Jet fuel range hydrocarbon synthesis through ethylene oligomerization over platelet Ni-AISBA-15 catalyst

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Abstract

Converting ethylene to biojet fuel range hydrocarbons via oligomerization is an important step in biojet production from ethanol. The present study investigates the catalytic ethylene oligomerization over platelet Ni-AISBA-15 mesoporous catalysts. The catalysts are synthesized and characterized using nitrogen adsorption–desorption isotherms, X-ray fluorescence and X-ray diffraction techniques. The catalytic performances are then evaluated in a continuous flow fixed-bed reactor under various conditions of reaction weight hourly space velocities ($0.56\text{--}4.5\text{ h}^{-1}$), temperatures ($150\text{--}350\text{ °C}$) and pressures ($1\text{--}20\text{ bar}$). Experimental results demonstrate that platelet Ni-AISBA-15 is a promising catalyst for the ethylene oligomerization to produce biojet fuel range hydrocarbons. It performs a good catalytic activity, yielding 98–99 mol% ethylene conversion and 34–42 wt% C_{8+} selectivity at 0.56 h^{-1} , $275\text{--}300\text{ °C}$ and 20 bar. The obtained products contain mainly $\text{C}_4\text{--C}_{10}$ olefins with low aromatic compounds. Moreover, the catalyst exhibits good stability of the activity during long periods of operation.

Keywords Ethylene · Oligomerization · Platelet Ni-AISBA-15 · Biojet fuel

1 Introduction

Emissions from both domestic and international global aviation account for approximately 2% of global anthropogenic CO_2 emissions [1, 2]. The prediction estimates that global air transportation demand will be increased approximately 5% per annum over the next several decades, which increasing fuel requirements as well as CO_2 emissions [3]. With the concern on the environmental impacts from the aviation sector, International Air Transportation Association (IATA) has set the target for the aviation industry to reduce 50% of CO_2 emissions as such of the 2005 emission level by the year 2050, via the implementations of various approaches [4]. The utilization of

biofuel in aviation sector, known as biojet, as a partial substitution of traditional petroleum jet fuel is one of the important approaches for reaching such a target. Biojet could be produced from a wide ranges of feedstock (i.e. vegetable oil, lignocellulosic biomass, sugar, and starch), using different conversion routes (i.e. chemical, thermochemical, and biochemical) [3, 5, 6]. Sugar/starch-base bioethanol is now produced on a large scale and is one of the most successful commercial biofuels mainly used for automobiles by partially blending with gasoline. However, the needs of ethanol for automobiles is expected to be stagnant or decreased in the foreseeable future, due to the ethanol blend-wall limitation as well as the incoming of electric and hydrogen-fueled vehicles [7, 8]. Thus, it is

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necessary to develop new technologies for utilizing the excess ethanol in advance.

Technology for converting bioethanol to biojet offers an environmentally friendly route to produce jet fuel, and it has received extensive interests recently. The American Society for Testing and Materials (ASTM) creates a specification known as ASTM D7566 for blends containing synthetic jet fuel with entitled as standard specification for aviation turbine fuel containing synthesized hydrocarbons [9]. An approved method to produce alcohol-to-jet synthetic paraffinic kerosene (ATJ-SPK) as substitute fuel for aviation turbine is described in ASTM D7566 Annex A5. Ethanol-derived jet fuel has been recently approved and specified under Annex A5 with blends permitted up to 50% [10]. Briefly, ethanol to biojet conversion technology involves 3-step chemical reaction process: (1) ethanol dehydration, (2) ethylene oligomerization, and (3) hydrogenation reaction [3, 6]. Ethanol is converted to ethylene by dehydration over an acid catalyst, and then ethylene will be further converted into long chain hydrocarbons by oligomerization. Olefin which is the main product from oligomerization reaction could not be used directly as a jet fuel due to its poor stability property. The hydrogenation reaction is therefore needed as an olefin upgrading process. Ethylene oligomerization is considered as an important step to define the carbon distribution of biojet product [11]. Thus, the development of highly active and stable catalyst for the ethylene oligomerization is crucial for converting ethanol to biojet fuel.

