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Olefin production from catalytic cracking of light fuel oil over different additives

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ABSTRACT

The catalytic cracking of a fuel oil over fluid catalytic cracking (FCC) catalyst has been investigated applying different additives. Catalyst mixtures consisting of a equilibrium FCC catalyst (E-Cat) blended with ZSM-5, MCM-41 and Mordenite additives were examined at the additive levels of 25 wt.%. The catalytic performance of the matrix was studied in a fixed-bed micro-activity test unit (MAT) at 600 ˚C and catalyst/oil ratio of 3.6. Two types of ZSM-5 with different Si/Al ratios were utilized. Results indicate that the yield of light olefins significantly increased by operating hybrid catalysts in comparison with the base E-Cat. The highest olefin yield of 61.46 wt.% in the gas phase products was achieved over E-Cat/ZSM-5 of low Si/Al ratio. The maximum propylene production was observed over MCM-41, besides applying mordenite as additive showed more propylene to ethylene ratio in products. Butenes were also increased by use of all additives, whereas iso-butene shows the maximum yield over all E-Cat/additives.

Keywords: FCC, Catalyst, Olefin, Propylene, Zeolite, Additive.

1. Introduction

Among the various downstream operations, fluid catalytic cracking (FCC) process is still one of the most important due to its widespread commercial use [1-3]. Through a FCC process, heavy feed stocks are converted to lighter and more valuable products such as gasoline and light olefins [4].

As we know, light olefins are the base feedstock for petrochemical industry [5]. The increasing demand for them is directing many FCC units to maximizing their yields, which offers considerable challenges to the conventional FCC catalyst design. Integrated petrochemical industry is continuously looking for processes with improved flexibility in producing various olefins (mainly propylene) from hydrocarbon feedstocks [6-7]. Currently, the easiest FCC operation to maximize light olefins is to utilize a catalyst system that minimizes hydrogen transfer reaction in order to preserve olefins. Furthermore, the production of light olefins as petrochemical feedstocks is economically attractive for refineries integrated with petrochemical industries [8].

At present, there is an increasing interest in maximizing propylene yield of FCC units and it is expected that worldwide propylene supply from FCC units will continuously increase [9,10].

So, new catalysts need to be developed to improve propylene yield of FCC process. Feed properties, operating conditions and the nature of the catalysts are the factors influence the FCC result. Besides, several additives may be applied in order to maximize the propylene yield.

In the present paper, four additives including two types of ZSM-5 (Si/Al ratios of 50 and 300), MCM-41 and also mordenite were investigated .The catalyst samples were evaluated in physical mixture of the corresponded commercial additives together with a base equilibrium catalyst (E-Cat) in a modified micro activity test (MAT) reactor [11]. The goal of this work was to study the role of the additives in enhancing the production of light olefins at constant operating conditions.

2. Experimental

2.1. Instrumentation

The X-ray diffraction (XRD) patterns of the catalysts were performed with Philips X'Pert MPD diffractometer using Cu Kα radiation (λ = 1.54056 Å) at 40 kV and 30 mA. The shape and size of the E-Cat and additives were determined by scanning electron

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microscopy (SEM) using a VEGA/TESCAN. Surface area measurements for the catalysts were obtained by N_2 adsorption at 77 K on a Quantachrome TPR Win v1.0 gas sorption apparatus following the BET procedure. Alumina, silica and sodium content of the additives were determined by atomic absorption spectroscopy. Gas chromatographic analysis of the MAT products was done to provide detailed results of the products and information from the selectivity of the catalysts tested. The gaseous MAT product was analyzed using Agilent technology 7890A fast RGA GC instrument equipped with FID and TCD detectors for the quantitative determination of all light hydrocarbons up to C_4 and fixed gases.

2.2. Materials

The base catalyst was a commercial equilibrium FCC catalyst (E-Cat) obtained from Abadan refinery. It was based on USY zeolite with a surface area of 210 m^2 g^{-1} and a pore volume of 0.35 cm^3 g^{-1}. It has a nearly spherical morphology with the particles of about 40-60 μm in diameter (Fig. 1). The amount of rare earth oxide on E-Cat was about 3-4.5 wt.% and loss of weight upon heating in air at 900°C for 3 h was 13. The E-Cat was calcined at 500°C for 3 h before further use. The additive contained catalysts were mixtures of 75 wt.% E-Cat together with 25 wt.% each of ZSM-5 (Si/Al ratios of 50 and 300), MCM-41 and mordenite as additives. Fig. 2 shows the SEM images of the four additives which have different morphological structure. The additives were air-calcined at 500°C for 4 h, in order to remove the impurities and the water molecules in the crystal lattice as well. The XRD patterns of all additives are shown in Fig. 3. All diffraction peaks are well indexed to the standard crystalline phases of the corresponded additives. The pure additives were physically mixed with the E-Cat sample. The obtained E-Cat/additive mixtures were pelletized, crushed and then sieved to obtain about three millimeter sizes catalyst particles. The total mass of the catalyst matrix applied for all tests was 4.0 g. The detailed characteristics of the E-Cat and the additives are listed in Tables 1 and 2, respectively. The hybrid catalysts were deactivated with 100% steam at 800°C for 4 h in a tubular furnace in order to equilibrate the activity of catalysts to what is expected under industrial conditions.

