Commercial test of the catalyst for removal of trace olefins from aromatics and its mechanism

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ABSTRACT

Twenty-two tons of catalyst was used in the 130kt/a industrial PX device at Sinopec Qilu Company for removing trace olefins from aromatics. The result showed it had an effective running time about 3 times as long as that of the commercial clay. The reaction mechanism was explored and it indicated that the weak L acid was the main reason for the enhancement of the catalyst activity. In addition, the process of the olefins reacted with the aromatics via the carbonium ion mechanism can be generalized by the alkylation reaction.

1. Introduction

The present paper is a continuation of our industrial application research on removing trace olefins from aromatics [1].

Aromatic hydrocarbon which can be obtained from reforming and cracking process is an important raw material in petrochemical processes and refineries. These aromatic streams always contain undesirable trace olefins [2] which are harmful to the following technological processes and the applications of aromatics [3]. For example, a 130kt/a PX device (Sinopec Qilu Company) was employed, using the Parex unit of UOP Company. Simulated moving bed technology was used to separate and produce PX with a highly selective adsorbent ADS-7. Unfortunately, the olefins are able to lead to the ADS-7 toxicosis. In order to protect the adsorbent, the product stream will have a bromine index which is an indicator of the presence of olefinic bonds less than 20. Therefore, the impurities must be removed with the suitable treatment technologies [4]. However, the particulate clay treating, a method of removing olefin, is widely used in mostly refineries with the drawbacks of limited lifetime and pollution.

Through the efforts of our research team, several new catalysts with longer lifetime have been developed and compared with the commercial clay by side-stream test [5].

In this work, catalyst production has been successfully scaled up from lab to industrial scale and 22 tons of catalysts had been used by Sinopec Qilu Company for this commercial test.

2. Experimental

2.1. Materials

The aromatic hydrocarbons used in this commercial test were obtained from the bottom of the naphtha reforming column at Sinopec Qilu Company. The bromine index (BI) is about 300–700 mg Br/100 g, and the components are shown in Table 1.

The active clay used as support in this commercial test was taken from Inner Mongolia.

The zeolite used in this test was MCM-22 purchased from Nanjing, China. The physicochemical properties of MCM-22 are presented in Table 2.

2.2. Catalyst preparation

As shown in Fig. 1, the procedures of industrial production were as follows: firstly, the clay and zeolite (the ratio of clay/zeolite was 4) were mixed completely in the stirring kneader, then the suitable amount of transition metal solution was injected; secondly, the raw materials which had been stirred for 0.5 h were sent to the twin-screw extruder by the conveying systems; thirdly, the strips were removed moisture in an oven, in an air atmosphere at 393 K for 2 h, and finally activated at 433 K for 2 h.

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Table 1
Aromatic hydrocarbon components.

Component	Content W (%)
Non-aromatics	2.5
Benzene	0.06
Toluene	0.09
Ethylbenzene	10.2
P-xylene	9.41
M-xylene	20.98
O-xylene	13.09
C9 and C9+	43.65

Table 2
Physicochemical properties of MCM-41.

	SiO_2/Al_2O_3	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
MCM-22	30	456	0.54	0.7

2.3. Characterization

The surface acidity was investigated by the adsorption of pyridine on the solid surface of samples. Prior to pyridine adsorption, sample wafers were evacuated at 753 K under high vacuum; followed by pyridine adsorption at room temperature. Finally, the wafers were desorbed at 473 K and 733 K. Fourier transform infrared (FT-IR) spectra were recorded using an FT-IR6700 spectrometer on sample wafers.

The BET surface areas, total volumes, and micropore volumes of the different clay samples were calculated by the data of N_2 adsorption and desorption isotherms which were conducted on a Micromeritics ASAP 2010.

The gas chromatography-flame ionization detection (GC-FID) analyses were carried out on a Hewlett-Packard Model HP5890 gas chromatograph equipped with a capillary column (AT-WAX, 50 m length, 0.32 mm inner diameter, and 0.30 μm film thickness) for investigating the changing of the content of the raw materials.

