



Short Communication

Hydrothermally stable mesoporous aluminosilicates as superior FCC catalyst: From laboratory to refinery

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ABSTRACT

Well-ordered aluminosilicates (MAs) were prepared by *in-situ* assembly of pre-crystallized units of zeolite Y precursors at a commercial scale, and applied in an industrial fluid catalytic cracking unit for the first time. Compared with incumbent equilibrium catalyst, the surface area of trial equilibrium catalysts (30% inventory ratio) increased from 110 m² g⁻¹ to 120 m² g⁻¹. Moreover, a significant increase of the mesoporous surface area of trial equilibrium catalysts (30% inventory ratio) from 33 m² g⁻¹ to 40 m² g⁻¹ (22% increase). Furthermore, the equilibrium catalyst that contain 80% LPC-65 yields significantly lower heavy oil (0.23%) and higher total liquids (0.53%) compared with LDO-70. The industrial results demonstrated excellent hydrothermal stability and superior catalytic cracking properties, showing the promising future in the industrial units.

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1. Introduction

Much attention was paid to the fluid catalytic cracking (FCC) of heavy oil due to its greatly enhanced processing difficulty because of the large molecules (Fu et al., 2006; Puente et al., 2007; Talmadge et al., 2014; Corma et al., 2017). It was well known that FCC of large molecules of heavy oil would be carried out in a successive way: (1) the large heavy oil molecules are precracked firstly in the macropores of the matrix, such as kaolin; (2) the products obtained in step (1) cracked further in the mesopores; (3) the intermediate products of step (2) cracked more selectively to valuable products, such as gasoline, diesel, and other chemical products (Ji et al., 2018). In addition to this, the improvement of FCC catalysts in the face of new challenges (such as new feeds and less polluting products) would be extremely urgent (Valle et al., 2019; Palos et al., 2021). Therefore, it is of vital importance to implant mesoporosity into FCC catalysts of heavy oil.

To date, many approaches to introducing mesoporosity into FCC

catalysts have been developed. A typical way is the so-called “top-to-down” method, which involves the removal of Al or Si species of zeolites (Verboekend et al., 2013; Jia et al., 2019). Unfortunately, this process suffers from zeolitic loss due to the destructive route. Another procedure “down-to-up” is a convenient approach to generating mesoporosity directly (Saxena et al., 2014; Kerstens et al., 2020). However, the low hydrothermal stability and high synthesis cost of the obtained materials still hinder its industrial application in severe conditions of FCC. Therefore, how to obtain hydrothermally stable MAs synthesized with low synthesis cost is still a great challenge in both FCC process and materials science.

Our group (Liu et al., 2013a; Cao et al., 2014; Jin et al., 2014; Mi et al., 2018a; Chen et al., 2021; Li et al., 2022) has obtained MAs with excellent hydrothermal stability by a novel strategy that introduces zeolite Y precursors (the primary and secondary structural unit of zeolite Y) into the walls of mesoporosity. Just in this idea, our group obtained MAs with hydrothermal stability comparable to that of USY (Liu et al., 2014a, 2021; Mi et al., 2017a, 2017b, 2018b). For example, the BET surface area of MAs decreased from 595.4 m² g⁻¹ to 153.9 m² g⁻¹ after a severe hydrothermal treatment in 100% water vapor at 800 °C for 12 h. Moreover, the materials showed excellent catalytic properties when it was employed in

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heavy oil FCC in the MAT unit (Liu et al., 2013b, 2014b, 2014c; Deng et al., 2022). Although the significant progress in synthesis and application of hydrothermally stable MAs, the commercial manufacturing of materials, preparation of industrial catalysts, and industrial application in pilot FCC unit are still a great challenge for the material scientists.

Herein, we report the most recent progress in commercial manufacturing and catalytic cracking performance in the FCC unit of 1.2-million tons in a refinery. To the best of our knowledge, the research progress represents the most advanced stage of commercial manufacturing and industrial application in FCC of MAs.