Oligomerization of ethylene could be efficiently catalyzed by homogeneous and heterogeneous catalysts having transition metals as active sites. Heterogeneous catalysis is an environmentally friendly alternative to the traditional homogeneous catalysis with respect to the green chemistry. Consequently, significant research efforts have been directed to the development of heterogeneous catalyst for the ethylene oligomerization process. Ni-containing catalysts are regarded as the promising heterogeneous catalyst for synthesizing higher olefins via the ethylene oligomerization as reported in many studies [12–15]. The ethylene oligomerization over Ni-based catalyst has been carried out in wide ranges of temperatures and pressures in both batch and flow reactors [8, 11–13, 16]. The reaction conditions such as temperature, pressure and space velocity, as well as, the catalytic properties have a strong effect on the activity and selectivity [12]. An activity in term of ethylene conversion of Ni-based catalyst is determined by the numbers of accessible Ni sites, while the stability, carbon number distribution and final structure of oligomers depend on the density and strength of the Bronsted acid sites and the porosity [17].

Severe catalyst deactivation is known to be a significant problem in the ethylene oligomerization over bifunctional

catalysts containing Ni and solid acid, i.e. Ni-ZSM-5 and Ni-H-beta zeolite. This is due to the strong acidity of zeolite and limited mass transfer of oligomeric products in heterogeneous catalysis [2, 14]. Coke is formed on the surface of acidic zeolite during the reaction, and then blocks the pores of zeolite causing the catalyst deactivation [8]. One of the approaches to overcome such a problem is to use a weak solid acidity catalyst with larger pores. SBA-15 is a mesoporous material with two-dimensional hexagonal, having uniform large pores with tunable size (5–30 nm), high specific surface area, and pore volume [14], which makes it versatile and suitable for a wide ranges of application. Nickel exchanged AISBA-15 mesoporous catalysts have been reported as an effective catalyst for synthesizing higher olefins from the ethylene oligomerization. Ni-AISBA-15 are selectively formed C_4 – C_{10} olefins due to large pores of SBA-15, and they showed high catalytic stability during the reaction, due to their weak acidity property [13, 14]. The large pore channels in SBA-15 support lead to a high diffusion of large molecules, and very good stability against deactivation [11].

Recent advances in the synthesis of platelet SBA-15 with the shorter channel pore support are of interest in the development of catalyst due to its enhanced mass transfer property and reduced diffusion limitation, comparing to conventional SBA-15 material. Platelet SBA-15 material is synthesized by adding appropriate amount of Zr(IV) ions to conventional SBA-15 synthesis solution. Zr(IV) ions are reported to accelerate the self-assembly of P123 micelles and tetraethyl orthosilicate (TEOS), which resulted in the formation of short-channeling pores [18]. Platelet SBA-15 mesoporous silica catalysts have high thermal stability, large surface area, and uniform-sized pores and shown excellent activity in a several catalytic reactions [18–20]. Ethylene oligomerization over conventional Ni-AISBA-15 catalyst with long channel pore and rod-like or fiber-like analogues have been reported in previous studies [17]. However, the catalytic activity of platelet SBA-15 for the oligomerization of ethylene has not been investigated and reported in the literature. Thus, the present study focuses on the oligomerization of ethylene over platelet Ni-AISBA-15 mesoporous catalysts to produce biojet fuel range hydrocarbons.

2 Materials and methods

2.1 Catalysts preparation

Platelet Ni-AISBA-15 catalyst was prepared by a sequence of three steps as follows. In the first step, the platelet SBA-15 mesoporous silica was synthesized by one-pot co-condensation method according to the procedure described

by Chen et al. [18]. The synthesis solution was prepared by dissolving 2 g of P123 Triblock copolymer ($\text{EO}_{20}\text{PO}_{70}\text{EP}_{20}$) and 0.32 g of zirconium chloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) into 80 g of 2 M hydrochloric acid (HCl) at 35 °C for 2 h with stirring. To this solution, 4.2 g of TEOS was added under stirring and then kept in static condition for 24 h. The synthesis gel was hydrothermally heated at 90 °C for 24 h in a static condition. The solid precipitate was filtered, washed with deionized water to remove the weakly adsorbed ions, and dried at 100 °C for 12 h. Removal of P123 was achieved by calcining the obtained solid product in air at 500 °C for 12 h at ramping rate of 1 °C min^{-1} . As a result, the platelet SBA-15 support was obtained.