2.4. Packing structure of reactor

Fig. 2 shows the packing structure of the testing reactor. The reactor is constructed as fixed bed reactor from stainless steel. For equal distribution of the feed, the reactor is equipped with a redistributer, Φ19 ceramic balls and quartz sand as shown in the figure. Catalysts were loaded in the center of the fixed-bed reactor, between two quartz sand. At the bottom of the reactor, there are also Φ19 ceramic balls and quartz, yet with the adverse turn compared with the top of the reactor, a stainless steel sieve is installed to hold the catalyst.

2.5. Flowchart of the commercial test process

Fig. 3 shows the flowchart of the commercial test in Sinopec Qilu Company. The tower FA-151A and FA-151B which can fill 6 tons of catalyst and the tower FA-161 with the capacity of 22 tons of catalyst are used to remove olefins in the PX device. This commercial
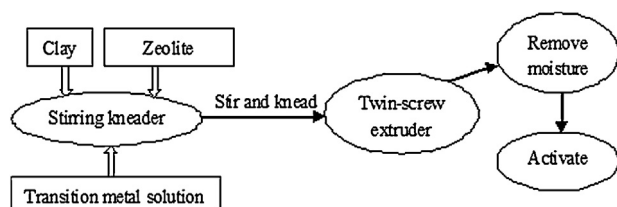

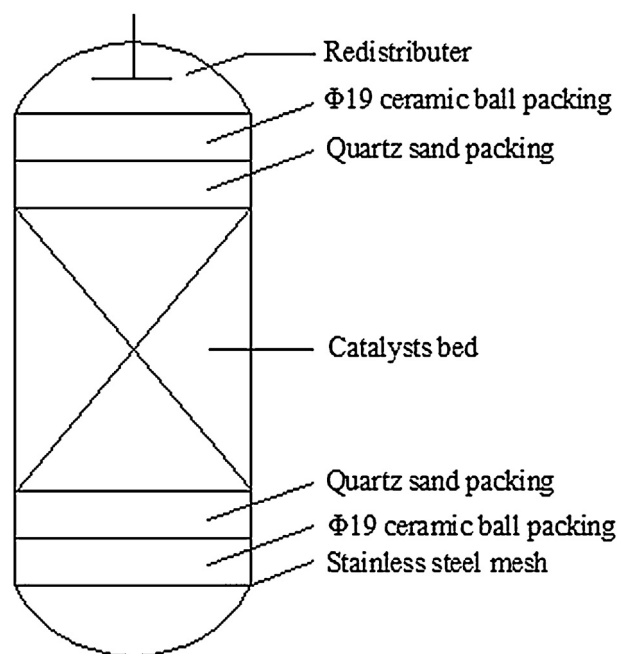**Fig. 1.** The procedure of industrial production.

Fig. 2. Packing structure of the reactor.

test was conducted in tower FA-161. Twenty-two tons of catalyst was loaded in FA-161. Aromatics stream enter into the reactors from the top, and flow out from the bottom of reactors after being treated in the reactor. The reactor operating temperature was about 433–443 K, controlled by regulating the steam flow. The reaction pressure was 1.0 MPa and the volume space velocity was about 0.59 h^{-1}. The samples were collected from the bottom of the reactor.

2.6. Study of the mechanism

In order to explore the mechanism of the reaction between aromatics and olefins, the aromatics which had added the trace 1-octene were used as the raw materials. At the same condition (the reactor operating temperature was about 433–443 K, the reaction pressure was 1.0 MPa and the volume space velocity was about 2.1 h^{-1}), the reaction was carried out in a fixed-bed tubular microreactor, equipped with a constant-flow pump to control flow rate and a controlled heating system to maintain the temperature. Two milliliters of the catalyst was loaded in the middle of the reactor; and the spare spaces were filled with quartz sand (40–60 mesh).