A light virgin fuel oil obtained from Tehran refinery was used as feedstock in all MAT tests. The specification of the corresponded fuel oil is presented in Table 3. Sulfur content in this feed was about 3.0 wt.%. The feed contains 13 wt.% of Conradson carbon and has a pour point of 5 and 15°C in winter and summer, respectively.
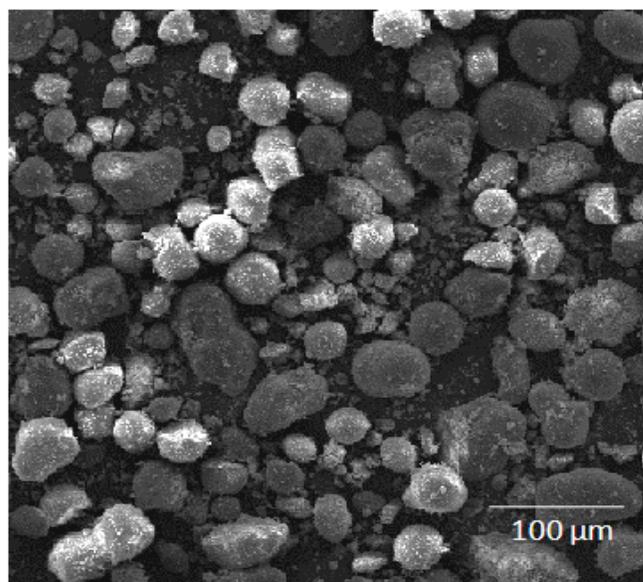

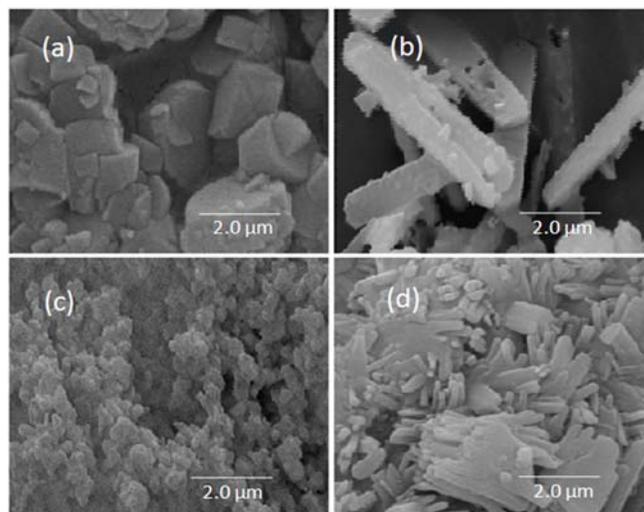**Fig. 1.** SEM image of the E-Cat, showing the spherical morphology.

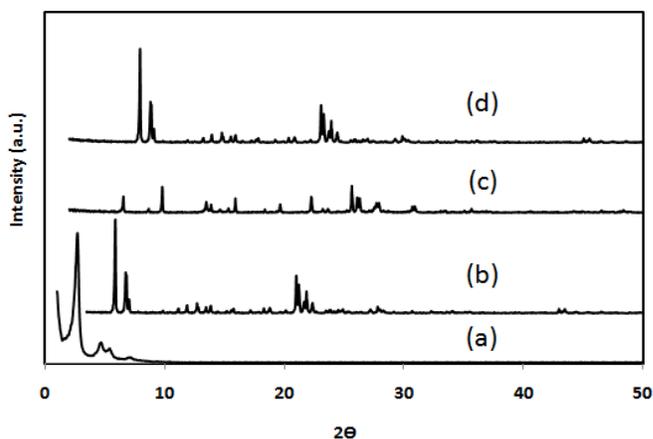**Fig. 2.** SEM images of: a) ZSM-5(50), b) ZSM-5(300), c) MCM-41 and d) Mordenite.