2. Experimental section

2.1. Chemical materials

Industrial reagent of Pluronic P123 triblock copolymer (EO₂₀PO₇₀EO₂₀) was obtained from Henan Ruiyi Chemical Company. Water glass (containing 27.78 wt% SiO₂ and 8.98 wt% Na₂O) was purchased from Tangshan Shihe Sodium Silicate Company.

2.2. Synthesis of zeolite Y precursors

The mixtures of Na₂SiO₃, Al₂(SO₄)₃·18H₂O, and NaOH solution with a molar ratio of Al₂O₃/SiO₂/Na₂O/H₂O = 1/16–19/15–20/300–320 were prepared. After rapidly stirring for 30–80 min, the prepared mixtures undergo an ageing with stirring at 80–100 °C for 4–20 h. The obtained sticky solution was denoted as “zeolite Y precursors”.

2.3. Industrial synthesis of MAs

- (1) P123 and water were added to the reactor. Zeolite Y precursors and H₂SO₄ (6 M) were slowly added to the above reactor to keep the pH of the system at about 1.0–3.0. The obtained solution was stirred at 30–60 °C for 10–40 h.
- (2) The liquid product of step (1) were transferred into crystallization autoclaves of 10 m³ for crystallization under 100–140 °C for 24 h. The as-synthesized products were processed by the subsequent filtering, washing, and drying at 120 °C for 2 h. Then, the resultant solid was calcined at 550 °C for 6 h in order to remove the organic template, the obtained product was denoted as “IS”
- (3) IS was hydrothermally aged under a severe condition (800 °C, and 100% water vapor) for 4 h and the product was named as “HIS”.

2.4. Characterization

Diffractionmeter Rigaku D/Max 2500VB2+/PC equipped with Cu K α radiation was used for the study of X-ray diffraction (XRD) patterns for the obtained samples. JEM 100CX instrument with 200 kV acceleration voltage was used to study the TEM images. A Micromeritics ASAP 2405N system was used to investigate the N₂ ad-desorption isotherms using liquid nitrogen at 77 K. Moreover, The curves of pore-size distribution of materials was obtained by the traditional Barrett-Joyner-Halenda (BJH) method.

The amount of acid and the type of acid are calculated using the following formula:

$$C_{\text{py-B}} = \frac{1.88I_{\text{A(B)}}R^2}{W}; \left(1.88 = \frac{\pi}{\varepsilon_{\text{B}}}, \varepsilon_{\text{B}} = 1.67 \pm 0.1 \text{ cm}^3/\mu\text{mol} \right)$$

$$C_{\text{py-L}} = \frac{1.42I_{\text{A(L)}}R^2}{W}; \left(1.42 = \frac{\pi}{\varepsilon_{\text{L}}}, \varepsilon_{\text{L}} = 2.22 \pm 0.1 \text{ cm}^3/\mu\text{mol} \right)$$

where $C_{\text{py-B}}$ and $C_{\text{py-L}}$ represent the concentration of Brønsted and Lewis acids, respectively. $I_{\text{A(B)}}$ and $I_{\text{A(L)}}$ represent the integrated absorbance of Brønsted and Lewis acids, respectively. R is the radius of the wafer (cm). W is weight of wafers (mg).

2.5. ACE testing

The catalytic properties of FCC catalysts were evaluated at Lanzhou Petrochemical Research Center, using the ACE unit Model R+MM from Kayser Technology. The fluidization of the reactor was achieved by a stream of nitrogen. 9 g catalyst was fluidized and stabilized at catalyst/oil ratio 5 and the reaction temperature 530 °C.

2.6. Properties of feeding heavy oil

The feeding heavy oil was characterized with viscosity 10.38–14.35 mm²/s, residual carbon 3.4–4.2 wt%, and density 900 kg/m³.

