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Polyolefins Journal, Vol. 8, No. 2 (2021)
DOI: 10.22063/poj.2021.2852.1176

ORIGINAL PAPER

Dual-templated synthesis of Si-rich [B]-ZSM-5 for high selective light olefins production from methanol

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Received: 20 February 2021, Accepted: 10 April 2021

ABSTRACT

Methanol dehydration is a high potential route for the production of light olefins (C_2-C_4). In this study, hierarchical Si-rich [B]-ZSM-5 catalysts (Si/Al= 200) were prepared through one-pot hydrothermal synthesis, including boron as a promoter and ethanol as a low-cost secondary template. N_2 adsorption-desorption, XRD, FE-SEM, and FT-IR techniques were applied to characterize the catalysts. The effect of different amounts of ethanol and different operating conditions was studied on the ZSM-5 catalyst preparation and performance in methanol-to-olefins (MTO) reaction. The results showed that the optimum amount of ethanol (ethanol/TPABr=5) led to the highest crystallinity (91.2%), the highest specific surface area (>400 m^2g^{-1}), and total pore volume (0.19 cm^3g^{-1}). The best catalytic performance was obtained at temperature of 480°C and methanol hourly space velocity (WHSV) of 7.2 h^{-1}. The optimum catalyst had the highest propylene selectivity (58%) and light olefin selectivity (85%). The results proved the high capability of the new strategy for the efficient and fast development of the MTO catalyst. **Polyolefins J (2021) 8: 93-103**

Keywords: Methanol-to-olefin; ZSM-5; dual template, ethanol, catalyst.

INTRODUCTION

Todays, non-oil techniques have been attracted more attention for light olefins production. Conventional methods for olefin production include steam cracking and fluid catalytic cracking (FCC) [1]. Methanol as renewable feedstock is converted to ethylene and propylene in methanol-to-olefin (MTO) reaction. The catalyst has a decisive role in efficiency of the MTO process [2]. One of the most important aspects of the zeolite catalyst (ZSM-5) is pore diameter, leading to the high catalytic activity and selectivity towards light olefins owing to the low mass transfer resistance and high diffusion rate of the light olefins through the catalyst structure [3]. Template is one of the most important reagents in ZSM-5 synthesis that highly interacts with

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aluminosilicates species, fills channels, and balances the framework charge [4]. TPA+ compounds are the common template, including several drawbacks like high cost and difficult treatment of the ammonium-containing wastewater [5]. In recent years, in addition to the primary template, a secondary template has been utilized for achieving controlled structural properties of ZSM-5 catalyst, including the high specific surface area and formation of mesopores [6, 7]. Different alcohols are proposed as secondary template for the preparation of ZSM-5 catalysts that are economical, easily accessible, and eco-friendly. It is worth noting that ethanol (EtOH) molecules are smaller, less toxic, and neutrally charged compared with tetrapropylammonium cation (TPA+), which can result in significant improvement in physic-chemical properties and catalytic performance of the ZSM-5 catalyst. Zhu et al. [8] applied polyvinyl butyral (PVB) as secondary template for synthesizing mesoporous ZSM-5 zeolite, resulting in ZSM-5 zeolites with high crystallinity and improved surface area. Aziz et al. [9] reported the application of tertiary butyl alcohol (TBA) as secondary template for the low silica ZSM-5 (Si/Al=25) synthesis. They found that TPAOH/TBA ratio of 1.5 led to the high crystalline ZSM-5. Ma et al. [10] studied the role of EtOH as primary template in the synthesis of low silica ZSM-5 (Si/Al<75). They reported the higher activity of the catalysts in the n-hexane cracking compared with the conventional catalyst. Zhang et al. [11] applied EtOH as primary template in the synthesis of ZSM-5 (Si/Al<45). It is accepted that the high adsorption of hydrocarbons on the MTO catalyst surface results in high catalyst activity and more cracking reactions. Sacchetto et al. [12] studied the adsorption of gaseous hydrocarbons on high silica ZSM-5. They found that high Si/Al ratio favored hydrocarbon adsorption on ZSM-5 surface. Furthermore, it is reported that the ZSM-5 with high Si/Al ratio include higher chemical and thermal stability and the more synthesis yield than the Al-rich ZSM-5 [13,14], favoring the economy of the catalyst development for the methanol conversion. On the other hand, promoter is necessary to achieve appropriate acidity properties as well as high catalytic performance. It is accepted that acid sites are responsible for the main and side reactions in the MTO process. Therefore, the well-adjusted acidity and structural properties of the catalyst play a crucial role in developing the improved catalyst for the MTO reaction. The minimizing of the synthesize steps, including post-treatment steps such as addition of a promoter and modification of catalyst structure, leads to the one-pot synthesize of the optimum catalyst as a cost-effective and fast route.

