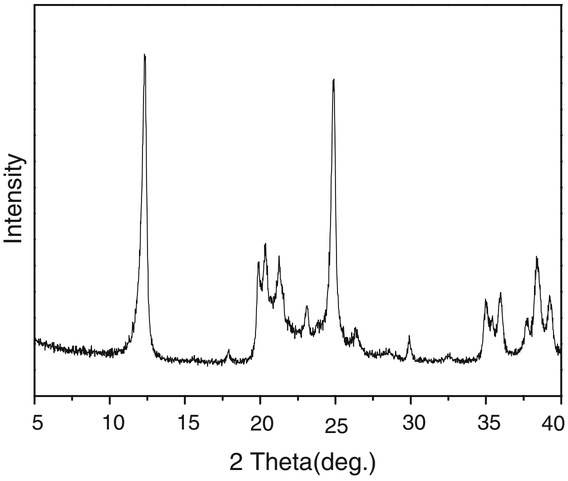

Figure 1. XRD pattern of kaolin.

At room temperature, the crystallization composites Y/kaolin microsphere were added to a stirred solution of rare earth chloride solution. The resulting slurry was adjust to a pH of 3.5 with 18% HCl and heated to 90 °C to achieve ion exchange in a water bath. After 1 h at 90 °C, the slurry was vacuum filtered and mildly calcined for 2 h at 650 °C. Then the calcined example were again treated with a fresh solution of $(NH_4)_2SO_4$ in a similar process of ion exchange and calcinations until a nominal 0.4% Na_2O and 1–5% RE_2O_3 was achieved. After that it was filtrated, dried and thus the ion exchanged samples were obtained.

2.3. Metal contamination

A certain amount of ammonium vanadate (NH_4VO_3) and nickel nitrate ($Ni(NO_3)_2$) were dissolved in distillation water, and the obtained solution was mixed with catalyst using the incipient wetness impregnation technique. The mixture was dried in the oven at 120 °C for 8 h and then calcined at 540 °C for 2 h.

2.4. Characterization

2.4.1. Element analysis

SiO_2 content was tested gravimetrically, Na_2O and K_2O by flame photometry, Al_2O_3 by complexometry and Fe_2O_3 and RE_2O_3 by spectrophotometry method.

2.4.2. X-ray diffraction analysis

Powder XRD patterns were recorded on a Rigaku D/max-3C X-ray diffractometer with Ni filtered CuK_α radiation.

2.4.3. Particle size distribution analysis

Malvern Micro-P particle size analyser was used for determining the size distribution in the samples.

Table 2
Main properties of of Xiniiang feedstock

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

2.4.4. *FT-IR test*

The samples were examined in Nicolet 510P Fourier transform IR spectrometer in the range 1350–1800 cm^{-1}.

2.4.5. *N_2 adsorption-desorption for pore characteristics*

The adsorption properties of the prepared samples as well as others that were comparable were studied via low-temperature nitrogen adsoption/desorption isotherms measured using as Coulter Omnisorp 360.

2.4.6. *Catalytic cracking testing*

Microactivity testing (MAT): The activity of catalyst was carried out at a microactivity test unit, which has been designed according to the ASTM D-3907 method using a naphtha feed. The MAT condition was: reactor temperature 460°C, reacting time 70s and catalyst to oil ratio 3.2.

Cracking performances of the catalyst, such as selectivity, conversion and liquid yield etc., were tested by circulating riser pilot plant (CRP), which simulates the conditions of commercial FCC units. The oil feed is the mixture of Xingjiang vacuum gas oil (VGO) and vacuum tower bottom (VTB) as shown in table 2. The blending weight ratio of VTB/(VGO + VTB) is 0.2. The catalyst was hydrothemally deactivated for 8 h at 800 °C with 100% steam before test. Runs were performed at 500°C under short contact times between 1.8 and 2.5 s, the mass of catalyst being 4 kg and the amount of feedstock injected 1.9 kg.