3. Results and discussion

3.1. Commercial test analyses

Fig. 4 shows the changing of the bromine index with the increasing time. For comparison, the data of the commercial clay also can be found from Fig. 4.

It could be seen from Fig. 4 that the bromine index of aromatics with commercial clay remained less than 20 for 22 days, wherein the effective reaction time of the commercial clay lasted 63 days. It should be noticed that the bromine index of aromatics after reaction over catalyst stayed less than 10 mg/100 g for about 43 days. While greatly increasing the lifetime of catalyst, treating of such process stream also does not significantly change the quantity or distribution of the aromatic hydrocarbons treated. Thus the catalyst showed great superiority in catalytic activity in removal of trace olefins from aromatics.
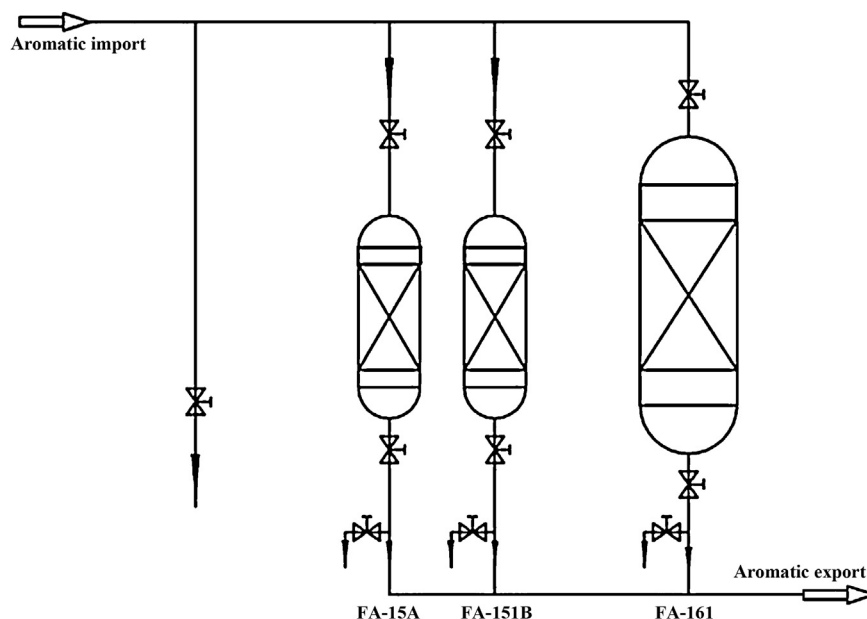
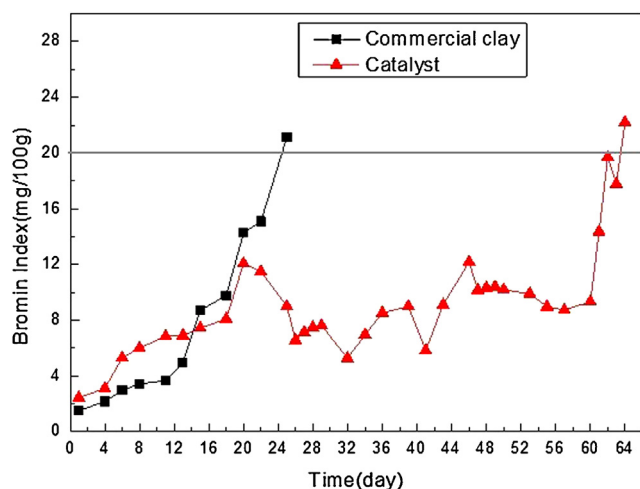**Fig. 3.** Flowchart of the commercial test process.

Fig. 4. The bromine index of aromatics after reaction over commercial clay and catalyst.