To the best of our knowledge, there is no report on the simultaneous utilization of the promoter and EtOH secondary template in the Si-rich ZSM-5 synthesis for the MTO reaction. In this study, we synthesized the bifunctional and mesoporous [B]-ZSM-5 catalysts (Si/Al=200) using EtOH as secondary template and boron as promoter. The catalysts were applied in the MTO reaction at different operating conditions to obtain the highest selectivity of light olefins.

EXPERIMENTAL

Materials

The precursors for the catalyst preparation were silicic acid (≥99 wt.%), sodium aluminate (55wt.% Al_2O_3), tetrapropyl ammonium bromide (≥99wt.%), ammonium nitrate (99wt.%), sodium hydroxide (99.6wt.%), sulfuric acid (98wt.%), boric acid (H_3BO_3), and ethanol (98wt.%), which were supplied from Merck Company (Germany).

Catalyst preparation

One-pot hydrothermal technique was applied to synthesize of the parent Si-rich [B]-ZSM-5 catalyst. Firstly, $NaAlO_2$, H_3BO_3, and TPABr were dissolved in NaOH solution for 30 min (solution A). Solution B was prepared by adding silicic acid and EtOH to NaOH solution. The solution A was gradually added to the solution B under stirring. After adjusting pH at 10.5 by concentrated sulfuric acid, the solution was stirred for 2h. The molar composition of the starting gel was $20SiO_2$: $0.05Al_2O_3$: 1TPABr: $1.5Na_2O$: $200H_2O$: $0.05B_2O_3$: yEtOH, where y represents the molar ratio of EtOH/TPABr (y= 0, 5, 10, 20, and 40). The crystallization was carried out at 180°C for 48 h in an autoclave. The sample was dried at 110°C for 12 h, followed by calcination at 540°C for 24 h with $3°Cmin^{-1}$ heating rate. In the final step, the catalyst was ion-exchanged with 1M NH_4NO_3 solution for 10 h at 90°C, dried at 110°C for 12 h, and calcined at 550°C for 12h. The parent [B]-ZSM-5 catalyst (Si/Al=200 and y=0) was denoted by ZSM-5 and the modified catalysts were represented by ZSM-5 (y). We tableted the catalysts and then crushed and sieved (16-25 mesh) before the catalytic evaluation in the reactor.

Catalyst characterization

The MTO reaction was carried out in a fixed bed reactor with a 450 mm length and 11 mm inner diameter (Figure. S1). The reactor was connected to a Gas Chromatograph (GC), which contained a flame ionization detector (FID) and HP-plot Q column with 30m length and 0.53 mm inner diameter. The applied catalyst had 16-25 mesh particle size. The reaction was carried out at different temperatures (450, 480, and 500°C) at atmospheric pressure. The feed was a 50/50 wt.% methanol/water solution, which was charged into the reactor with determined weight hourly space velocity (WHSV). The methanol conversion and product selectivity were defined by the following equations:

$$x_{\mathrm{MeOH}} = \frac{N^{i}_{\mathrm{MeOH}} - N^{o}_{\mathrm{MeOH}}}{N^{i}_{\mathrm{MeOH}}} \times 100 \qquad (1)$$

$$S_{C_xH_y} = \frac{x \times N^{o}_{C_xH_y}}{N^{i}_{\mathrm{MeOH}} - N^{o}_{\mathrm{MeOH}}} \times 100 \qquad (2)$$

Where, N is the mole number of components. The superscript i and o stand for components at the inlet and outlet of the reactor, respectively.

RESULTS AND DISCUSSION

Characterization

The XRD patterns of the catalysts are shown in Figure. 1, which are in consistent with the standard pattern of MFI structure (JCPDS NO. 00-042-0023) [15]. The relative crystallinity is determined by the peak intensity at 2θ=23.2° based on the parent catalyst. The results show the highest crystallinity (91.2%) for the ZSM-5(5) among the modified catalysts (Table 1). The high amounts of ethanol dilute the synthesis solution and reduce the rate of both crystallization steps, including nucleation and crystal growth [10]. It is reported that the structure-directing effect of EtOH is weaker than TPABr [10]. The lowest crystallinity (34.8%) is obtained for the ZSM-5(40) sample.

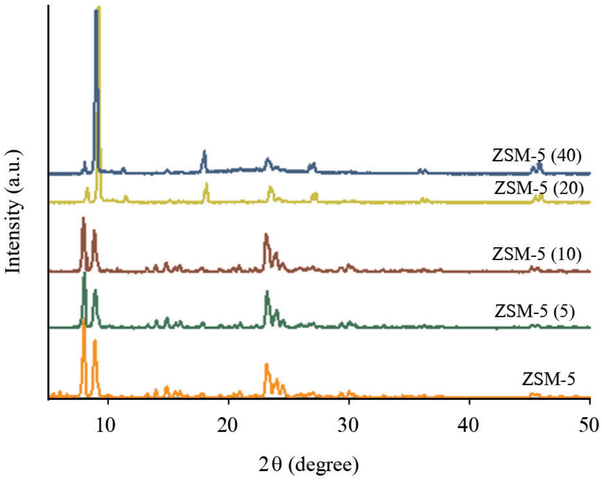


Figure 1. XRD patterns of the catalysts.

