ISSN 0965-5441, Petroleum Chemistry, 2018, Vol. 58, No. 5, pp. 457–463. © Pleiades Publishing, Ltd., 2018.
Published in Russian in Neftekhimiya, 2018, Vol. 58, No. 3.

Catalytic Cracking of *n*-Hexane and *n*-Heptane over ZSM-5 Zeolite: Influence of SiO_2/Al_2O_3 Ratio[1]

N. Afroukhteh-Langaroudi[a, *#], **S. Tarighi**[b, *#], **and H. A. Khonakdar**[a]

[a] *Department of Chemical Engineering, Faculty of Engineering, Central Tehran Branch, Islamic Azad University, P.O. Box, Tehran, 19585-466 Iran*
[b] *Faculty of Petrochemicals, Iran Polymer and Petrochemical Institute, Tehran, Iran*
**e-mail: s.tarighi@ippi.ac.ir*

Received March 15, 2017

Abstract—The performance of two types of ZSM-5 zeolite catalysts (MFI-type zeolite, SiO_2/Al_2O_3 = 50 and 300) was studied in the catalytic cracking of *n*-hexane and *n*-heptane as a model compound of light naphtha for production of light olefins at 500, 550, and 600°C. The physicochemical properties of ZSM-5 catalysts were characterized by means of XRD, BET, SEM and NH3-TPD. The influence of SiO_2/Al_2O_3 molar ratio was investigated on conversion and product selectivity. ZSM-5 zeolite yielded higher conversion in the cracking of *n*-hexane compared to *n*-heptane and maximum conversion was achieved over ZSM-5(50) at 600°C. ZSM-5(50) showed higher alkane selectivity rather than olefins. It was found that ZSM-5(300) was more desirable in terms of having significant selectivity to light olefins as well as producing high propylene to ethylene ratio. The maximum propylene to ethylene ratio of 2.7 and 2.48 was observed over ZSM-5(300) at 500°C for *n*-hexane and *n*-heptane cracking, respectively.

Keywords: catalytic cracking, ZSM-5 zeolite, *n*-alkane, light olefins

DOI: 10.1134/S096554411805002X

INTRODUCTION

Light olefins such as ethylene and propylene are the most important materials in chemical industry [1, 2] that are used as feedstock for polyethylene, resins, polypropylene, ethylene oxide and other materials [3, 4]. The main routes for production of light olefins are thermal and steam cracking, that is energy intensive processes [5] and operate at high temperature [3]. The control of light olefins selectivity in these processes is difficult [4]. Through increasing demand for light olefins every year [6, 7], catalytic cracking has been proposed to obtain these materials under moderate conditions and higher yields [8]. In order to study the reactions related to naphtha cracking and explain the performance of catalyst and reaction mechanism, the catalytic cracking of light alkanes (C_5—C_8) over various zeolites was investigated by several research groups [5, 9]. The catalytic cracking of alkanes has a significant impact in petrochemical industry; because it produces valuable olefins from low cost saturated hydrocarbons [10]. This is one of the most common reactions which are widely used to investigate the zeolite activity [11]. It is accepted that the cracking of alkanes occur via two mechanisms including monomolecular and bimolecular pathways. The first one involves a carbonium ion and the latter includes a carbonium-chain mechanism [4, 11]. Many zeolites have been used for hydrocarbons cracking to the lower molecular weight products, such as light olefins [12]. Among various zeolite catalysts, ZSM-5 (MFI type zeolite) has been recognized as prime candidate for catalytic cracking because of its strong acidity, high thermal and hydrothermal stability and the considerable resistance to deactivation caused by coking during cracking process [13, 14]. ZSM-5 is a synthetic zeolite with high silica content [15]. It has SiO_2/Al_2O_3 ratio from around 20 to almost infinity [16]. Rownaghi et al. [3] studied the catalytic cracking of *n*-hexane over a series of HZSM-5 zeolites with different characteristics.

