CRACKING OF MIXED C4s TO PROPYLENE AND ETHYLENE OVER MODIFIED ZSM-5 CATALYSTS

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ABSTRACT

Catalytic cracking of mixed C4s to propylene and ethylene was investigated over ZSM-5 with different acidity, crystallite size, modification technique and various feed composition in a continuous fixed-bed reactor. It was found that the acidity of zeolites plays important role in the catalytic activity and stability. In high acidity ZSM-5 catalysts, the high activity but low stability were obtained. Deactivation is ascribed to a consecutive reaction of hydrogen transfer and oligomerization. While, the ZSM-5 with low acidity exhibits good stability. Moreover, the crystallite size of zeolite was markedly influenced the stability of catalysts. The high stability of zeolite could be gained on smaller (< 0.5 micrometer) crystallite size. Modification of ZSM-5 possessed low Si/Al ratio by alkaline and alkaline earth ion exchange was remarkable decreased the conversion of mixed C4s. While, platinum impregnated provide a higher activity, as compared to the parent ZSM-5. In the reaction using olefin-rich as feed, it was found a higher conversion over acid catalyst, as compared to that of higher paraffinic hydrocarbons. Moreover, the suppression of hydrogen transfer by reduction acid site and reaction temperature, can enhance the ethylene and propylene selectivity. After the catalyst was regenerated by air, it was found that the higher activity was obtained, as compared to the fresh one, owing to the formation of Lewis acid site.

KEYWORDS: Catalytic cracking, ZSM-5 catalyst, C4 Hydrocarbons

1. INTRODUCTION

The demand of light olefins, especially propylene, are growing rapidly due to important raw materials for polymer and various other petrochemicals [1]. However, traditional process for propylene production cannot provide this growing demand. For instance, co-product propylene production from steam cracker is determined largely by the feeding condition and most of the new steam cracking capacity is based on ethane feed, which produces the low selectivity of propylene [2]. Hence, the development of technology for propylene production was driven by the need for increased volumes of propylene which currently produced as Fluid Catalytic Cracking (FCC) of higher hydrocarbons. However, propylene is obtained with a relatively low yield [3]. New on-purpose propylene technologies are available, such as propane dehydrogenation and metathesis, however such processes have seen only limited applicability due to a high investment [4]. In addition, both technologies require opportunistic feedstock economics. A recently emerging technology involving catalytic cracking of light naphthas to produce propylene can now be considered, particularly the C4 recycle stream which is resistant to steam cracking process.

Several researches have been investigated the technology of catalytic cracking of C4+ olefins [1,3-5]. However, the effect of acidity of the ZSM-5, types of modified ZSM-5, crystallite size and effect of olefinic/paraffinic feed on the performance of mixed C4s cracking, have not been highlighted

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so far. In this research was attempted for selective propylene production from the C4 hydrocarbons consisting of olefinic feeds such as butylenes and paraffinic feeds such as *i*-butane. The olefinics can readily produced carbonaceous materials, i.e., coke, during hydrocarbon conversion reactions. While, the paraffinics are difficultly converted [6].

Fixed-bed reactor was chosen for this study. This is because the process requires the low cost of investment, as compared to the FCC [7]. Therefore, catalyst stability is also focused. Lower deactivation rate of catalyst can be achieved by side reactions limiting such as hydrogen transfer and oligomerization. Consequently, we expected that the selectivity of product is significantly affected by variation of acidity and crystallite size. In addition, effect of feed composition, reaction temperature, regeneration and modification of ZSM-5 catalyst by alkaline and alkaline earth ion exchange or metal loading are also mentioned.

2. MATERIALS AND METHODS

2.1 Catalysts preparation

Various types of HZSM-5 were commercially obtained from several suppliers. Specifications of the obtained catalysts were shown in Table 1. The modified ZSM-5, by ion exchange which applied from Subhash [8], were prepared by exchanged HZSM-5 with NaCl, KCl, and $CaCl_2$ (aq) followed by activating in air 550 °C for 4 hours. These catalysts will be referred to as NaZSM-5, KZSM-5, and CaZSM-5, respectively. Metal incorporated zeolite namely [Pt]HZSM-5 was prepared by impregnation of $(NH_4)_2[PtCl_4]$ (aq) which also applied from Subhash [8]. After impregnation, [Pt]HZSM-5 was activated by air, nitrogen and followed with hydrogen at 300 °C for 4 hours.