Table 3 shows the parameters of last 6 tons commercial test and this 22 tons commercial test. The catalyst of last commercial test was loaded in tower FA-151B with the amount of 6 tons and the volume space velocity was about 2.1 h^{-1}. The last result showed that the effective reaction time of the catalyst was 6 times as long as that of the commercial clay. The ratio of this 22 tons commercial test was about 3. The difference was caused by the volume space velocity. When the volume space velocity was 2.1 h^{-1}, the bromine index of aromatics with commercial clay remained less than 20 only for 3 days [1]. It can be concluded that the catalyst for

Table 3
The parameters of the commercial tests.

Test	Tower used[a]	Space velocity (h^{-1})	Loading quantity (t)
6 tons commercial test	FA-151B	2.1	6
22 tons commercial test	FA-161	0.59	22

[a] The code name of towers were showed in Fig. 3.

Table 4
Textural properties of different clay samples.

	Surface area (m^2/g)	Micropore area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
Clay	198.7	25.16	0.1857	4.479
Catalyst	149.3	8.3	0.1936	4.458

removing trace olefins from aromatics would perform with greater superiority for the situation of a higher volume space velocity.

3.2. BET analysis

As shown in Table 4, the pore structures of the synthesized catalyst and commercial clay were investigated by N$_2$ adsorption–desorption isotherms. The BET surface areas of the clay decreased from 198.7 to 149.3 m^2/g after modification, the average pore diameter was decreased from 4.479 to 4.458 nm, and the micropore area was reduced from 25.16 to 8.3 m^2/g, while the pore volume increased from 0.1857 to 0.1936 cm^3/g.
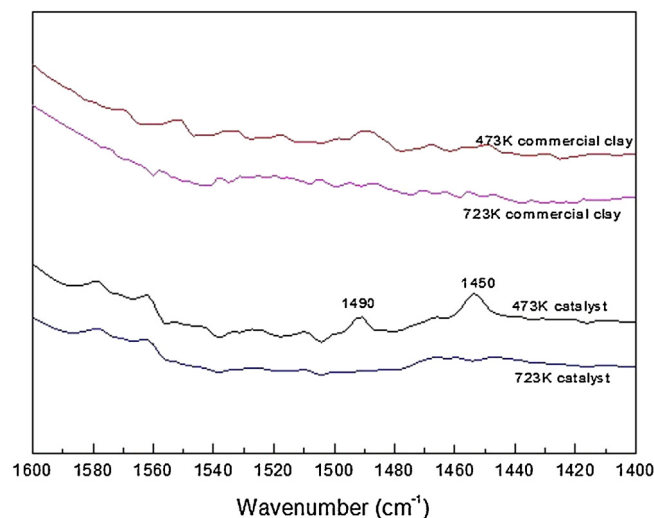

Fig. 5. FT-IR spectra of pyridine adsorbed at 473 K and 723 K.

Table 5
Acidic properties of different samples.

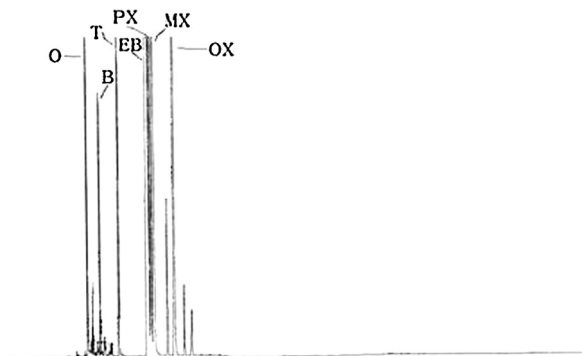| Sample	Acidity ($\times 10^{-4}$ mol g^{-1})		
	Total L acid sites	Strong L acid sites	Weak L acid sites
Catalyst	3.1005	0.2543	2.8462
Commercial clay	0.3312	0.1435	0.1877
MCM-22	25.39	18.69	6.7