They observed that the acid site on the external surface effects the olefins production. The HZSM-5 with nano-sized crystals containing less Al on the external surface area showed a better catalytic performance compared to the micro-sized catalyst [3]. Konno et al. [6] investigated ZSM-5 zeolite in catalytic cracking of *n*-hexane. Nano-zeolite crystals exhibited high conversion with stable activity in comparison with the macro-zeolites. It was suggested that the large external surface area and low diffusion resistance of the nano-zeolite reduce the effect of pore plugging due to coke deposition [6]. It is known that acidity of the zeolite is

---

[1] The article is published in the original.
[#] Equally First Authors.

dependent on SiO_2/Al_2O_3 molar ratio. Wang et al. [5] carried out the cracking of *n*-hexane over MCM-22 with various SiO_2/Al_2O_3 molar ratios. They found that the higher propylene selectivity is observed for HMCM-22 with the higher SiO_2/Al_2O_3 molar ratio [5]. Fully literature survey indicates that there is no report comprising investigation and comparison of *n*-hexane and *n*-heptane in various temperatures simultaneously. As at similar work reported by Kubo et al. [17] the catalytic cracking of *n*-heptane have been investigated individually and the relationship between selectivity and reaction temperatures was just investigated for Si/Al = 31 and a comparison of different Si/Al ratios at various temperatures was not investigated [17].

In the present study, the catalytic cracking of both *n*-hexane and *n*-heptane have been investigated simultaneously over two types of ZSM-5 zeolite with SiO_2/Al_2O_3 ratios of 50 and 300 at reaction temperatures 500, 550, and 600°C in a fixed-bed micro-activity test (MAT) unit. Also, the influence of Si/Al ratio on the catalyst performance and products selectivity was fully explained and compared over different reaction temperatures for two zeolites with different Si/Al ratio.

EXPERIMENTAL

Reactant and Materials

n-Heptane (97% purity, Merck) and *n*-hexane (95% purity, Merck) were used as the feedstock without further purification. Two types of Commercial ZSM-5 zeolite with SiO_2/Al_2O_3 molar ratios of 50 and 300 were used as catalysts which were denoted as ZSM-5(50) and ZSM-5(300), respectively. Both zeolites were used as their H-forms.

Instruments

The catalysts were characterized by various techniques. The X-ray diffraction (XRD) patterns of the catalysts were recorded with a SIEMENS D5000 diffractometer using Cu-K_α radiation. The specific surface area were calculated according to Brunnaur-Emmettt-Teller (BET) equation and measured by N_2 adsorption at liquid nitrogen temperature. The Particle size and morphology of the zeolites were investigated by scanning electron microscope (SEM) using a VEGA/TESCAN. The acidity of the catalysts (amount and strength) was determined by the stepwise NH3-Temperature Programmed Desorption (NH3-TPD) technique. The experiments were carried out using a NanoSORD NS91 apparatus. The NH3-TPD experiments were performed on 90 mg of each catalyst placed in a U-shaped quartz reactor. Prior to each TPD run, the catalyst was degassed in a flow of 10 sccm N_2 at 500°C for 2 h, and cooled down to 120°C. This was followed by the adsorption of 5% NH_3/He at 120°C for 30 min, sample were then purged in a He stream for 30 min at 120°C in order to remove loosely bound Ammonia. Then, the sample was heated again from 120 to 900°C at a heating rate of 10°C/min in a flow of He (10 sccm). The gaseous products of the catalytic reaction were analyzed using Agilent Technology 7890 fast RGA GC instrument equipped with FID/TCD detectors. This GC is configured to analyze the refinery gas within 7 minutes. The system has five valves and three detectors. The FID channel is configured to analyze the C_1 to C_5 hydrocarbons, while C_6/C_{6+} components are back flushed and measured as one peak at beginning of analysis. The first TCD channel is configured to analyze fixed gases. Last the second TCD channel is dedicated to analyze hydrogen only. The columns used in this analyzer are Hayesep Q and Molecular sieve (packed column, 1/8 stainless steel) and capillary columns are DB-1 (2 m × 0.32 μm) and HP-Al/S (25 m × 0.32 μm). The inlet column pressure was 14.2 psi and the column temperature increased from 35 to 120°C during the analysis.