2.2 Catalysts characterization

SEM technique was used to determine shape and size of the crystal. XRD of the catalysts which confirmed MFI structure, were detected at 2-theta angle range of 5 to 60. Moreover, XRF was used to investigate elemental composition. ^1H MAS NMR spectra were recorded at 300 MHz on a Bruker spectrometer with 5 mm ZrO_2 rotor using spin echo pulsed sequence for acidity measurement. All catalysts reveal signals for Brønsted acid site (3.9 ppm) and silanol (1.7 ppm). Gas adsorption analyzer was investigated surface area (BET method). Zeolite characteristics are shown in Table 1.

2.3 Catalytic testing

Catalytic reaction were performed by feeding mixed C4s gas regulated by mass flow controller. 30 mL/minute of mixed C4s gas (Feed 1 and Feed 2 composition were shown in Table 2.) was passed through a catalyst bed set in a catalytic reactor, which is located inside a temperature-regulated furnace. The gaseous mixture flowing out of the reactor was passed through a gas sampling loop and detected with on-line GC equipped with FID.

The preferred reaction conditions used in the experiments [9] were as follows: temperature 500-600 °C; total pressure = 1 atm; catalyst weight = 0.15 g (W/F = 1.3 g hr/mol).

3. RESULTS AND DISCUSSION

3.1 Influence of Si/Al ratio

The characteristic of various zeolites were shown in Table 1.

Table 1. Zeolite characteristic with various Si/Al ratio.

Type of catalyst	Si/Al ratio	Crystallite size (micrometers)	Surface area (m^2/g)
HZSM-5(1)	25	0.1	502
HZSM-5(2)	28	1.0	545
HZSM-5(3)	122	3.0	457
HZSM-5(4)	165	0.4	439
HZSM-5(5)	188	2.0	496
HZSM-5(6)	314	2.0	456

Table 2. Feed composition of mixed C4s.

Feed composition	Feed 1	Feed 2
Butane	15.46	46.17
Butene	84.54	53.83

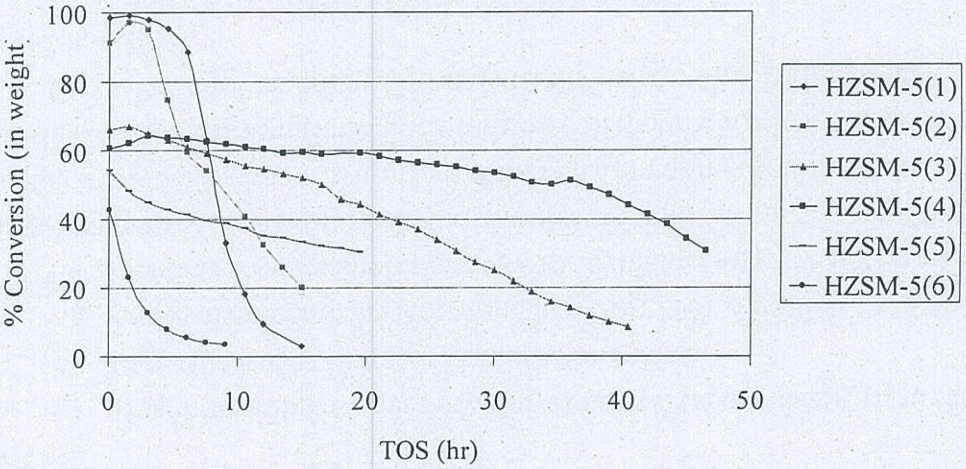


Fig.1 Stability of zeolite ZSM-5 with various Si/Al ratio using Feed 1.
(Catalyst = 0.15 g, Feed flow rate = 30 mL/min, Temperature = 600 °C)

Table 3. % Conversion and selectivity of Feed 1 cracking over various type of HZSM-5.