Fig. 3. XRD patterns for: a) MCM-41, b) ZSM-5(50), c) Mordenite and d) ZSM-5(300).

Table 1. Properties of the FCC catalyst (E-Cat).

Total surface area ($m^2 g^{-1}$)	210
Al_2O_3 (wt.%)	40
SiO_2 (wt.%)	55.5
Re_2O_3 (wt.%)	3.0-4.5
Na (wt.%)	0.15
Fe (wt.%)	0.40
Loss on ignition (900 ˚C, 3h)	13
Pore volume ($cm^3 g^{-1}$)	0.35
Bulk density (g cm^{-3})	0.7-0.8
Particle distribution (%)	
0-20 μm	2
0-40 μm	10-20
0-80 μm	70-80

Table 2. Additive compositions.

Additive	Na_2O (%)	Si/Al ratio (mol/mol)	Surface area (m^2/g)
ZSM-5 (50)	0.05	50	425
ZSM-5 (300)	0.05	300	400
MCM-41	0.08	-	900
Mordenite	0.08	20	500

2.3. Reaction procedure

The evaluation was performed in a modified fixed-bed micro activity test reactor according to ASTM-D3907. The operating conditions of the MAT unit are listed in Table 4. All cracking reactions were performed at 600˚C with constant catalyst to oil ratio of 3.6 and the catalyst time on stream in all experiments was 50 s.

Fig. 4 shows the schematic flow diagram of the experimental set-up which was employed for the activity tests. The main parts of the set-up were a tubular quartz reactor with a WHSV of 30 h^{-1} and an injection system consists of a syringe and a syringe pump. Preheated Tehran refinery light fuel oil was injected in the reactor by the syringe pump at the rate of 55 ml h^{-1}. The catalysts were mixed with quartz particle to ensure its heat capacity being constant during the endothermic reaction. Before each test, the system was purged under N_2 flow of 60 cm^3 min^{-1} for about 20 min at the reaction temperature, and then 1.11 g of the fuel oil was fed through the syringe pump.

After that, stripping of the catalyst was carried out for 20 min using 60 cm^3 min^{-1} of N_2. During the reaction, liquid products were collected in a glass receiver at the end of the reactor which was kept in an ice-bath. The gaseous products were collected in a gas sampling bag.

The amount of carbon on catalyst was calculated by total burning of the deposited carbon with air in an electrical furnace for about 5 h at 500˚C for each sample.

3. Results and Discussion

In recent years, many research groups have focused on FCC modified processes to improve light olefins production [12-14]. The effect of operating conditions such as temperature and catalyst to oil ratio was investigated and interesting results were reported [15,16]. Continuing to the published researches, herein the effect of catalyst bed composition was investigated in constant operating conditions. Catalyst mixtures including E-Cat blended with 25% of the commercial

Table 3. Properties of the light fuel oil feedstock.

Density @ 15°C (g cm^{-3})	0.97
Kinematic viscosity @ 50°C (c.St)	230
Sulfur (wt.%)	3.0
Conradson carbon (*wt*.%)	13
Pour point (°C)	Winter 5.0 Summer 15.0
Flash point (°C)	65

Table 4. Operating conditions of the MAT test.

Parameter	Value
Reactor temperature (°C)	600
Fuel oil weight (g)	1.11
Catalyst weight (g)	4.0
Catalyst/oil ratio (g/g)	3.6
Contact time (s)	75
WHSV (h^{-1})	30

ZSM-5 (Si/Al ratios of 50 and 300), MCM-41 and mordenite were investigated at the 600°C and catalyst to oil ratio of 3.6. The results obtained in the MAT tests with the E-Cat and different E-Cat/additive mixtures are shown in Table 5. Comparing the results obtained from the base catalyst (E-Cat) with those of E-Cat/additives in Table 5, it is observed that an apparent increase promote in total olefins yield for hybrid catalysts in comparison with the base E-Cat. This increase could be assigned to the more pore sizes and shape versatilities due to hybrid catalysts, allowing more hydrocarbons to enter the pores and then cracked properly. Therefore, the fact observed by other similar researches is fulfilled by this observation [17].

On the basis of results of Table 5, it is deduced that besides the increasing total olefins yield by adding additives rather than the base catalyst, among the different additives tested, ZSM-5 of lower Si/Al ratio (ZSM-5(50)) resulted in the maximum value of total olefin production. The effect of additives in total olefin production is plotted in Fig. 5. The high yield of light olefins obtained over ZSM-5(50) is attributed to its low hydrogen transfer activity which is due to its lower acidity as well as the three-dimensional and highly accessible pore structure. So this additive offered easier transport and accessibility to the active sites. Such an effect was well known and previously reported by Arandes and co-workers on cracking a commercial feedstock [18].