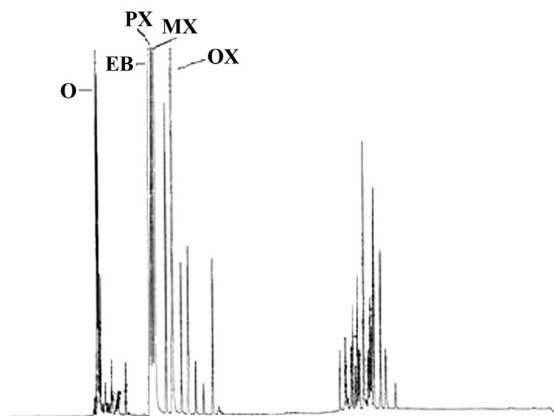**Fig. 6.** The chromatogram of raw material.

Fig. 7. The chromatogram of reaction product.

The commercial clay has large surface area and can remove trace olefin from aromatics, while once the commercial clay reaches adsorption equilibrium, it will be deactivated soon. In the process of clay treating, the running time depends on the textural properties of the clay. The higher surface areas can lead to a better result for removing olefin [6].

The catalyst has a better performance with the lower surface areas than the clay. It demonstrated that the catalyst treating main owing to the reaction while that of clay was adsorption as an adsorbent.

3.3. Study on the acidity of samples

To investigate the type and number of surface acidic sites, FT-IR spectra for the adsorption of pyridine at 473 and 723 K were obtained (see Fig. 5). The spectrum displayed many bands in the wavenumber range of 1400–1600 cm^{-1}, which was attributed to the interaction of pyridine with Lewis (L) and Brønsted (B) acid sites on the sample surfaces. As shown in Fig. 5, the spectra present bands of adsorption at 1450 and 1490 cm^{-1}, which is typical of adsorbed pyridine [7]. It mainly observed the band at around 1450 cm^{-1}, arising due to 19b ν(C—C) vibration of pyridine adsorbed at Lewis acid sites. Another band could be seen at around 1490 cm^{-1} due to contributions of both the Lewis and Brønsted acid sites [8]. There is no band that is observed at 1540 cm^{-1}, so the amount of total B acid could not be calculated. Table 5 shows the amount of the total L acid, weak L acid and strong L acid.

According to Table 5, it is obvious that catalyst was higher than commercial clay in the amount of the weak L acid, with 2.8462 $\times 10^{-4}$ mol g^{-1} weak L acid. This was in accordance with the catalytic activity data and can be concluded that the increase in activity of the catalyst had contributed to the increase in the amount of the weak L acid.

The total amount of L acid in the zeolite was 25.39 $\times 10^{-4}$ mol g^{-1}, and the amount of weak L acid was 6.7 $\times 10^{-4}$ mol g^{-1}. It should be noticed that the amount of strong L acid was 18.69 $\times 10^{-4}$ mol g^{-1}. When the clay mixed with the zeolite, the amount of L acid in the catalyst became higher than that of the clay. The zeolite can adjust the amount of acid in the catalyst. The zeolite has large strong L acid which can cause the olefins polymerize with each other [9]. This was why we only add 20% zeolite in catalyst.

The amount of the weak L acid in the commercial clay was only 0.1877 $\times 10^{-4}$ mol g^{-1} and this explained why the commercial clay activity was much poorer than the catalyst in Fig. 4. The commercial clay has large surface area and relatively high pore volume, wherein once the commercial clay reaches adsorption equilibrium, it will be deactivated soon.