	Type of HZSM-5					
	(1)	(2)	(3)	(4)	(5)	(6)
% Conversion						
5 min	98.62	91.13	65.93	60.71	54.45	42.97
3 hr	97.89	95.03	64.75	64.32	44.98	12.85
15 hr	2.88	19.99	52.00	59.47	33.30	0.00
% Selectivity*						
Ethylene	0.79	1.75	18.12	16.00	13.72	4.56
Propylene	1.24	3.00	36.88	37.63	58.47	48.81
Yield ratio*						
Propylene/Ethylene	1.57	1.72	2.04	2.35	4.26	10.69
Ethylene/Ethane	3.10	5.07	13.92	15.81	20.00	4.91
Propylene/Propane	1.25	1.91	4.51	7.40	25.85	51.46

*At 3 hours time on stream, (Catalyst = 0.15 g, Feed flow rate = 30 mL/min, Temperature = 600 °C)

Mixed C4s cracking to ethylene, and propylene is a complicated reaction. The sequential conversion of cracked products to paraffins, aromatics, naphthenes and higher olefins, is well known from hydrocarbon chemistry over acid catalysts [6]. These reactions proceed via classical carbocation mechanisms with concurrent hydrogen transfer. The product namely, methane, ethane, propane, and higher hydrocarbon are also formed in the catalytic reaction. The main reaction involved in the mixed C4s cracking was shown in Scheme I.

$$C4^{=}\text{ (or }C4^{\circ}) \longrightarrow [C8]^{+} \longrightarrow C3^{=} + C2^{=} \quad (1)$$
$$C4^{=}\text{ (or }C4^{\circ}) \longrightarrow C3^{=} + C5^{\circ} \quad (2)$$
$$C4^{=}\text{ (or }C4^{\circ}) \longrightarrow [C5]^{+} \longrightarrow \text{Aromatics} \quad (3)$$
$$C3^{=}\text{ (or }C2^{=}) \longrightarrow C3^{\circ}\text{ (or }C2^{\circ}) \quad (4)$$
$$C3^{=}\text{ (or }C4^{=}) \longrightarrow \text{Aromatics} \quad (5)$$

Scheme I. The main reaction involved in the mixed C4s cracking ($Cn^{=}$ represents olefin hydrocarbon, Cn° represents paraffin hydrocarbons)

From the Fig. 1, this indicates that the active acid site is significant for catalytic cracking process, determining both catalytic activity and stability. It can be seen that, initial conversion of mixed C4s cracking is proportional to number of acid site in the catalyst. HZSM-5(1) and HZSM-5(2) possessed low Si/Al ratio and hence high acidity, providing a high activity for Feed 1. However, this leads to the rapidly deactivation after 1-3 hours time on stream (Table 3). This is ascribed that by the side reaction, such as oligomerization, was also promoted. Over such catalytic system, the high molecular weight products were typically formed and blocked the pore-entrance of the zeolite leading to a reduced conversion, as observed from HZSM-5(1) and HZSM-5(2). On the other hand, lower activity of Feed 1 cracking was obtained from the reaction using zeolite ZSM-5 with higher Si/Al ratio, as catalyst. However, higher stability was observed over 24 hours time on stream except, that from the reaction using HZSM-5(6), as catalyst. This is because HZSM-5(6) possesses a very high Si/Al ratio, where small amounts of active sites are present. With difficulty in diffusion due to its large crystallite size, a rapid loss of activity is expected over this catalyst. From the above results, it is found that HZSM-5 with Si/Al ~ 122-188 (HZSM-5(3), HZSM-5(4) and HZSM-5(5)) are an appropriate catalyst for this reaction providing the suitable activity and stability.

It is well recognized that an enhancement of catalytic activity can be observed for high acidity zeolite. However, the yield of ethylene and propylene over high acidity zeolite of HZSM-5(1) and HZSM-5(2) was found to be lower than that obtained from the low acidity zeolites. Hydrogen transfer between reactant paraffin and carbenium ion occurs easily over high acidity zeolite producing more paraffin fraction. While, the yield of olefin was observed over lower acidity zeolites. From the above results, it can be deduced that the suppression of hydrogen transfer and side reaction can enhance selectivity of ethylene and propylene.

3.2 Influence of crystallite size

When we compare the activity of HZSM-5(4) and HZSM-5(5), it was found that the activity of HZSM-5(5) was dramatically dropped. Although, both of them possess the same Si/Al ratio. This is can be ascribed by the difference of crystallite size (Fig. 2). The large crystallite size does not only inhibit the diffusion of reactant into the active site, but also the diffusion of product out of the catalyst pore. This leads to the consecutive side reaction and formation of coke deposits. Therefore, a relatively rapid deactivation is observed over HZSM-5(5), as compared to HZSM-5(4).