Investigating the propylene production, it can be concluded that additives have significant influence in the propylene yield. The corresponded column curve is shown in Fig.6. The addition of MCM-41 increased the propylene yield up to 32.52 wt.% in the gas phase products which was the highest value among all additives tested. This observation could be attributed to its mesopores which suppressed secondary and hydrogen transfer reactions. Other hybrid catalysts resulted in 27.64, 27.87 and 29.63 wt.% for ZSM-5(50), ZSM-5(300) and mordenite, respectively. It is noteworthy that the propylene yield which obtained via

the base E-Cat was 21.53 wt.%, much lower than all E-Cat/additive mixtures.

In the case of ZSM-5, it can be seen that increasing the Si/Al ratio caused to decrease in total olefin yields, which could be attributed to greater thermal cracking due to the higher acidity obtained with high Si content. Applying mordenite as additive shows lower total olefins yield of 50.33 wt.% rather than both MCM-41 and ZSM-5. One-dimensional pores of mordenite are easily blocked even with a small amount of carbon deposit through the reaction. However, it shows high selectivity to propylene, even more than MCM-41. The propylene to ethylene ratio (P/E) against different catalyst mixtures studied is plotted in Fig. 7. As it is clear from the figure, it is notable that mordenite leads to the highest P/E ratio while ZSM-5 as additive conducted the minimum P/E ratio through increasing the ethylene yield. High P/E ratios of 2.26 and 2.33 obtained by MCM-41 and mordenite, respectively, is
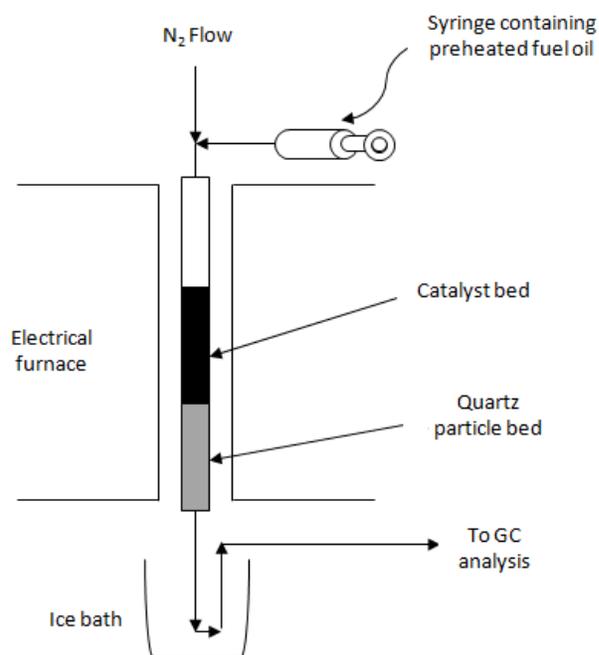

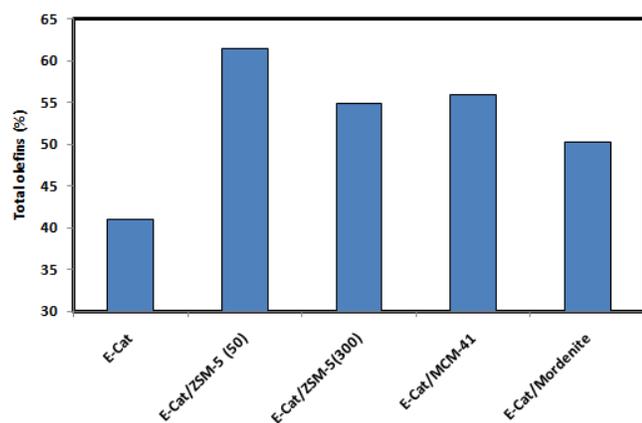**Fig.4.** Schematic flow diagram of the experimental set-up.

Table 5. Comparative MAT data over E-Cat and E-Cat/additives

Product yields (wt.%)	E-Cat	E-Cat/ZSM-5(50)	E-Cat/ZSM-5(300)	E-Cat/MCM-41	E-Cat/Mordenite
Ethylene	16.65	26.88	22	14.34	12.7
Propylene	21.53	27.64	27.87	32.52	29.63
Butenes	2.82	6.94	5	9.04	8
Total olefins	41	61.46	54.87	55.9	50.33
Dry gas	44	23	39.74	31.22	35.11
Coke	4.08	2.94	2.79	2.87	3.11

of considerable importance in comparison with the values obtained by conventional steam cracking processes. Moreover, the previous works using catalytic cracking processes reported the maximum P/E ratio of 1.8 by adjusting the acidity as well as reaction temperature [19]. So, the results of this work show considerable increase in P/E ratio with respect to the similar works.