Reaction Procedure

The catalytic cracking was performed over ZSM-5 zeolite in MAT unit according to ASTM-D3907. Zeolites were calcined at 550°C in air for about 4 h. Both ZSM-5 zeolites were tested with two feedstocks, *n*-hexane and *n*-heptane. The experiments were carried out under atmospheric pressure in a down-flow fixed-bed reactor with 18 mm inner diameter. The catalyst powder was pressed, pelleted without any binder, crushed and sieved to specific particle sizes. The reactor was tubular made of quartz and was heated in an electric furnace equipped with temperature controllers and thermocouple to monitor the temperature. The catalytic cracking experiments were performed at 500, 550, and 600°C and the time on stream was 70 s. A rotameter and a syringe pump were applied to control the flow rates related to carrier gas and feedstock, respectively. A known amount of catalyst (4.0 g) was loaded in the reactor and activated at 550°C under dry air for 30 min before each run. Before each test, the system was purged for 20 min with a N_2 flow of 50 mL/min at the reaction temperature and then *n*-hexane and *n*-heptane were fed. At the end of the reaction process, stripping of the catalyst was done for 20 min to strip the entrapped hydrocarbons in the catalyst bed. The effluent was cooled in an ice-bath and separated into liquid and gas product. Gaseous products were collected in gas sampling bag and the liquid products were collected in a glass receiver kept in ice-bath. A thorough gas chromatographic analysis of gaseous MAT products was conducted to provide detailed yield patterns and information on the selectivity and conversion of the catalysts being tested.

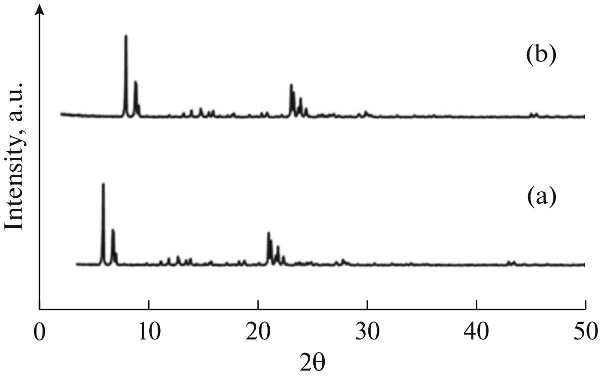

Fig. 1. XRD patterns of (a) ZSM-5(50) and (b) ZSM-5(300).

RESULTS AND DISCUSSION

Catalyst Characterization

The XRD patterns are shown in Fig. 1. From the XRD patterns, it can be seen that the X-ray powder patterns of two zeolites are typical of MFI zeolites and two patterns are in good accordance.

The specific surface area was obtained 269.73 and 339.7 for ZSM-5(50) and ZSM-5(300), respectively. The SEM micrographs of ZSM-5(50) and ZSM-5(300) are showed in Fig. 2.

ZSM-5 zeolites exhibited regular cuboidal morphology with crystal sizes of about 24 μm and 2 μm.

Figure 3 presents the NH3-TPD profiles of ZSM-5(50) and ZSM-5(300). The profiles exhibited two desorption group peaks for both zeolites, one centered in low-temperature region at around 200°C and the other in high temperature region from 400–700°C, corresponding to weak acid sites and the strong acid site, respectively.

The calculated values of both NH_3 adsorbed together with the desorption peak area are reported in Table 1. ZSM-5(50) showed 43 $\mu mol\ g^{-1}$ total acidity, which was higher as compared to ZSM-5(300) with 33.2 $\mu mol\ g^{-1}$ NH_3. The higher total concentration of acidic sites for ZSM-5(50) in terms of desorbed peak area is concluded which is in consistent with the general principles of the relationship between SiO_2/Al_2O_3 ratio in the zeolites and their acidic properties. Increasing Al sites as active acidic sites in zeolites increases the zeolite acidity [18, 19].

Catalytic Cracking

The catalytic performance of two ZSM-5 zeolites were studied in the cracking of light alkanes including *n*-heptane and *n*-hexane in MAT unit according to ASTM-D3907 to produce light olefins at 500, 550, and 600°C. Light olefins includes ethylene, propylene and butenes in which butenes were mainly 1-butene, 2-butene (including trans-2-butene and cis-2-butene) and isobutylene. The catalyst to oil ratio was 3.0 and the time on stream for all cracking tests was 70 sec. The results are shown in Table 2. The reaction performance of the catalysts was evaluated by conversion of *n*-hexane and *n*-heptane as well as the selectivity of the gaseous products. The calculation formulas were as follows:

$$\text{Conversion} = \frac{W_\text{i} - W_\text{o}}{W_\text{i}} \times 100\%,$$

$$\text{Selectivity} = \frac{W_\text{p}}{W_\text{i} - W_\text{o}} \times 100\%.$$