Figure. 2 represents FT-IR spectra of the catalysts in the range of 400-4000 cm^{-1}. The peak at 454 cm^{-1} is attributed to the vibration of internal AlO_4 and SiO_4 tetrahedral units [16]. The peak at 549cm^{-1} is assigned to the 5-membered rings. The peak at 795 cm^{-1} is resulted from the external symmetrical stretching vibrations. Anti-symmetrical stretching vibrations of T-O resulted in a peak at 1098 cm^{-1} [17]. The peak at 1232 cm^{-1} is assigned to the anti-symmetrical stretching vibrations of external bonds of TO_4. The weak peak at 2880-2980 cm^{-1} is attributed to the stretching absorption bonds of C-H, confirming the complete calcination procedure and sufficient removal of template molecules from the zeolite structure. Vibration of bonds in Si-OH-Al and Al-OH groups is characterized by the peaks at 3610 cm^{-1} and 3680 cm^{-1}, respectively.

Table 1. Textural data of the catalysts.

Catalyst	Relative crystallinity (%)	S_{BET} (m^2g^{-1})	V_{total} (cm^3g^{-1})	V_{micro} (cm^3g^{-1})	V_{meso} (cm^3g^{-1})
ZSM-5	100.00	321.10	0.15	0.13	0.02
ZSM-5(5)	91.20	404.60	0.19	0.14	0.05
ZSM-5(10)	88.51	419.10	0.20	0.14	0.06

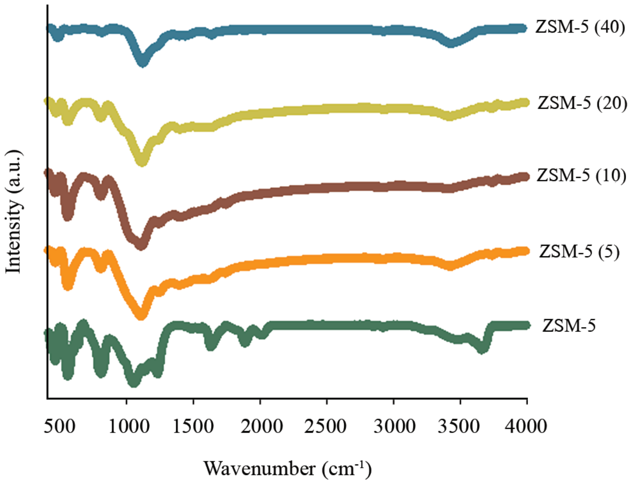


Figure 2. FT-IR spectra of the catalysts.

The peak at 3740 cm^{-1} is attributed to Si-OH groups [18]. The SEM image of the catalysts is represented in Figure. 3. The catalysts have a spherical morphology, and particle size distribution is uniform, including the smooth external surface. The surface morphology of both parent and modified catalysts shows micro-spherical aggregation of individual nanocrystals. According to intra crystal spaces, this type of morphology provides mesoporous structure and eventually improves diffusion of the compounds inside the catalyst structure. It is obvious that the samples with high EtOH/TPABr ratio (>10) include some impurity, which is in line with their low crystallinity and XRD results. Therefore, the ZSM-5(20) and ZSM-5(40) are rolled out for more characterization. N_2 adsorption-desorption isotherm of the catalysts is Langmuir isotherm (type IV) that is attributed to micro and mesopore structures (Figure. 4a). The large adsorption volume at the pressure range of $0.1<P/P0<0.2$ reveals the microporous structure [19]. Furthermore, the increased adsorption at the pressure range of $0.4<P/P0<1$ has resulted from adsorption of nitrogen inside and intra crystalline mesopores due to agglomeration of the nanocrystals. Table 1 shows the textural properties of the catalysts. The data show the high specific surface area for the modified catalysts.

The incorporation of EtOH favors the formation of mesopore structure. According to the reaction between silica and hydroxyl groups, hydroxyl of EtOH disperses homogenously in silica structure. Under hydrothermal synthesis conditions, silica converts into crystalline zeolite and EtOH diffuses into zeolite pores during the crystallization process. EtOH burns at the first step of calcination, leading to the forma-