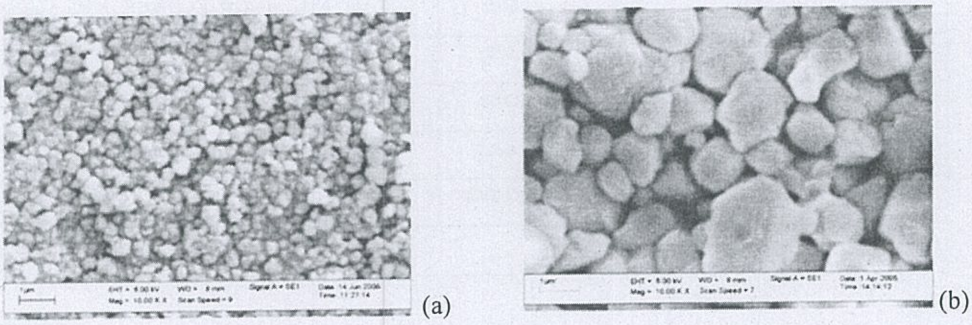


Fig. 2 SEM micrograph of a) HZSM-5(4) and b) HZSM-5 (5)

From the above results, it can be concluded that the conversion of mixed C4s in this catalytic cracking process is governed by both the catalyst acidity and the crystallite size.

3.3 Modification techniques

In order to improve the yield of olefin products in the cracking of olefin-rich feed (Feed 1), it is important to suppress hydrogen transfer which often take place over catalysts with high site density. We expected that the alkaline or alkaline earth exchanged zeolite can reduce the active acid sites which would pronounce high selectivity of light olefins. Hence, ZSM-5(2) was chosen to study the effect of acid site reduction.

The catalytic conversion and product distribution of modified zeolite were shown in Table 4. From the Table 4, it can be seen that the conversion over the catalysts is in the order of NaZSM-5(2) (100 % Na exchange) < KZSM-5(2) (75 % K exchange) < CaZSM-5(2) (11 % Ca exchange) < HZSM-5(2), agreeing with the dependence of number acid sites on catalytic activity. However, ethylene and propylene selectivity is increased when the acid amount was reduced. This is clearly explained by the reduction of side reaction. Although, the selectivity of ethylene and propylene were obtained from the alkaline and alkaline earth exchanged zeolite, the conversion of these modified catalyst were exceedingly low. Therefore, these modified zeolites shall not be used in this process.

In the case of incorporated metal, ([Pt]HZSM-5(2)) (2.0 % Pt loading), a similar activity as HZSM-5(2) is observed. However, it was found that yield of ethylene and propylene is relatively lower, while higher yield of higher hydrocarbons was obtained (Table 4). This is clearly because the side reaction (oligomerization, reforming, and aromatization) is likely to be promoted over acid sites associated with the metal loaded. In particular, dehydrogenation is largely enhanced over this bifunctional catalyst. It has been well-accepted that using Pt loading catalyst leads to a high activity for conversion of olefin-rich feed. However, this catalyst selectively promoted formation of higher molecular weight hydrocarbons which increase the deactivation rate of the catalyst.

Table 4. % Conversion and product distribution of Feed 1 cracking over modified ZSM-5(2)

% Weight of hydrocarbon	Type of active sites				
	H	Na	K	Ca	Pt/H
% Conversion	95.03	1.23	8.52	89.01	96.03
Methane	0.24	0.22	0.32	0.46	0.21
Ethane	0.33	0.00	0.08	0.43	0.32
Propane	1.49	0.00	0.05	1.80	1.42
Ethylene	1.66	0.13	0.32	3.33	1.47
Propylene	2.85	0.59	3.87	6.49	2.37
Unconverted feed	4.97	98.77	91.48	10.99	3.97
C5+	88.46	0.30	3.88	76.52	90.23
% Selectivity of ethylene	1.75	10.58	3.80	3.74	1.53
% Selectivity of propylene	3.00	47.69	45.44	7.29	2.47

(Catalyst = 0.15 g, Feed flow rate = 30 mL/min, Temperature = 600 °C
Product at 3 hours time on stream)

From the above results, HZSM-5(4) is an appropriate catalyst for catalytic cracking. This is because it possesses the lower acidity (Si/Al = 165), and small crystallite size (0.4 micrometers). This provides the good catalytic activity and stability for continuous fixed bed reactor which requires a long life time catalyst. Therefore this catalyst was chosen to test the effect of feed composition.