Where W_i represents the weight of feed at the inlet and W_o indicates the weight of unreacted feed at the outlet of the reactor [20]. W_p stands for content of each component in the products. It is worth noting that the

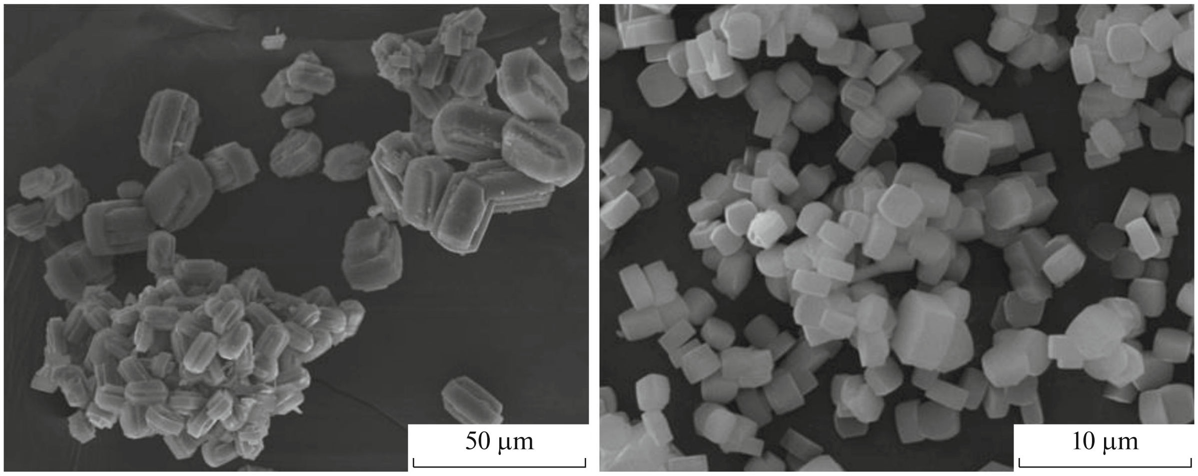

Fig. 2. SEM images of zeolites. ZSM-5(50) (left) and ZSM-5(300) (right).

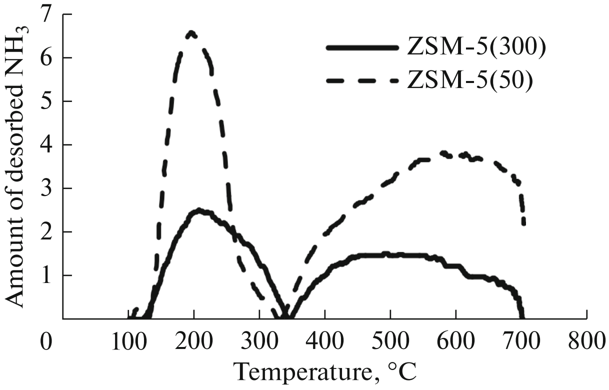

Fig. 3. NH_3-TPD profiles of the ZSM-5 catalysts.

amount of coke formed on the catalyst bed was insignificant, so that there was no significant change in appearance of catalyst.

Table 2 shows that temperature has a significant influence on the behaviour of the catalysts. The conversion of *n*-hexane and *n*-heptane at different reaction temperatures are plotted in Fig. 4 showing an ascending correlation with temperature over either zeolites. Both trend lines have the same slope, yet the conversion values for *n*-hexane are greater than *n*-heptane regardless of SiO_2/Al_2O_3 molar ratio. Despite this similar pattern for both zeolites, ZSM-5(50) yielded greater conversion values independent of feedstock (Fig. 4). The slope of the trend line between 550 to 600°C in case of ZSM-5(50) was higher than the slope between 500 to 550°C, while for ZSM-5(300) a reverse trend was observed. In general, catalytic cracking occurs at the acidic sites of zeolites and the conversion depends on the acidity of the catalyst [21]. On the other hand, acidic property of the zeolites highly depends on SiO_2/Al_2O_3 molar ratio [5, 18]. The higher the Al content, the more acid sites become available on the zeolite [19]. Therefore, lower conversion values in case of ZSM-5(300) were expected. Overall, maximum conversion of 93.84 and 88.93 was achieved over ZSM-5(50) at 600°C for *n*-hexane and *n*-heptane, respectively.