3. Results and discussion

3.1. Hydrothermal stability

~25 tons of MAs were manufactured at a commercial zeolite manufacturing corporation by using the existing production equipments. This is the first time that MAs are manufactured at an industrial scale. Characterization results (Fig. 1 and Fig. 2) showed that the industrial product had similar physicochemical properties with those obtained at the laboratory. With a BET surface area of 769 m² g⁻¹, the industrial product has a narrow mesopores centered around 3.5–4.5 nm (Fig. 3). After the hydrothermal deactivation at 800 °C for 10 h under 100% water vapor, the total surface area decreased from 769 m² g⁻¹ to 154 m² g⁻¹, the total pore volume decreased from 0.77 cm³/g to 0.32 cm³/g, while the mesopore volume dropped from 0.57 cm³/g to 0.25 cm³/g (Table 1). Interestingly, the diameter and the size distribution of mesopores became wider (Fig. 3). All these results demonstrated the excellent hydrothermal stability of industrial products. TEM images (Fig. 4)

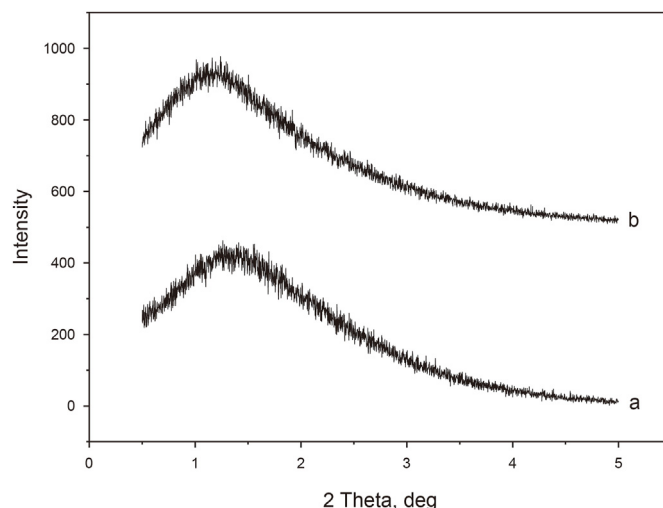


Fig. 1. XRD patterns for the obtained materials: (a) IS, and (b) HIS.

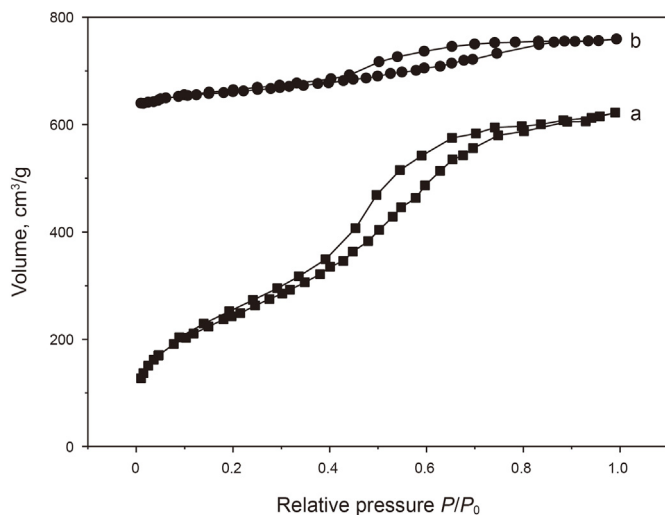


Fig. 2. N_2 ad-desorption isotherms of the obtained products: (a) IS, and (b) HIS.