Bronsted sites were introduced to SBA-15 support in the second step by grafting sodium aluminate on SBA-15. 3.8 g of SBA-15 is added into aqueous solution of sodium aluminate and stirred for 15 h. The obtained sample in sodium form was filtered, washed with water, then dried at 80 °C in air and calcined at 550 °C for 6 h to generate NaAISBA-15. Then, it was treated with an aqueous solution of NH_4NO_3 to obtain the sample in an ammonium form ($\text{NH}_4\text{AISBA-15}$). In the third step, Ni sites were introduced to $\text{NH}_4\text{AISBA-15}$ by impregnation with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor solution. The sample was dried and calcined at 550 °C for 5 h to attain platelet Ni-AISBA-15 catalyst. It was granulated, crushed and then sieved to obtain 425–1000 μm particles size.

2.2 Catalyst characterization

X-ray diffraction (XRD) patterns of the catalysts were defined by a SmartLab (Rigaku Corporation, Japan) using Cu rotating anode X-ray source (1.5406 Å). The sample was scanned from $2\theta = 0.5$ to 3° with a scan speed of 0.0001° s^{-1} at 50 kV and 50 mA for small angle analysis and from $2\theta = 5$

to 90° with a scan speed of 0.005° s^{-1} at 40 kV and 40 mA for wide angle analysis. The Si:Al molar ratio and the amount of Ni loading on catalysts were analyzed through wavelength dispersive X-ray fluorescence (XRF) technique using S8 Tiger (Bruker AXS, Germany). The physical properties of samples were evaluated by N_2 adsorption–desorption isotherms on Autosorb iQ station 1 (Quantachrome, USA). The Braunauer-Emmett-Teller (BET) equation was applied to calculate the specific surface area, while the pore diameter and pore size distribution were calculated by Barret-Joyner-Halenda (BJH) method.

2.3 Ethylene oligomerization

The catalytic performances of the prepared platelet Ni-AISBA-15 catalysts on ethylene oligomerization were evaluated under various conditions of pressures, weight hourly space velocities and reaction temperatures. Catalytic ethylene oligomerization was performed in electric heated fixed bed stainless steel reactor (i.d. 10 mm) as shown schematically in Fig. 1. Prior to the experiment, 2 g of fresh catalyst was loaded into the reactor and pretreated in situ at 550 °C under N_2 flow at atmospheric pressure for 6 h and cooled to room temperature. Temperature and pressure were then raised to the desired ranges of 150–350 °C and 1–20 bar. A mixture of ethylene and nitrogen gas was fed into the reactor at weight hourly space velocity (WHSV) in the ranges of 0.56–4.5 h^{-1} . WHSV was calculated based on the mass flow rate of ethylene per weight of catalyst in an hourly basis (i.e. $\text{g}_{\text{ethylene}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$). Gaseous and liquid products were separated and depressurized to atmospheric pressure. The gaseous products were continuously analyzed using an online gas chromatograph (GC) system (Agilent 7890B, Japan), equipped with Porapak Q, Mol-sieve 13X, HP-AL/S, GS-Oxyplot columns, flame ionization

Fig. 1 Schematic diagram of ethylene oligomerization experimental system

detector and thermal conductivity detector. Accumulated liquid products in condenser (i.e. cooled by a mixture of ethylene glycol and water at 0 °C) were collected, weighed and analyzed offline by GC–MS (Agilent 7820A and 5975 MSD, Japan) equipped with a DB-Petro column. The peak areas shown on the GC spectra were used to calculate the composition of liquid product and the compounds were identified by comparison with the NIST database. The carbon numbers distribution of the product was estimated for the overall experiment by combining results from both online and offline GC analyses.

The ethylene conversion at given time on stream (denoted as X) was defined as the amount of ethylene consumed compared to the total ethylene fed. Product selectivity (denoted as S_i) was calculated by comparing amount of interested product with amount of all measured compounds in product. Liquid hydrocarbons yield was defined by amount of the obtained liquid product compared to the total ethylene fed. Ethylene conversion, product selectivity, liquid hydrocarbon yield, and deactivation rate were calculated based on previous researches [14, 21] by the following equations:

$$X(\text{mol}\%) = \frac{\text{molar flow rate of ethylene in} - \text{molar flow rate of ethylene out}}{\text{molar flow rate of ethylene in}} \times 100 \quad (1)$$

$$S_i(\text{wt}\%) = \frac{\text{mass of compound}_i}{\text{mass of all measured compounds}} \times 100 \quad (2)$$

$$\text{Liquid hydrocarbon yield}(\text{wt}\%) = \frac{\text{mass of liquid product collected}}{\text{mass feed rate of ethylene} \times \text{time}} \times 100 \quad (3)$$

$$\text{Deactivation rate}(\text{h}^{-1}) = \frac{(\text{initial conversion} - \text{conversion after 96 h time on stream})}{(\text{initial conversion} \times 96 \text{ h})} \quad (4)$$