It can be concluded that for both zeolites and both feedstocks, the selectivity of ethylene increased at higher reaction temperatures (Table 2). This can be attributed to the fact that ethylene was formed via primary carbonium ions which requires high activation energy [5]. Higher temperature fulfils the high activation energy requirement.

Table 1. NH_3-TPD results of ZSM-5 zeolites

Catalyst	Desorption peak area	NH_3 (μmol g^{-1}) adsorbed
ZSM-5(300)	5966	33.22
ZSM-5(50)	7723	43.00

The data presented in Table 2 show that the selectivity of ZSM-5 zeolite for propylene production using any SiO_2/Al_2O_3 molar ratio or any type of feed was higher compared to ethylene and butenes. However, ZSM-5(300) showed higher selectivity to propylene compared to ZSM-5(50). Propylene selectivity of about 30 and 28 wt % was obtained over ZSM-5(300) for *n*-hexane and *n*-heptane cracking, respectively. Maximum propylene to ethylene ratio of 2.7 and 2.48 was observed over ZSM-5(300) at 500°C for *n*-hexane and *n*-heptane cracking, respectively.

The distribution of products obtained from cracking of *n*-hexane and *n*-heptane over both ZSM-5 zeolites at different temperatures is plotted in Figs. 5 and 6. As shown in Figs. 5 and 6, the selectivity of ethylene, dry gas and total olefins obeys an ascending trend by increasing the reaction temperature for both zeolites, while selectivity to alkanes decreased at high temperatures. No considerable changes were observed for butenes selectivity at different temperatures. As opposed to other products, propylene follows a different trend over the two ZSM-5 zeolites. Under ZSM-5(50), a linear increase was observed for propylene selectivity correlated with temperature whereas under ZSM-5(300) there is no considerable difference in terms of propylene selectivity at different temperatures for both feedstocks.

The selectivity for alkanes and total olefins are summarized in Table 2. Regardless of feed type, ZSM-5(50) is significantly selective for alkanes while ZSM-5(300) was much more selective for light olefins. This observation may be attributed to the less acidic properties of ZSM-5(300) which reduces H-transfer reactions [5, 18] inhibiting the conversion of olefin products to alkanes leading to olefins selectivity of the catalyst. ZSM-5(50) becomes less selective for alkanes at high temperature leading to maximum alkane selectivity 79.97 and 78.21 at 500°C for *n*-hexane and *n*-heptane cracking, respectively. To further understand, the alkanes to olefins ratios were calculated which was about 4.5, 3, and 2 under ZSM-5(50) for both feedstocks at reaction temperatures 500, 550, and 600°C, respectively while the ratio under ZSM-5(300) is about 1 at all reaction temperatures. The direct relationship between olefins selectivity and conversion of *n*-hexane and *n*-heptane to the products are shown in Fig 7.

As it is shown, the olefins selectivity increased with enhancing the conversion at 500, 550, and 600°C. Therefore, temperature enhancement has desirable influence on ZSM-5 performance at catalytic cracking process. It causes increasing both conversion and olefins selectivity. Consequently, the catalytic cracking process over ZSM-5 at higher temperature is more

Table 2. The conversion and selectivity of ZSM-5 catalysts in *n*-hexane and *n*-heptane carcking

Feed	Catalyst	*T*, °C	Conversion, %	Selectivity, wt %					
				dry gas[a]	ethylene	propylene	butenes	total olefins[b]	total alkanes[c]
Hexane	ZSM-5(50)	500	88.2	3.1	5.5	8.4	3.1	17.0	80.0
		550	88.9	6.1	9.4	10.9	2.7	23.0	70.9
		600	93.8	10.9	14.3	15.4	4.7	34.4	54.5
	ZSM-5(300)	500	42.1	3.0	11.4	31.0	5.3	47.7	47.6
		550	56.7	4.8	15.0	30.3	4.8	50.1	43.6
		600	64.0	6.0	19.5	27.4	4.7	51.6	42.3
Heptane	ZSM-5(50)	500	83.1	1.9	5.5	10.1	4.2	19.8	78.2
		550	84.2	4.4	7.7	11.2	4.1	23.0	72.5
		600	88.9	8.2	9.9	13.7	4.1	27.7	64.1
	ZSM-5(300)	500	32.1	2.1	11.4	28.2	8.3	47.9	50.0
		550	53.9	3.7	18.5	28.1	6.3	52.9	43.4
		600	57.4	4.4	20.4	28.0	7.4	55.8	39.8

[a] Dry gas included hydrogen and methane.