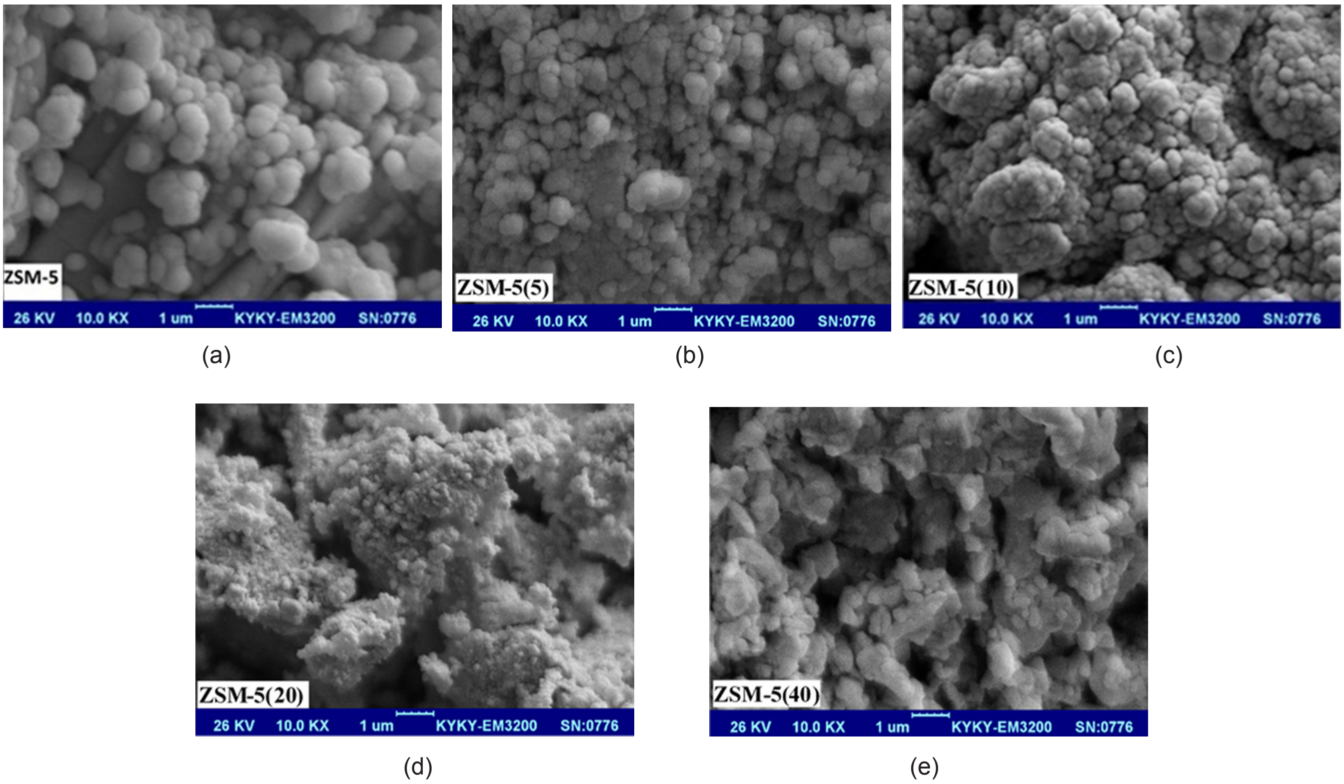
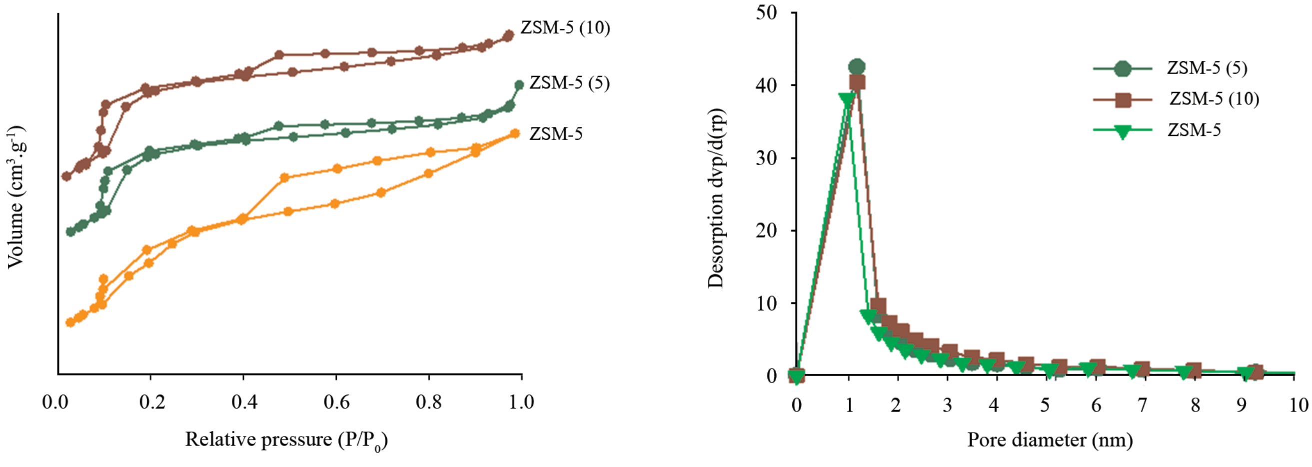


Figure 3. FE-SEM images of the catalysts.