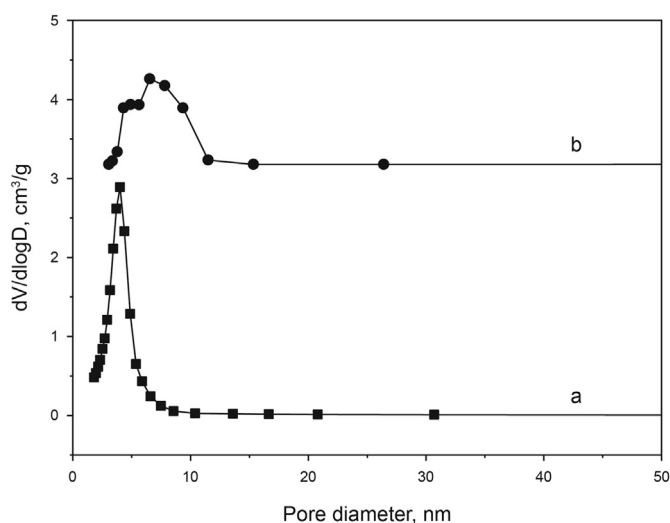


Fig. 3. Curves of pore size distribution of the obtained products: (a) IS, and (b) HIS.

showed that IS after the severe hydrothermal ageing still exhibited mesoporous structure which is typically wormlike, suggesting the high hydrothermal stability of IS.

3.2. Acidity characteristics

The MAs was milled and then mixed with kaolin, rare earth salts, pseudo-boehmite, and alumina sol. The mixtures are spray-dried into 429 tons of FCC catalysts microspheres with the diameter of 75 μm . The final catalyst was named “LPC-65”. The incumbent catalyst applied in the industrial FCC unit LDO-70 was used to compare with LPC-65.

To study the acidity characteristics of LDO-70 and LPC-65,

Brønsted acid sites (BAS) and Lewis acid sites (LAS) were calculated from Py-FTIR spectra in the temperature range of 473–623 K, and the corresponding results were depicted in Fig. 5, Fig. 6 and Table 2. From Table 2, we could see that both the total acid sites and the BAS of LPC-65 are much higher than those of LDO-70. In this sense, it could be reasonably deduced that the conversion of heavy oil would increase greatly.

3.3. Catalytic cracking properties of catalysts in ACE

The final catalyst LPC-65 exhibited a total surface area of 258 $\text{m}^2 \text{g}^{-1}$, including micropores area of 173 $\text{m}^2 \text{g}^{-1}$ and mesopores area of 85 $\text{m}^2 \text{g}^{-1}$ (Table 3). As for comparison, the incumbent industrial catalyst LDO-70 has a total surface area of 239 $\text{m}^2 \text{g}^{-1}$, including micropores area of 169 $\text{m}^2 \text{g}^{-1}$ and mesoporosity surface area of 70 $\text{m}^2 \text{g}^{-1}$.

LPC-65 and LDO-70 were hydrothermally deactivated at 800 $^\circ\text{C}$ for 4 h under 100% water vapor to simulate the catalytic properties of equilibrium catalysts. The mesoporous surface area of steamed LPC-65 is 195 $\text{m}^2 \text{g}^{-1}$, in which the mesoporous surface area is 64 $\text{m}^2 \text{g}^{-1}$, much higher than that of the reference catalyst (49 $\text{m}^2 \text{g}^{-1}$), indicating that the remaining ratio of mesoporosity is high even after severe hydrothermal treatment. ACE test of the two deactivated catalysts using the same heavy oil feed suggested the clear advantage of LPC-65 in selectivity, mainly in increased conversion of 3.36%, reduced heavy oil yield of 1.39% and increased total liquid yield of 0.67% (Table 4). The lower coke factor of LPC-65 compared with that of LDO-70 exhibited much enhanced selectivity, which was the most important factor for FCC catalysts. These interesting results could be reasonably ascribed to the presence of enhanced hydrothermally stable mesoporosity.

It is well known that vanadium and nickel will cause damage to zeolites in FCC conditions (Trujillo et al., 1997; Xu et al., 2002; Hagiwara et al., 2003; Cerqueira et al., 2008). The ACE test of the contaminated LPC-65 and LDO-70 (deactivated with 3000 ppm Ni and 5000 ppm V) suggested the clear advantage of contaminated LPC-65 in selectivity, mainly in increased conversion of 4.48%, reduced heavy oil yield of 2.82% and increased total liquid yield of 2.14% (Table 5). These results demonstrated that the obtained MAs could withstand the severe conditions in industrial FCC units. To the best of our knowledge, this is the first time that a mesoporous aluminosilicate demonstrated excellent hydrothermal stability in FCC units. Moreover, it is the first time that a mesoporous aluminosilicate is employed in FCC catalysts with good activity and selectivity.