[b] Total olefins included ethylene, propylene and butenes.

[c] Total alkanes included ethane, propane and butane.

advantageous. It should also be noticed that the cracking reaction over ZSM-5(50) is more effective at higher temperature and more reasonable results could be obtained while passing the temperature from 550 to 600°C don't have a significant impact on ZSM-5(300) performance.

CONCLUSIONS

This study examined the catalytic cracking of *n*-hexane and *n*-heptane over two different ZSM-5 zeolites, ZSM-5(50) and ZSM-5(300) using two SiO_2/Al_2O_3 molar ratios, 50 and 300 under atmospheric pressure. The catalysts performance at three different reaction temperatures, 500, 550, and 600°C was evaluated. The data showed that increasing temperature enhances both conversion and olefins selectivity. Among the olefin products, the highest selectivity belonged to propylene while ZSM-5(300) had higher propylene selectivity in comparison with ZSM-5(50). ZSM-5 catalysts with higher Si/Al ratio showed higher propylene selectivity in catalytic cracking of *n*-hexane and *n*-heptane. This could be attributed to the lower acid amount which prevents the secondary reaction of pro-

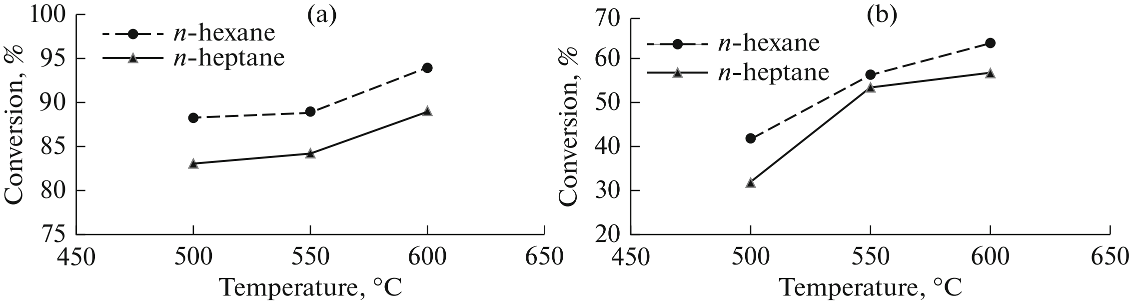

Fig. 4. The conversion of *n*-hexane and *n*-heptane as a function of the reaction temperature over (a) ZSM-5(50) and (b) ZSM-5(300).