(a) (b)

Figure 4. (a) N_2 adsorption-desorption isotherm and (b) BJH pores size distribution of the catalysts.

tion of mesopores. Furthermore, it is reported that the crystal formation in the ZSM-5 synthesize by EtOH is followed by in situ desilication, which results in generation of mesopores [10]. This phenomenon is quite similar to the alkali-treatment of ZSM-5 zeolite after synthesis, which is a common route to mesopore generation [15].

Figure. 4b shows the BJH pore size distribution of the catalysts. The peak pore size of the modified catalysts (1.21nm) is larger than that of the parent catalyst (1.01nm), favoring the low mass transfer resistance as well as the better catalytic performance.

Catalytic performance

Effect of EtOH/TPABr ratio

The modified catalysts provide higher product selectivity than the parent catalyst (Figure. 5). Sevell et al. [20] explained propylene and ethylene production with two different cycles: i) propylene is produced by methylation of alkenes and cracking cycle ii) ethylene is formed through (poly)methylbenzene methylation and alkylation cycle. The ethylene selectivity follows an increasing trend for all catalysts. After 8 h time on stream, coke content decreases the acidity of the catalyst and inhibits cracking reactions, decreasing the ethylene selectivity (according to dual-cycle mechanism). The lowest ethylene selectivity is obtained for the ZSM-5(10) catalyst (6%).

The propylene selectivity of the ZSM-5(10), ZSM-5(20) and ZSM-5(40) catalysts increases at first, and then decreases gradually. This trend is due to gradual activation of the acid sites during the reaction. According to Figure. 5, the ZSM-5(5) catalyst has the highest propylene selectivity (58%), which is in agreement with its appropriate structural properties. The high specific surface area and pore volume lead to the low diffusion resistance inside the catalyst and so enhance the permeability of the products out of the catalyst's pores [21]. Therefore, the potential of coke formation and side reactions like secondary cracking and hydrogen transfer reactions is reduced.

Zhu et al. [22] reported the application of H-[B]-MFI borosilicate (Si/Al=41) in the MTO reaction. They found that B promoter improved the propylene selectivity owing to the methylation of ethylene with methanol. Furthermore, Wang et al. [23] reported that bulkier methyl benzenes (tetraMB and pentaMB) and light methyl benzenes (p/m - diMB) improved the propylene and ethylene formation, respectively. The less adsorption of light MBs (due to mesoporous structure) increases the propylene formation because light MBs diffuse out of zeolite channel quickly and bulkier MBs remain longer in the catalyst.

It is clear that the ZSM-5(5) catalyst has superior catalytic performance, which provides the total olefin selectivity of 85%. Compared with the other catalysts, the ZSM-5(5) catalyst is more stable through the process, resulting from the high crystallinity and specific surface area. During the process, the acidity of the catalysts is decreased owing to blockage of active sites and pores by coke content. The low acidity prevents hydrogen transfer, alkylation, cyclization and