3.4. Catalytic cracking properties of catalysts in industrial FCC unit

LPC-65 was added to 1.2-million tons equipment at the same addition rate with that of the incumbent catalyst. As a result of this, a constant catalyst inventory of 429 tons was maintained in the industrial unit. The change-over from the incumbent catalyst to LPC-65 resulted in an 83.37% inventory ratio at the end of 68 days trial. Equilibrium catalyst samples in different inventory ratios were collected and characterized periodically. Interestingly, the surface area of trial equilibrium catalysts (30% inventory ratio) increased from 110 $\text{m}^2 \text{g}^{-1}$ to 120 $\text{m}^2 \text{g}^{-1}$, consistent with the higher

Table 1
XRD and BET characterization results of IS, and HIS.

Sample	2-Theta	Area	$S_{\text{BET}}, \text{m}^2 \cdot \text{g}^{-1}$	$S_{\text{MES}}, \text{m}^2 \cdot \text{g}^{-1}$	$S_{\text{MIC}}, \text{m}^2 \cdot \text{g}^{-1}$	$V_{\text{Total}}, \text{cm}^3 \cdot \text{g}^{-1}$	$V_{\text{MES}}, \text{cm}^3 \cdot \text{g}^{-1}$	$V_{\text{MIC}}, \text{cm}^3 \cdot \text{g}^{-1}$	$D_{\text{avg}}, \text{nm}$
IS	1.16	913	769	713	56	0.77	0.57	0.20	3.2
HIS	1.41	255	154	125	29	0.32	0.25	0.07	6.5

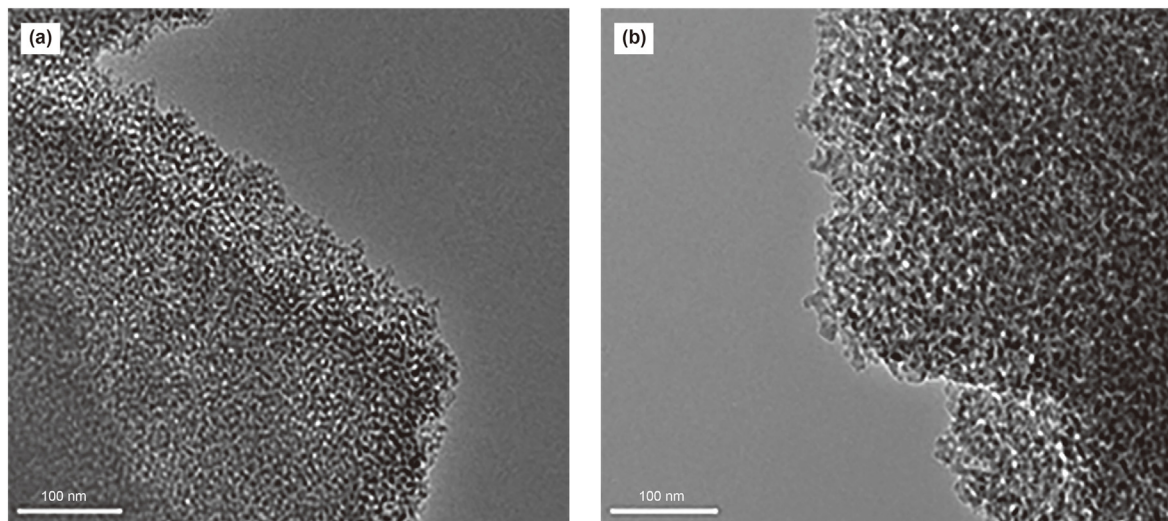


Fig. 4. TEM images of samples: (a) IS, and (b) HIS.