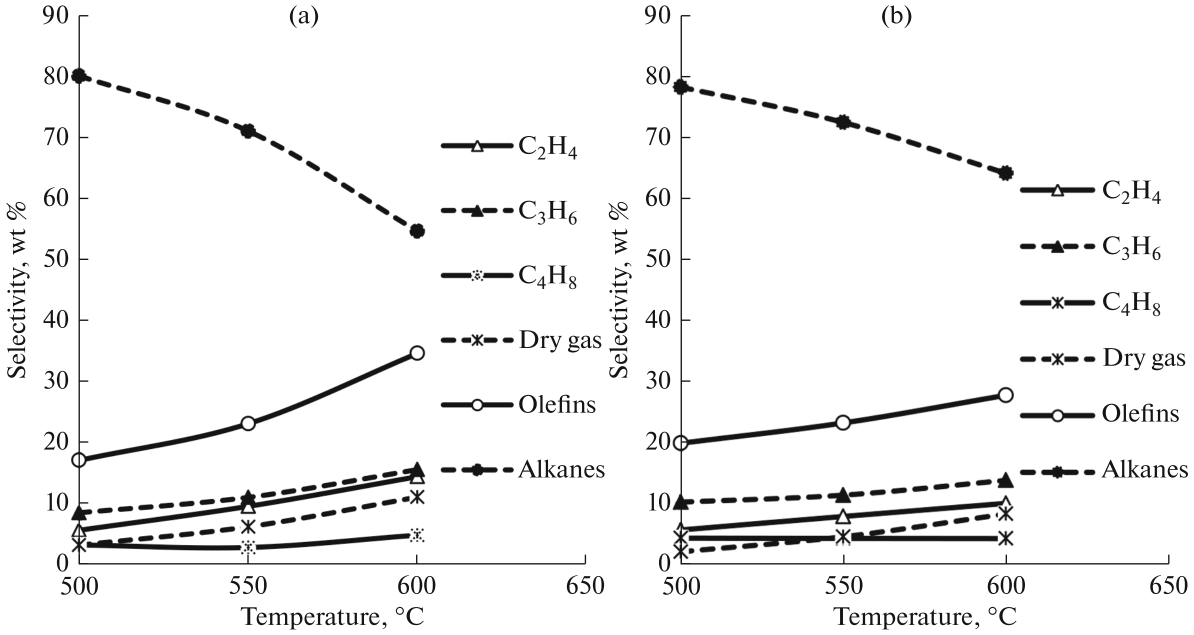

Fig. 5. Products selectivity as a function of temperature over ZSM-5(50) for (a) *n*-hexane and (b) *n*-heptane cracking.

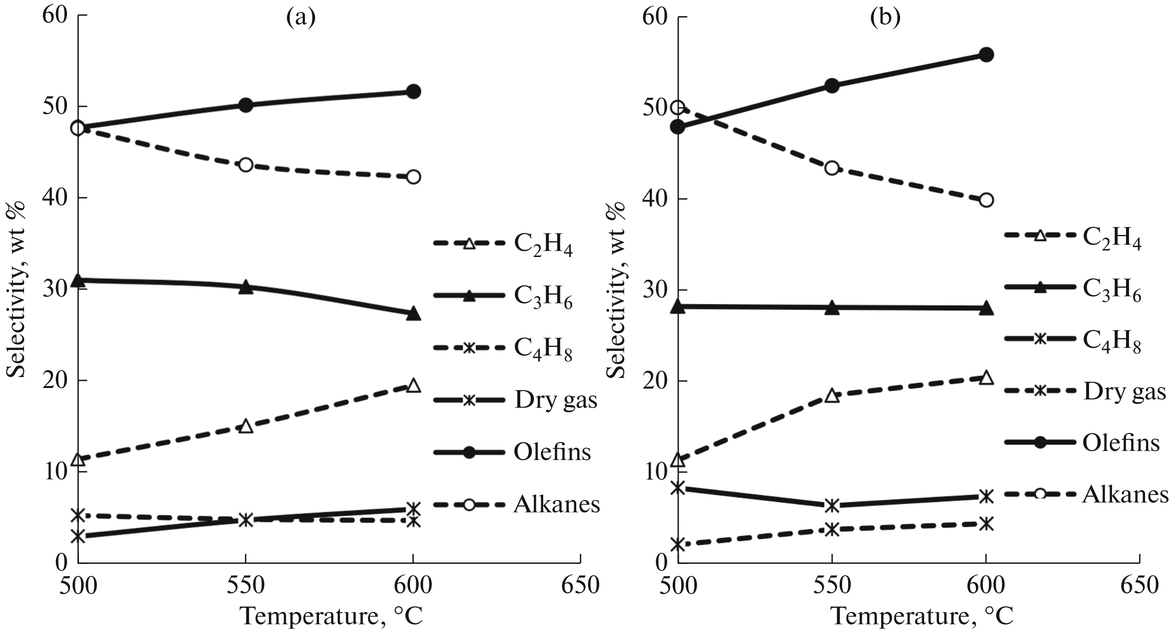

Fig. 6. Products selectivity as a function of temperature over ZSM-5(300) for (a) *n*-hexane and (b) *n*-heptane cracking.

pylene and butenes. The highest propylene to ethylene ratio was observed over ZSM-5(300) at 500°C for both feedstocks. ZSM-5(50) was found to be highly selective for alkane products rather than olefins. ZSM-5(50) resulted in greater conversion values compared to the other catalyst for both feedstocks. Maximum conversion was achieved over ZSM-5(50) at 600°C while highest selectivity to light olefins was obtained over ZSM-5(300). Also, olefins selectivity was directly correlated with the conversion. In conclusion, SiO_2/Al_2O_3 molar ratio and temperature had significant influence on the performance of the catalysts.