3. Results and discussion

3.1. *Crystallization of the in situ catalyst*

In the process of *in situ* NaY crystals' growth, the metakaolin microspheres and fully calcined kaolin microspheres are reacted with sodium hydroxide to form active Al–O and Si–O structures which are dissolved in the alkali solution and they will become a part of reactants in *in situ* hydrothermal synthesis under the caustic condition [4]. At the same time a microspheroidal amorphous material formed becomes matrix which comprises alumina-silica residue of caustic leached kaolin. Lots literatures reported this kind of residue of caustic leached kaolin with ideal mesoporous distribution may effectively improve activity and stability of FCC catalyst [5, 6]. For these reasons, the catalyst appears better performances by *in situ* route on cracking heavy hydrocarbons [7] and feedstocks contaiminated with metal [8]. In the present work, by using the unique combination of metakaolin microspheres and fully calcined kaolin microspheres, a much higher Y type zeolite content was obtained, 24–28 h of crystallization afforded at least about 40% by weight Y-faujasite into/on the microspheres. And the physical properities (such as the attrition index) of the *in situ* catalyst are much better than those of the commercial (reference) catalyst, which usually have about 30–35% (wt) Y-faujasite in the microspheres. It is known that the higher content of zeolite in the catalyst microsphere, the lower its attrition resistance.

3.2. *Chemical compose and properties*

Here in this work, we chose a comparable commercial resid catalyst as base reference catalyst. Physicochemical characteristics of the two kinds catalysts are listed in table 3. Compared to the commercial catalyst, *in situ* catalyst has higher surface area, activity and stability. These advantages make the catalyst appeared good performances in FCC process.

3.3. *Py-IR testing*

As it is known that the number and strength of acid sites present in Y-zeolite are responsible for the activity and selectivity in the FCC reactions [9]. The acidity properties of samples were determined using pyridine-adsorption method by FT-IR. The concentration of Bronsted-acidic sites (B acid) and Lewis-acidic sites (L acid) of samples was measured on the bands at 1540 and

Table 3
Catalyst composition and properties

Catalyst	Reference catalyst	*In situ* catalyst
Chemical compose (wt%)		
Na_2O	0.15	0.35
RE_2O_3	4.20	4.86
Al_2O_3	49.82	36.91
Properties		
Surface area (m^2/g)	259	510
Pore volume (cm^3/g)	0.37	0.39
Bulk density (g/cm^3)	0.75	0.74
Attrition index (wt%)	1.2	0.8
Microactivity (wt%)*	66	73

* Hydrothemally deactivated for 17 h at 800 °C with 100% steam.

1450 cm^{-1}, respectively. The acid amounts could be expressed as absorbance in the indicated bands of the unit weight of sample. This article define that total acid amount and strong acid amount respectively is unit absorbance (u.a./g) above 200 °C and 400 °C. As seen from table 4, the strong B acid amount, total B acid amount and ratio B/L for the *in situ* catalyst is much higher compared to the reference catalyst, its total B/L acid type ratio increased by 2.4 times. As known that the higher B type of acid site is favorable to resid cracking [10], thus compared with the reference catalyst, the characteristic of acid amount, acid strength and acid type ratio (B/L) of *in situ* catalyst is more suitable for resid cracking.

3.4. NH_3 temperature-programmed desorption

NH_3-TPD spectra of the catalysts were shown in figure 2. It is obvious that the shapes of the corresponding desorption curves of the commercial catalyst(a) and *in situ* catalyst(b) are different. These differences are ascribed to that the reference catalyst owns less acid sites, especially strong acid sites, compared with *in situ* catalyst, which has been proven by the results of pyridine-IR desorption data in table 4. The NH_3-TPD experimental results further confirm that even strong acid sites were available on the surfaces of *in situ* catalyst.

3.5. Nitrogen adsorption

The nitrogen adsorption/desorption isotherms for *in situ* catalyst and reference catalyst depicted in figure 3. It is indicated in figure 3 the existence of equilibrium Langmuir branches at low P/P^o values and hysteresis loops over higher values, i.e. in the mesopore range. Such isotherms are typical for zeolite particles embedded in a matrix phase [11] and the materials with a mesoporous structure [12]. However, the isotherm for reference catalyst was somewhat different.