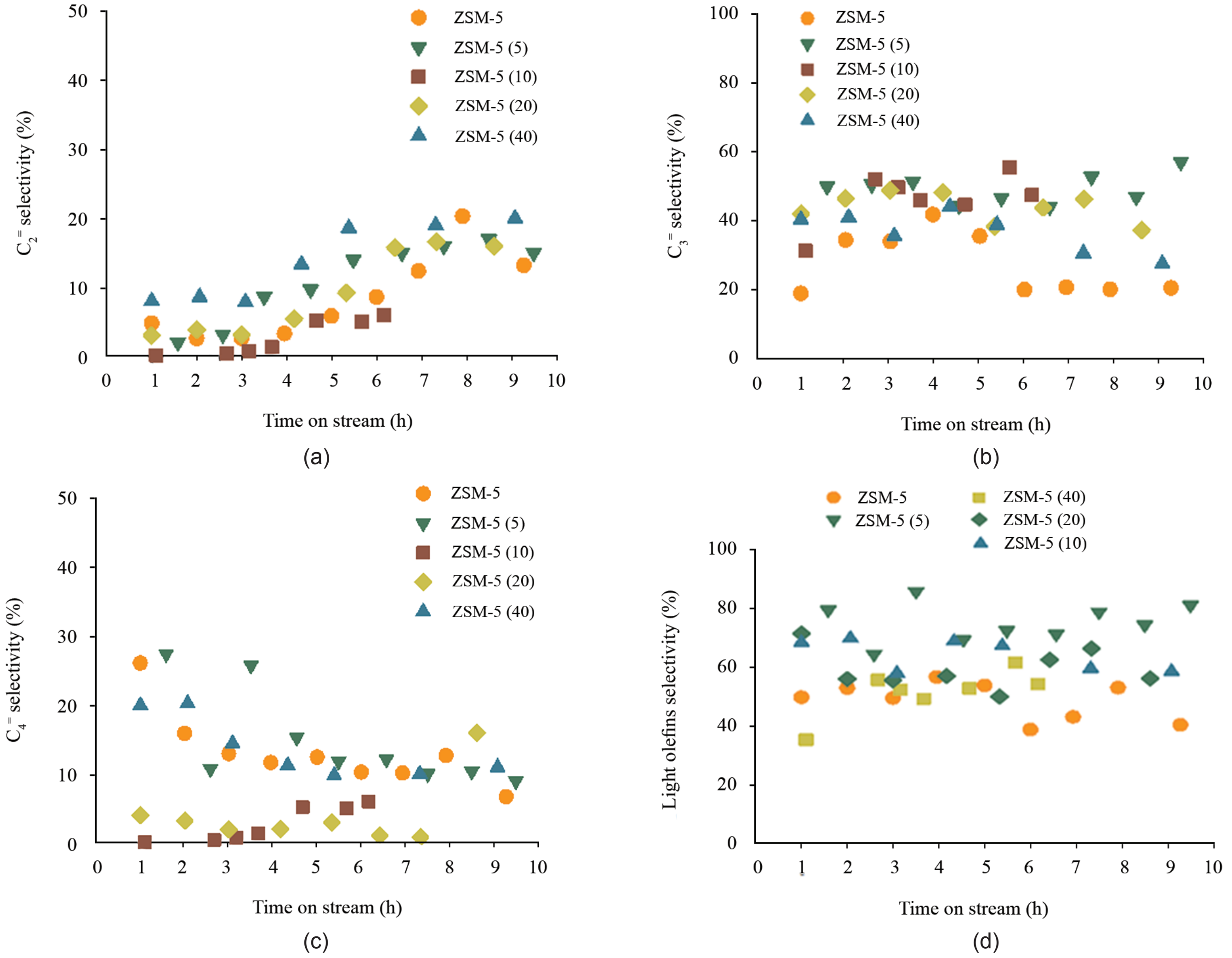


Figure 5. Product distribution variation over the catalysts with different EtOH/TPABr ratios; Reaction conditions: T= 480°C and WHSV=7.2 h^{-1}.

compressive polymerization reactions. Based on the results, the ZSM-5(5) catalyst is selected as optimum catalyst for further investigation.