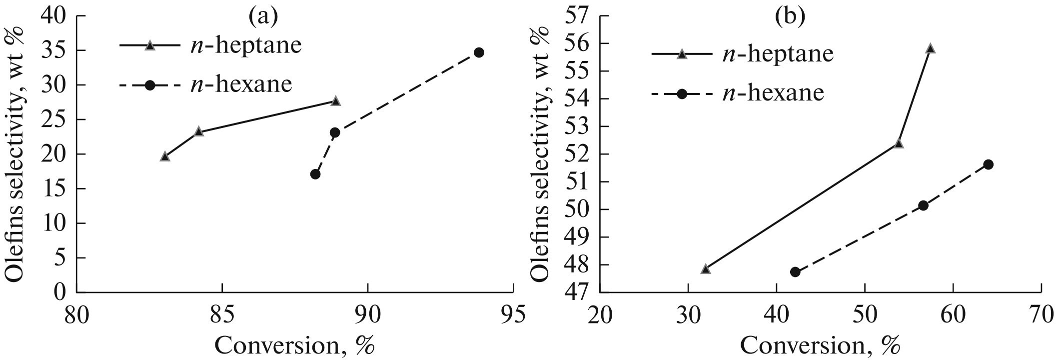

Fig. 7. Total olefins selectivity as a function of conversion over (a) ZSM-5(50) and (b) ZSM-5(300).

ZSM-5(300) under optimized conditions can be introduced as a valuable catalyst for the production of light olefins especially propylene.

ACKNOWLEDGMENTS

The financial support from Iran Polymer and Petrochemical Institute (IPPI) is acknowledged.

REFERENCES

1. K. Urata, S. Furukawa, and T. Komatsu, Appl. Catal., A **475**, 335 (2014).
2. X. Gao, Z. Tang, H. Zhang, D. Ji, G. Lu, Z. Wang, and Z. Tan, J. Mol. Catal. A: Chem. **325**, 36 (2010).
3. A. Rownaghi, F. Rezaei, and J. Hedlund, Chem. Eng. J. **191**, 528 (2012).
4. S. M. Alipour, Chin. J. Catal. **37**, 671 (2016).
5. Y. Wang, T. Yokoi, S. Namba, J. N. Kondo, and T. Tatsumi, Appl. Catal., A **504**, 192 (2015).
6. H. Konno, T. Okamura, T. Kawahara, Y. Nakasaka, T. Tago, and T. Masuda, Chem. Eng. J. **207–208**, 409 (2012).
7. Y.-K. Park, C. W. Lee, N. Y. Kang, W. C. Choi, S. Choi, S. H. Oh, and D. S. Park, Catal. Surv. Asia **14**, 75 (2010).
8. G. Jiang, L. Zhang, Z. Zhao, X. Zhou, A. Duan, C. Xu, and J. Gao, Appl. Catal., A **340**, 176 (2008).
9. Y. Nakasaka, J. Nishimura, T. Tago, and T. Masuda, Chem. Eng. J. **278**, 159 (2015).
10. B. M. Weckhuysen and R. A. Schoonheydt, Catal. Today **51**, 223 (1999).
11. A. Corma, J. Mengual, and P. Miguel, J. Catal. **330**, 520 (2015).
12. A. Janda and A. T. Bell, J. Am. Chem. Soc. (JACS) **135**, 19193 (2013).
13. Y. Wang, T. Yokoi, S. Namba, J. N. Kondo, and T. Tatsumi, J. Catal. **333**, 17 (2016).
14. F. Chen, L. Ma, D. Cheng, and X. Zhan, Catal. Commun. **18**, 110 (2012).
15. R. Sadeghbeigi, *Fluid Catalytic Cracking Handbook, Design, Operation and Troubleshooting of FCC Facilities* (Gulf Professional Publishing, 2000).
16. A. W. Chester and E. G. Derouane, *Zeolite Characterization and Catalysis: A* (Springer, 2009).
17. K. Kubo, H. Iida, S. Namba, and A. Igarashi, Microporous Mesoporous Mater. **149**, 126 (2012).
18. Y. Nakasaka, T. Okamura, H. Konno, T. Tago, and T. Masuda, Microporous Mesoporous Mater. **182**, 244 (2013).
19. D. Bhattacharya, M. Chatterjee, and S. Sivasanker, React. Kinet. Catal. Lett. **60**, 395 (1997).
20. Q. Meng, B. Liu, J. Piao, and Q. Liu, J. Catal. **290**, 55 (2012).
21. N. Rahimi and R. Karimzadeh, Appl. Catal., A **398**, 1 (2011).