Table 4
Bronsted and Lewis type acid sites of catalysts

Samples	Reference catalyst			*In situ* catalyst		
	B	L	B/L	B	L	B/L
Weak acid amount (u.a./g)	8.555	8.405	1.018	7.505	2.170	3.459
Strong acid amount (u.a./g)	2.626	8.090	0.325	6.247	6.283	0.994
Total acid amount (u.a./g)	11.181	16.495	0.678	13.752	8.453	1.627

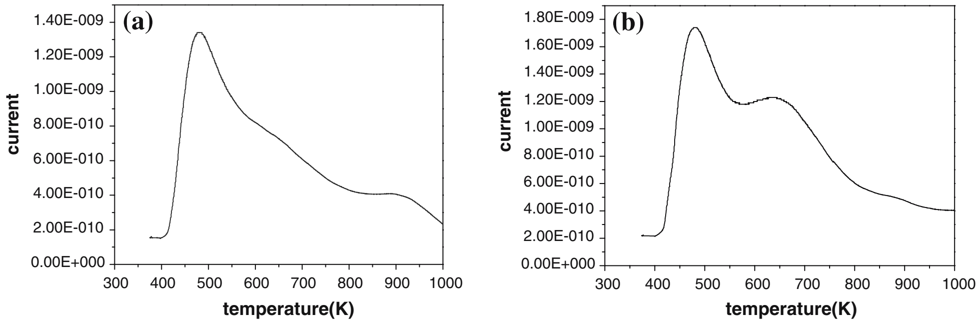

Figure 2. NH_3-TPD spectra of (a) reference catalyst and (b) *in situ* catalyst.

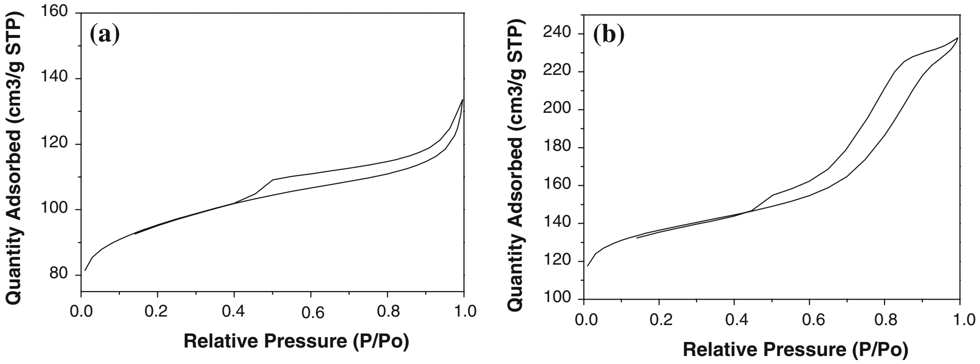

Figure 3. Nitrogen adsorption/desorption isotherms for (a) reference catalyst and (b) *in situ* catalyst.

Form a comparison of the shapes of two isotherms presented in figure 3, it may be deduced that *in situ* catalyst has more meso- and macrostructures than commercial catalyst. Table 5 listed the main pore structure data of the two kinds of catalysts and it demonstrated that *in situ* catalyst has higher surface area, more larger mesopore volume and average pore diameter because the metakaolin microspheres and fully calcined kaolin microspheres are reacted with sodium hydroxide during *in situ* crystallization process, in which some amount of silica and alumina was dissolved from the pore wall of kaolin microsphere, it promoted the development of meso- and macropores. The meso- and macropores provides more accessible active sites for resid cracking [13]. This architecture will benefit to shorten the secondary diffusion of the cracked primary products to the unique pore structure of the zeolite, and thus lead to more effective zeolite utilization, high bottoms conversion to high yield of desired products, and less over cracking to coke and gas. The pore size distributions profile as shown in figure 4 supported the above point of view, it clearly show macropore information from BJH desorption calculation.