3.4 Influence of feed composition

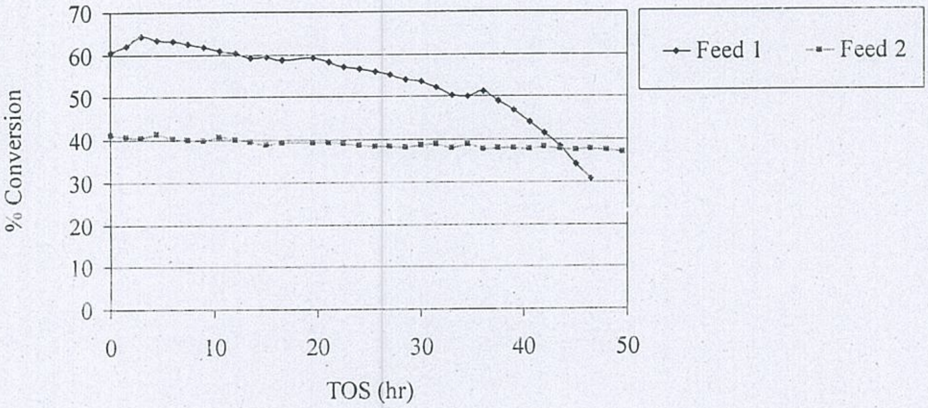
From the Fig. 3, the conversion of Feed 2 over HZSM-5(4) is lower than the reaction using Feed 1 as feed. However, the stability of the reaction using Feed 2 is higher than that of Feed 1.

This is clearly because Feed 2 is composed of large amounts of inert C4s such as *i*-butane and *n*-butane, while the major composition of Feed 1 is an easily converted of C4 olefins (Table 2). Therefore, the olefin-rich feed can be easily converted leading to higher activity for high molecular weight hydrocarbons formation, as compared to the paraffinic nature of Feed 2. When the higher hydrocarbon is formed, the catalytic activity is also dropped.

Regarding to the ethylene and propylene selectivity over HZSM-5(4) catalyst (Fig. 3), it was observed that ethylene and propylene selectivity obtained the reaction using Feed 2 is higher than the reaction using Feed 1 as feed. This is clearly because the olefinic feed which contained in the Feed 1, can facilitate the side reaction. Therefore, non-selective products other than ethylene and propylene were obtained.

3.5 Effect of reaction temperature over HZSM-5(4)

From the above results, we expected that a reduction of temperature can suppress the hydrogen transfer which is thermodynamically favored at high temperature. Decrease in reaction temperature may well increase the olefin/paraffin ratio. From the Table 5, it was found that a lower temperature provides the lower conversion of Feed 2, as compared to that at high reaction temperature. Since cracking is endothermic, the reaction prefers the high reaction temperature. Therefore, at 600 °C higher conversion of C4s can be promoted. As expected, the high selectivity of olefin/paraffin ratio were obtained at lower temperature (500 °C). This is consistent with the above suggestion that at lower temperature, hydrogen transfer was suppressed leading to an increased olefin/paraffin ratio. This is further evidence supporting the fact that the suppression of hydrogen transfer can enhance the ethylene/ethane and propylene/propane ratio, as observed in the reaction using alkaline and alkaline earth exchanged zeolite.



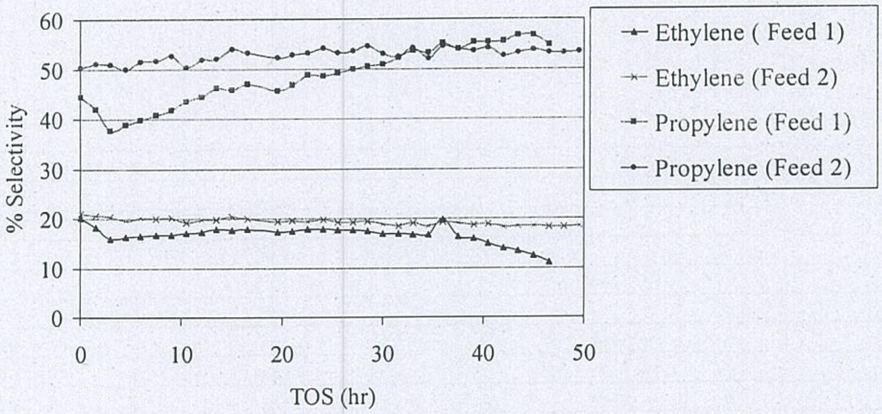


Fig.3 Stability of zeolite HZSM-5(4) with variation of feed composition (Catalyst = 0.15 g, Feed flow rate = 30 mL/min, Temperature = 600 °C)