The evaluation of butenes yield indicates that among four butenes produced, isobutene showed the maximum yield in all catalyst systems tested. Yields of all butenes including 1-butene, cis-2-butene, trans-2-butene and isobutylene, obtained over all catalyst systems under the same conditions are compared in Fig. 8. The same as other olefins produced, additives increase the butenes yield in comparison with the base E-Cat.

The yield of coke, calculated by total burning of the deposited carbon on catalyst after reaction, was slightly lower for hybrid catalysts in comparison with the base catalyst. This could be a consequence of lower conversion mainly because of dilution of the base catalyst. These results agree with those obtained by several authors under different experimental conditions [20].
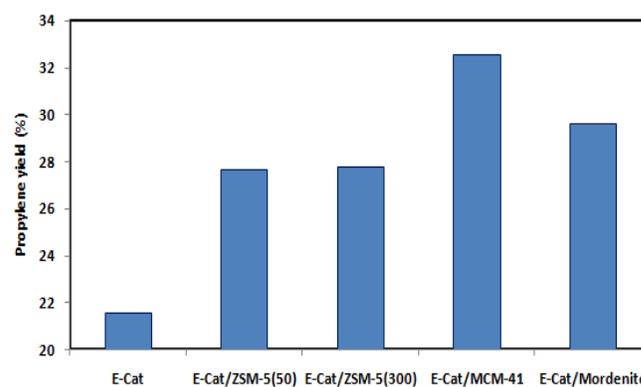
4. Conclusions

This study has demonstrated the important effect of additives including ZSM-5, MCM-41 and mordenite for FCC catalyst to enhance light olefins production. Using Tehran refinery light fuel oil and a USY equilibrium cracking catalyst, propylene yield increased from 21.53 wt.% over E-Cat (base catalyst) to 29.63 wt.% over mordenite and to 27.64 and 27.87 wt.% over ZSM-5(50) and ZSM-5(300), respectively. The maximum propylene yield of 32.52 wt.% was obtained using MCM-41 as additive. The highest propylene to ethylene ratio of 2.33 generated via applying mordenite as additive. ZSM-5(50) could be regarded as the most efficient additive in production of light olefins (C_2-C_4) by producing total olefins yield of 71.54 wt.%. ZSM-5 of higher Si/Al ratio induced thermal cracking in the reactor and increases the dry gas content, resulted in lower olefin production. Among butenes, isobutene created as the main product in all catalyst compositions.

Acknowledgement

Fig. 5. Variation of total olefins yield obtained by different catalysts.

Fig. 6. Propylene yield obtained over different catalysts.
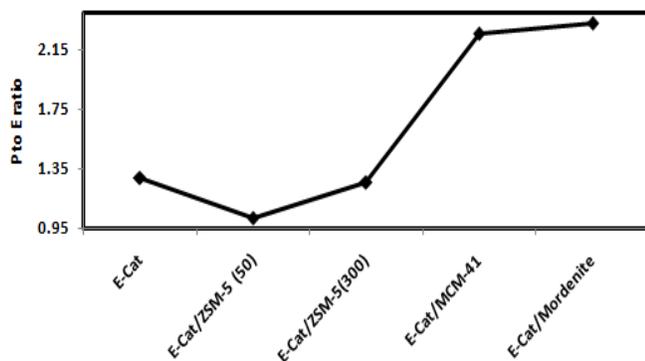
Fig. 7. Effect of catalyst composition on propylene to ethylene (P/E) ratio.
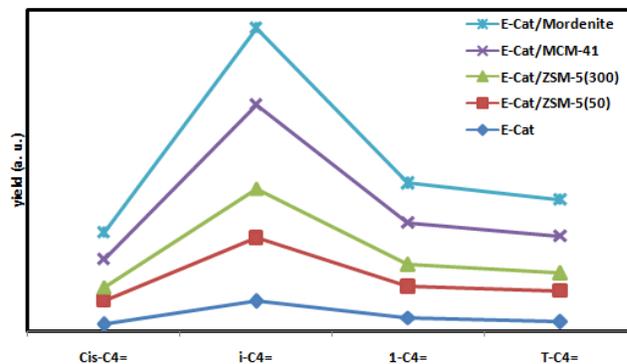

Fig. 8. Comparison of four butenes produced by different catalysts.

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