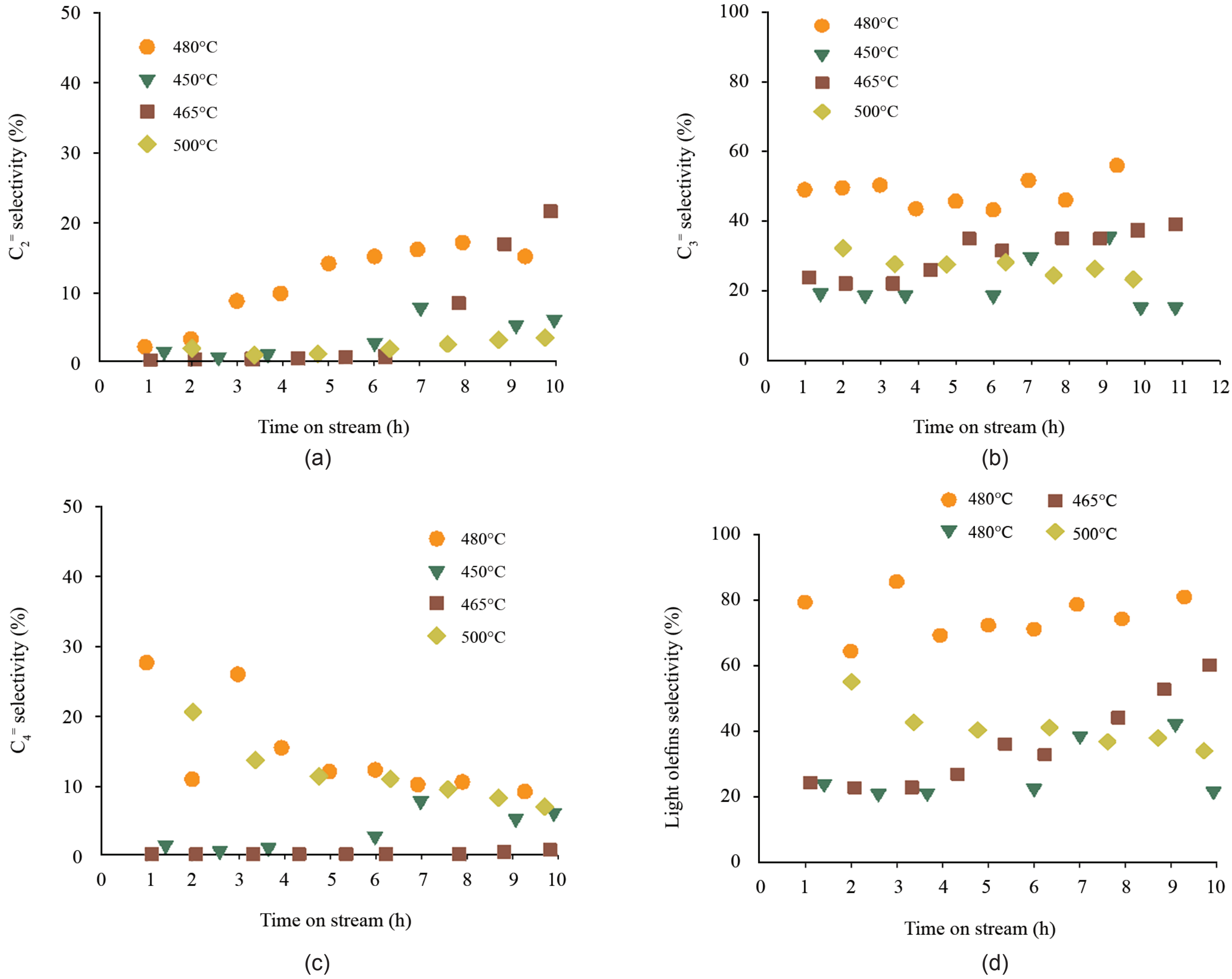
Effect of reaction temperature

Figure. 6 shows effect of reaction temperature on the performance of the ZSM-5(5) catalyst in the range of 450-500°C. The highest propylene selectivity (58%) is obtained at 480°C. At low temperature (450°C), the propylene production rate is slow owing to the low rate of reactions. The higher temperature (500°C) increases the rate of the side reactions such as cracking and decreases the propylene selectivity. Therefore, it is expected that propylene decomposes to the lighter molecules at high temperature. These results are in accordance with the literature [24, 25].

The highest ethylene selectivity (11.2%) is obtained at 480°C. This can be explained by cracking of the heavier molecules such as butylene and enhanced permeation of ethylene molecules out of the pores. By increasing temperature, the butene selectivity first increases and then decreases. This is in agreement with the results of the propylene selectivity at lower temperatures, which cracking reaction rates are low and the higher amount of butene is produced. Also, the highest total olefins selectivity (85%) is achieved at 480°C. Therefore, the optimum MTO reaction temperature over the ZSM-5(5) catalyst is 480°C.

Effect of WHSV

Figure. 7 shows the effect of methanol WHSV on the product distribution over the ZSM-5(5) catalyst. It is clear that high WHSV favors more light olefins production. The highest propylene (58%) and light olefins