The conversion and product distribution of HZSM-5(4) at the various temperature were shown in Table 5.

Table 5. % Conversion and product distribution of Feed 2 cracking over HZSM-5(4)

% Weight of Hydrocarbon	HZSM-5(4) 500 °C	HZSM-5(4) 550 °C	HZSM-5(4) 600 °C	re-HZSM-5(4) 550 °C
Methane	0.07	0.39	0.90	0.32
Ethane	0.06	0.20	0.49	0.19
Ethylene	3.59	6.30	8.28	6.63
Propane	2.38	2.94	3.42	3.56
Propylene	18.28	19.71	20.64	21.94
Unconverted feed	66.09	63.43	59.50	59.82
C5+	9.53	7.04	6.78	7.55
% Conversion	33.91	36.57	40.50	40.18
% S of ethylene	10.58	17.22	20.43	16.51
% S of propylene	53.91	53.88	50.96	54.59
Propylene/Ethylene	5.10	3.13	2.49	3.31
Ethylene/Ethane	55.45	31.29	16.93	35.40
Propylene/Propane	7.70	6.71	6.04	6.17

(Catalyst = 0.15 g, Feed flow rate = 30 mL/min, Temperature = 500-600 °C, Product at 3 hours time on stream), S = Selectivity

3.6 Effect of regeneration

From the above results, we choose the reaction at 550 °C for regeneration study. After 300 hours time on stream, HZSM-5(4) catalyst was cooled down and activated in air for 4 hours. The results of this reaction over regenerated catalyst (re-HZSM-5(4)) were shown in Table 5. It was found that the activity of the re-HZSM-5(4) is higher than the fresh one. However, the selectivity of ethylene and propylene were slightly changed. The higher conversion obtained over re-HZSM-5(4) can be explained by the synergistic effect between of Brønsted acid and Lewis acid site [10]. The water produced from the combustion of coke during the regeneration, can drive off the aluminum framework and coordinatively unsaturated aluminum species can be formed in the catalyst's pores. This produces strong Lewis acid site, which enhance the conversion. An enhancement of catalytic activity can be typically observed for dealuminated zeolite under mild conditions.

4. CONCLUSIONS

The acidity of zeolite plays important roles in catalytic activity and stability. This is observed that the high acidity (low Si/Al ratio) catalyst can enhance the catalytic cracking and also side reaction such as hydrogen transfer. This allows the formation of high molecular weight hydrocarbons leading to low stability of the catalyst. On the other hand, the high selectivity of ethylene and propylene were obtained over the low acidity (high Si/Al ratio) catalyst. In this research, it was found that the zeolite possessed Si/Al = 165 provides the good activity and stability. In addition, the small crystallite size may also gain catalyst stability of catalyst by facilitated diffusion and hence, reduction of coke deposits. With various modification technique, the low activity of Feed 1 cracking was observed over the alkaline or alkaline earth exchanged zeolite ZSM-5(2). However, these exchanged zeolites can increase the selectivity of ethylene and propylene owing to the suppression of hydrogen transfer. While, incorporated platinum over HZSM-5(2) catalyst in the reaction using Feed 1 as feed, provides a high activity and consequently, high deactivation rate, due to the formation of high molecular weight product. In the effect of feed composition, catalytic cracking over Feed 1 which is rich in olefinic C4 hydrocarbons leads to a high deactivation rate, as compared to that over Feed 2 which contained number of paraffinic C4 hydrocarbons. Moreover, in the reaction at low temperature, the hydrogen transfer was suppressed leading to the increase olefin/paraffin ratio. The catalyst can be regenerated and then reused without lost of activity.

5. ACKNOWLEDGEMENTS

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