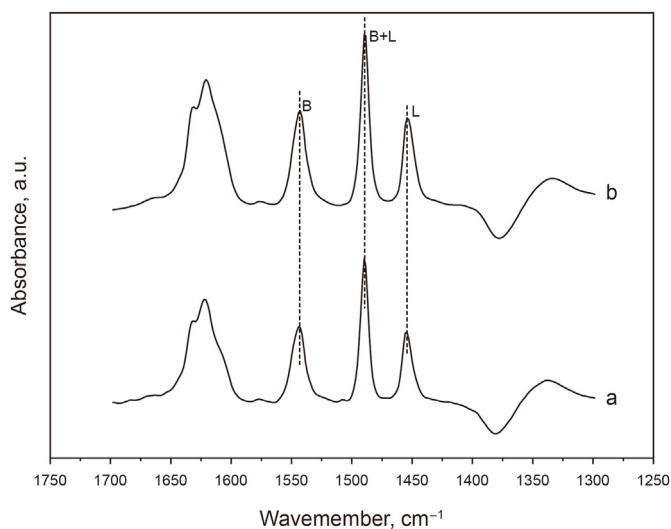


Fig. 5. Py-IR spectra of (a) LDO-70, and (b) LPC-65 at 200 °C.

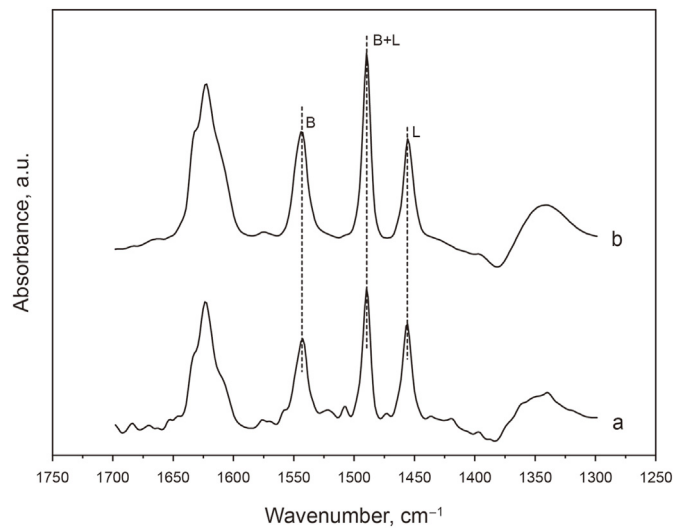


Fig. 6. Py-IR spectra of (a) LDO-70, and (b) LPC-65 at 350 °C.

surface area of fresh LPC-65. Surprisingly, a significant increase in the mesoporous surface area of trial equilibrium catalysts (30% inventory ratio) from $33 \text{ m}^2 \text{ g}^{-1}$ to $40 \text{ m}^2 \text{ g}^{-1}$ (22% increase), indicating the high hydrothermal stability of the mesoporosity in this industrial unit.

Table 6 summarized the industrial results of equilibrium catalysts of the incumbent and LPC-65. Compared with LDO-70, the equilibrium catalyst that contain 80% LPC-65 yields significantly lower heavy oil (0.23%) and higher total liquids (0.53%). These results are very close to those obtained from laboratory ACE testing. Generally, the activity of equilibrium catalyst could be considered as the average activity of all the catalyst in FCC unit, which included fresh catalyst and deactivated catalyst. Therefore, it could be suggested that LPC-65 was an ideal FCC catalyst.

Mechanical resistance is another important quality of FCC catalyst, because it reduces the flow of catalyst that must be purged. Interestingly, the abrasion index of LPC-65 is 1.6, much lower than the prerequisite value 3.0. These results indicated that LPC-65 developed in this paper had comprehensive advantages compared with the commercial catalysts.

Table 2

Acid amount and acid type of LDO-70, and LPC-65.