3.4. The mechanism of the reaction

From the comparison of Fig. 6 and Fig. 7, some new organic matter was produced after reaction. According to Table 6, there
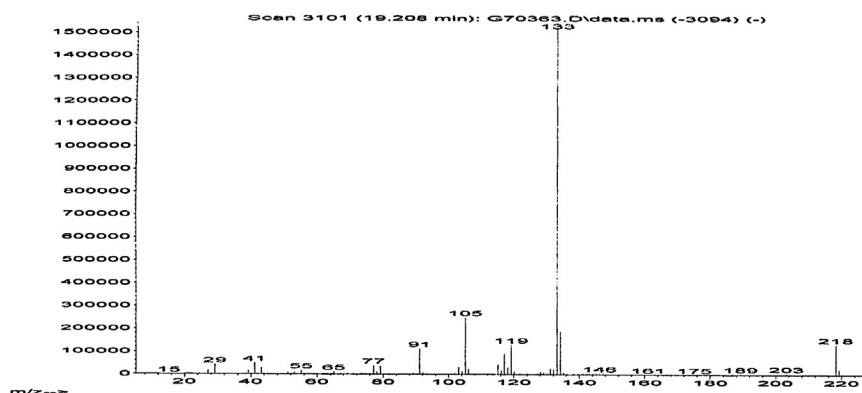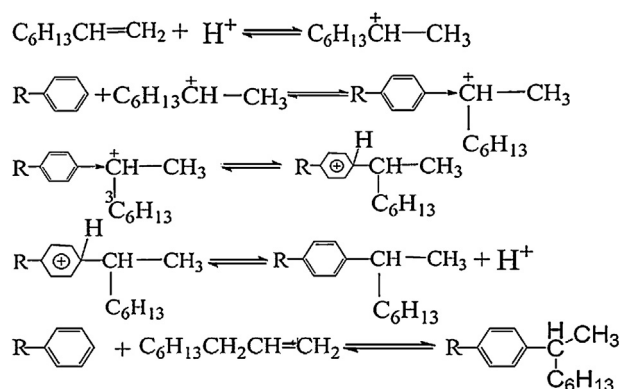

Fig. 8. The mass spectrum of reaction product.

Table 6
The comparison between product and raw material.

	1-Octene	Benzene	Toluene	Ethylbenzene	Xylene	Outcome
Raw materials	3.41%	0.60%	2.16%	57.43%	34.58%	–
Product	1.34%	0.18%	0.09%	57.03%	34.27%	4.4%

Scheme 1. The reaction mechanism between 1-octene and aromatics.

were some chemical reactions of the 1-octene with the benzene and toluene with the markedly changing of theirs content after reaction.

On the other hand, the product was investigated through the mass spectrum (Fig. 8). It could be concluded that the products mainly contained $C_{14}H_{22}$, $C_{15}H_{24}$ and $C_{16}H_{26}$, furthermore, the 1-octene reacted with the benzene to form $C_{14}H_{22}$, when it reacted with toluene and ethylene to form $C_{15}H_{24}$ and $C_{16}H_{26}$ separately.

It was well known that the alkylation of aromatic with olefins over solid acid catalyst obeyed the generally accepted carbonium ion mechanism [10]. On the basis of this mechanism the reaction mechanism between 1-octene and aromatics was illustrated in Scheme 1. The olefins molecule was protonated by the B acid sites or L acid sites to a carbonium ion that generated, by electrophilic attack on the aromatic π-electrons, a mono or polyalkylbenzenium ion. The desorption process and the loss of the proton gave the alkylated aromatic and restored the B acid sites and the L acid sites.

4. Conclusions

(1) The commercial test showed that the effective reaction time of the catalyst lasts 63 days, about 3 times as long as that of the commercial clay. By reducing the frequency of clay replacement and landfill quantity, this catalyst will significantly reduce production cost and protect the environment and it should conduct large scare application.
(2) The comparison of the 6 tons and 22 tons commercial tests indicated that the catalyst developed by our research team was more suitable for treating the higher volume space velocity.
(3) The acidity of the catalyst and the commercial clay was evaluated, indicating that the amount of the weak L acid sites of the catalyst was larger than the commercial clay, and the enhancement of the efficiency on removing olefins in aromatics though catalytic reaction had contributed to the increase in the amount of the weak L acid.
(4) The mechanism of the olefins reacts with the aromatics in accordance with the carbonium ion mechanism and the reaction is the alkylation reaction.

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