Table 5
Adsorption properties of catalysts by two routes

Characteristic	Reference catalyst	*In situ* catalyst
BET surface area (m^2/g)	298.2	423.5
Mesopore surface area (m^2/g)	98.6	118.4
Micropore surface area (m^2/g)	199.6	305.1
Total pore volume (cm^3/g)	0.207	0.368
Mesopore pore volume (cm^3/g)	0.091	0.208
Micropore pore volume (cm^3/g)	0.104	0.159
Average pore diameter (0.1 nm)	27.7	34.8

Table 6
Product distribution (wt%) of FCC catalysts with Ni and V loaded in CRP

Catalysts	Reference catalyst	*In situ* catalyst
Dry gas	1.19	1.67
LPG	13.91	17.74
Gasoline	41.00	46.42
LCO	17.89	16.24
Slurry	19.05	10.37
Coke	6.56	7.33
Loss	0.40	0.23
Conversion	63.06	73.39
Liquid yield	72.80	80.40
Coke/conversion	10.40	9.99

3.6. CRP evaluation

For closely simulating operation conditions of commercial FCC unit and making the catalyst closer to the equilibrium catalyst in industry, catalysts were impregnated with 5000 ppm vanadium and 3000 ppm nickel according to the Mitchell method. Catalysts were underwent hydrothermal treatment at 800 °C with 100% steam for 8 h before being evaluated in a CRP. The testing results were shown in tables 6 and 7.

From table 6 we can see that the *in situ* catalysts of the present study show good cracking performance and contaminating metal tolerance in the presence of 5000 ppm vanadium and 3000 ppm nickel. Compared to reference catalyst under same operation conditions and similar coke selectivity, the *in situ* catalyst have evident advantages on slurry yield (8.68% lower), conversion rate (10.33 higher) and liquid yield (7.6%

Table 7
PONA analyses of gasoline in CRP

Catalysts	Commercial catalyst	*In situ* catalyst
n-Paraffin (%)	4.17	3.51
i-Paraffin (%)	26.73	25.77
Olefin (%)	51.51	42.08
Naphthalene (%)	7.05	5.98
Aromatic (%)	10.55	21.95
MON	79.6	79.9
RON	89.9	92.6

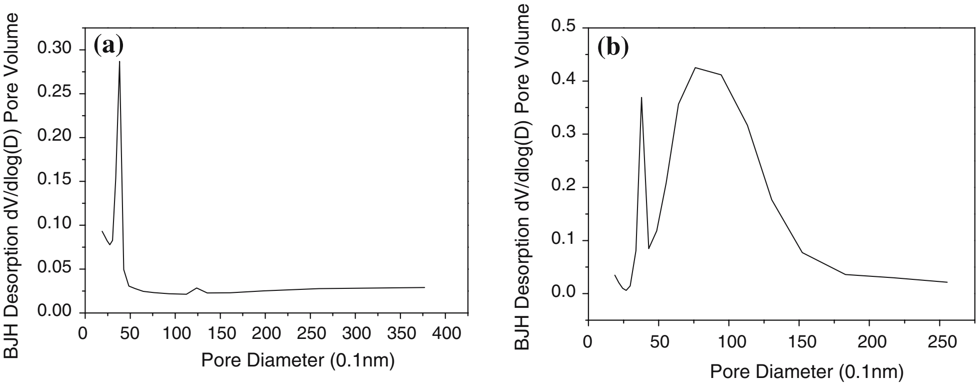

Figure 4. Pore size distributions for (a) reference catalyst and (b) *in situ* catalyst.

higher). This attractive product distribution may attributed to the nice combination of suitable acidity and the meso-macropore system of the *in situ* catalyst. So we can conclude that the FCC units will have more profit by employing this new *in situ* catalyst even if catalysts were contaminated by high quantity nickel and vanadium. From PONA analyses (table 7), we can also clearly see that the olefins reduced greatly and RON rise markedly with *in situ*catalyst because of its higher zeolite content. Therefore, this novel *in situ* catalyst with higher zoelite content has more adaptability for resid cracking.

4. Conclusion

An active Y/kaolin microsphere composite were successfully synthesized by *in situ* crystallizing process with at least 40% Y-faujasite content. After modification, the as-made FCC catalysts shows excellent performances on activity, stability, bottoms cracking ability, metal tolerance and good yield of valuable products in heavy crude oil processing.

Acknowledgments

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