Sample	Weak acid sites, $\mu\text{mol/g}$			Strong acid sites, $\mu\text{mol/g}$			Total acid sites, $\mu\text{mol/g}$
	B	L	B + L	B	L	B + L	
LDO-70	84	41	125	50	35	85	210
LPC-65	139	77	216	72	39	111	327

4. Conclusions

For the first time, mesoporous aluminosilicates with excellent hydrothermal stability were manufactured at the commercial scale by a unique process. FCC catalysts obtained from the MAs exhibited high stability in an industrial FCC unit. The catalyst showed improved product selectivity compared with the incumbent catalyst, at a high inventory ratio of 80%. Gasoline oil yield with 80% LPC-65 equalized catalyst enhanced by 1.22% and the total liquid yield enhanced by 0.53%. The results of synthesis and application

Table 3
Physicochemical properties of catalysts.

Sample	Na ₂ O, wt%	RE ₂ O ₃ , wt%	S _{BET} , m ² /g	S _{MIC} , m ² /g	S _{MES} , m ² /g	V _{Total} , cm ³ /g
LPC-65	0.10	2.64	258	173	85	0.42
LDO-70	0.11	2.81	239	169	70	0.38
Steamed LPC-65 ^a			195	131	64	0.30
Steamed LDO-70 ^a			168	119	49	0.26
Incumbent equilibrium catalyst			110	77	33	0.15
Catalyst change-out, 30%			120	80	40	0.17
Catalyst change-out, 50%			121	79	42	0.16
Catalyst change-out, 80%			126	79	47	0.19

^a LPC-65 and LDO-70 were hydrothermally deactivated at 800 °C for 4 h under 100% water vapor.

Table 4
ACE testing results of catalysts.

	Steamed LDO-70 ^a	Steamed LPC-65 ^a
Dry gas, wt%	2.04	2.24
LPG, wt%	19.60	20.75
Gasoline, wt%	53.11	54.49
Diesel, wt%	12.60	10.75
Heavy oil, wt%	5.81	4.42
Coke, wt%	6.83	7.36
Conversion, wt%	81.58	84.94
Total liquids, wt%	85.32	85.99
Coke factor ^b	1.54	1.30

^a LPC-65 and LDO-70 were hydrothermally deactivated at 800 °C for 4 h under 100% water vapor.

^b Coke factor = $Y_{\text{Coke}} \times (100 - X) / X$, which Y_{Coke} is coke yield, X is conversion ratio.

Table 5
ACE testing resulting of contaminated LPC-65 and contaminated LPC-70.

	Contaminated LPC-65 ^a	Contaminated LDO-70 ^a
Dry gas, wt%	3.13	3.14
LPG, wt%	19.72	16.35
Gasoline, wt%	41.28	40.60
Diesel, wt%	15.07	16.99
Heavy oil, wt%	10.68	13.50
Coke, wt%	9.87	9.43
Conversion, wt%	73.99	69.51
Total liquids, wt%	76.07	73.93
Coke factor	3.465	4.136

^a Contaminated with 3000 ppm Ni and 5000 ppm V, and hydrothermally aged in 800 °C, 100% water vapor for 4 h.

Table 6
Catalytic performance of LDO-70 and catalyst with change-out of LPC-65.

Catalyst change-out	LPC-65			
	LPC-65	LPC-65	LPC-65	LPC-65
	0	30%	50%	80%
	Equilibrium catalyst LDO-70			
Dry gas, wt%	3.75%	3.45%	3.38	3.52%
LPG, wt%	17.64%	18.08%	18.32	18.07%
Gasoline, wt%	48.46%	49.26%	49.08	49.68%
Diesel, wt%	17.31%	16.23%	16.07	16.19%
Heavy oil, wt%	3.25%	3.15%	3.25	3.02%
Coke, wt%	9.59%	9.83%	9.9	9.52%
Total liquids, wt%	83.41%	83.57%	83.47	83.94%

represent the most advanced development of MAs in heavy oil FCC to date, which bring a ray of hope for the industry-scale application of MAs in heavy oil FCC.

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