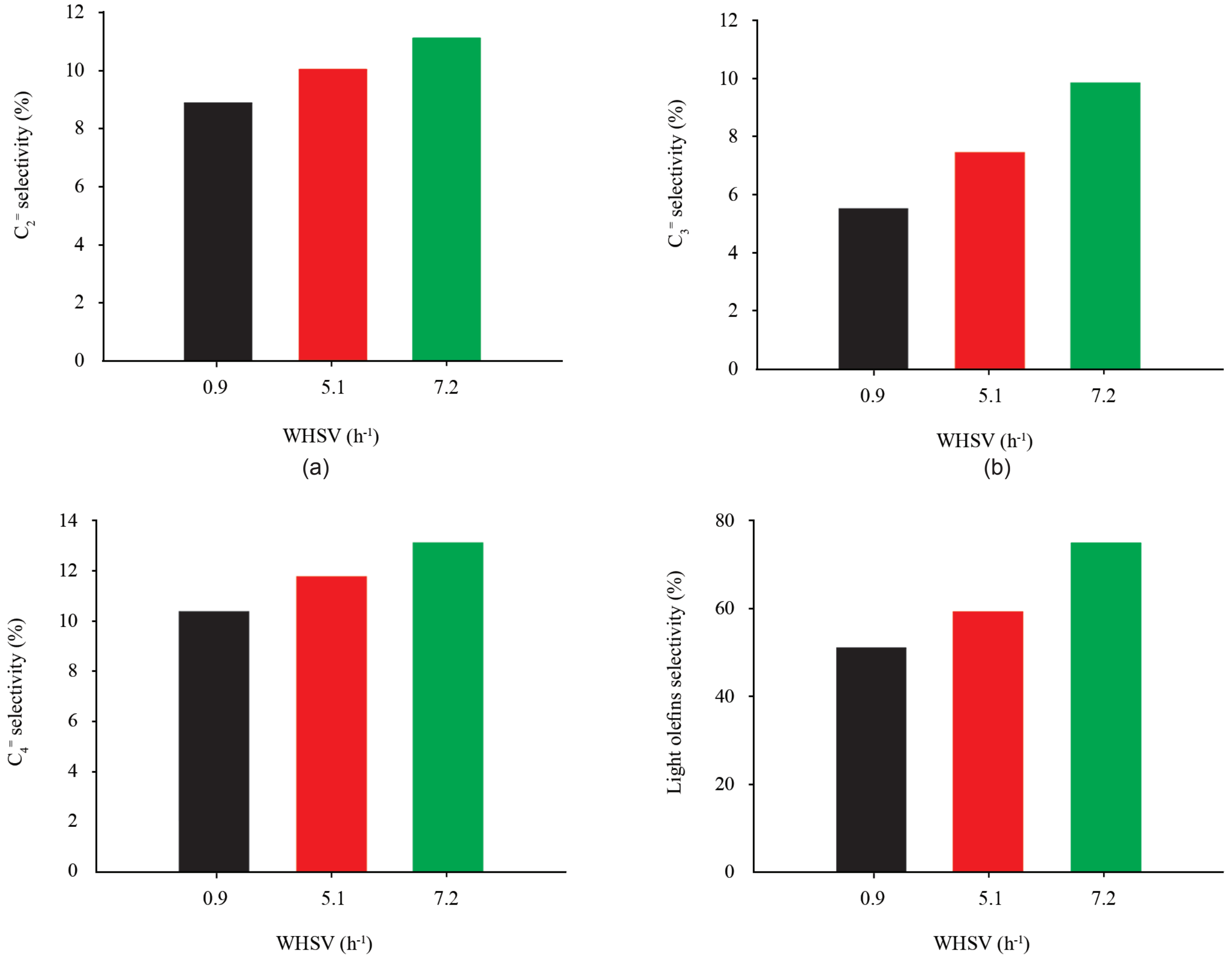


(a) (b) (c) (d)

Figure 6. Product distribution over the ZSM-5(5) catalyst at different temperatures and WHSV of 7.2 h^{-1}.

selectivity (85%) are obtained at WHSV of 7.2 h^{-1}. It is worth noting that increasing WHSV could have dual effect on the MTO reaction. The high WHSV results in more methanol feeding and low conversion. On the other hand, it leads to short residence time in the catalyst bed, reducing the possibility of the side reactions to convert the light olefins. Therefore, the acidity and structural properties of the catalyst significantly influence WHSV effects and the resulted product distribution. The preferred properties, including the high specific surface area and uniform pore size distribution, can compensate negative effects of the reduced feed residence time and increase production rate without methanol conversion drop. The high WHSV over the ZSM-5(5) catalyst bed results in more products without methanol conversion reduction, which can be attributed to appropriate properties of the catalyst. It is accepted that the high WHSV in the MTO reaction can evaluate catalyst resistance towards coke formation and rapid deactivation owing to the high possibility of the side reactions like oligomerization. The catalytic performance of the ZSM-5(5) catalyst shows the high resistance towards coke formation even at the high WHSV. These results are attributed to the high specific surface area, the high pore volume, and mesopore size that lead to the low diffusion resistance and hinder coke formation.

The ethylene selectivity decreases by increasing WHSV due to the cracking of oligomers [26, 27]. Zhu et al. [22] reported the methylation of ethylene with methanol to produce propylene over ZSM-5 catalyst. Their results showed that the weak acidity hindered the formation of ethylene oligomers and the methylation of ethylene with methanol resulted in high pro-



(a) (b)

(c) (d)

Figure 7. Product distribution over the ZSM-5(5) catalyst at different WHSVs and at 480°C.

pylene selectivity. The hydrogen transfer has a significant effect on the product of the MTO reaction [28]. At the low WHSV, the hydrogen transfer reactions are accelerated owing to the long contact time, leading to more conversion of the light olefins. Therefore, there is no time for ethylene and propylene conversion to paraffins and aromatics through the secondary reaction at the high WHSV [26, 27].

Table 2 compares the propylene selectivity of the ZSM-5(5) catalyst and the results reported in literature. As can be seen, the developed catalyst has the high performance, including the fast and one-pot synthesis process. The simultaneous incorporation of EtOH secondary template and B promoter improves the physicchemical properties of the catalyst, suppressing coke formation and the side reactions. Furthermore, EtOH

Table 2. Comparison of the propylene selectivity in literature.

No.	Catalyst	Si/Al	Propylene selectivity (%)	Reference
1	ZSM-5	200	37.35	[29]
2	ZSM-5/SiC	44	44.87	[30]
3	ZSM-5	78	42.03	[31]
4	ZSM-5	175	41.96	[32]
5	ZSM-5	30	44.04	[33]
6	ZSM-5	200	43.56	[5]
7	ZSM-5(5)	200	58.00	This study

template results in the mesopore structure, which reduces the mass transfer resistance and coke formation possibility. In fact, hierarchical ZSM-5 catalyst shifts coke formation from inside of the micropores to the external surface and/or mesopores, increasing the acid sites accessibility as well as the catalyst life time.

CONCLUSIONS

In summary, hierarchical high silica ZSM-5 catalysts were synthesized hydrothermally in one-pot, including different amounts of ethanol as the low-cost second template and boron as a promoter. It was obtained that the EtOH/TPABr molar ratio of 5 was the best, resulting in the optimum textural and acidity properties as well as the catalytic activity in the MTO reaction. The results showed the high surface area, mesoporous structure, high crystallinity, and well-adjusted acidity for the modified catalyst. The optimum operating conditions were 480°C and WHSV of 7.2 h^{-1}, which led to the highest propylene selectivity (58%) and the highest light olefins selectivity (85%) in the MTO reaction. The results confirmed the significant role of ethanol and boron introduction in the MTO catalyst development.

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