3 Results and discussion

3.1 Catalyst characterization

Small and wide angle XRD patterns of as-synthesized SBA-15 and Ni-AISBA-15 catalysts are shown in Fig. 2. XRD pattern of SBA-15 shows a strong diffraction peak d_{100} (at $2\theta = 0.93^\circ$) and two weak diffraction peaks d_{110} (at $2\theta = 1.60^\circ$) and d_{200} (at $2\theta = 1.84^\circ$). Such a pattern implies the existence of the well-ordered two-dimensional hexagonal structure in SBA-15 [22]. There is no significant change in intensity of XRD peaks of Ni-AISBA-15, suggesting that the mesopores are not affected by alumination and subsequently impregnation with Ni. Only one broad diffraction peak is observed at $2\theta = 22^\circ$ in wide angle XRD patterns, which is the characteristic peak of amorphous silica. No peak corresponding to NiO in the profile of Ni-AISBA-15 is observed. This is consistent with the result reported by Jan et al. [21]; in which Ni is ion-exchanged with the support and might be presented at level lower than the detection limit of XRD.

The textural properties of the support and catalyst are summarized in Table 1. The Si/Al molar ratio determined from XRF analysis is 7.8 for NaAISBA-15 and there is no

Fig. 2 **a** Small angle and **b** wide angle XRD patterns of SBA-15 and Ni-AISBA-15

Table 1 Textural and chemical properties of the support and catalysts

Samples	Si/Al ^a (mol/mol)	Ni ^a (wt%)	S _{BET} (m ² g ⁻¹)	V _{Total} (cm ³ g ⁻¹)	φ _p (nm)	d ₁₀₀ -spacing (nm) ^b
SBA-15	–	–	605	1.07	8.9	10.6
NaAISBA-15	7.8	–	394	0.68	8.5	9.5
Ni-AISBA15	7.2	2.2	292	0.57	7.9	10.9

^aXRF measurements^bXRD measurements (at 2θ = 0.93°)

significant change in Si/Al ratio after Ni impregnation. The XRF measurement also shows that the Ni content in the catalyst is 2.2 wt%. The specific surface area of the samples is in a range of 292–605 m² g⁻¹. The Ni-AISBA-15 has a reduced specific surface area compared to SBA-15 and NaAISBA-15, as shown in Table 1. Loss in BET area is related to the reduction of pore size and pore volume, suggesting that the loading of Ni in the support is partially blocked the pores of the support.

Figure 3 shows the N₂ adsorption–desorption isotherms, and pore size distribution profiles of SBA-15, AISBA-15 and Ni-AISBA-15 catalysts. All samples exhibit type IV isotherm corresponding to mesoporous solid materials. The SBA-15 support shows a H₁ hysteresis loop at relative high P/P₀ region of 0.6–0.8, indicating the presence of large and channeling pores. On the other hand, the AISBA-15 support and Ni-AISBA-15 present the H₂ hysteresis loop due to pore-blocking. A uniform distribution of pore size is observed for SBA-15 support. While the broader pore size distributions are obtained for AISBA-15 and Ni-AISBA-15 catalysts.

3.2 Catalytic activity in ethylene oligomerization reaction

Typically, the compositions of jet fuel are C₈–C₁₆ hydrocarbons, which consisted of 70% paraffins, 25% aromatics, and 5% olefins [2]. Thus, it is necessary to synthesize hydrocarbons product with C₈ or higher carbon chain length in order to produce biojet via ethylene oligomerization. The catalytic performances of Ni-AISBA-15 catalysts, in terms of ethylene conversion, selectivity toward jet fuel range hydrocarbons (C₈₊), and liquid product yield, on ethylene oligomerization are investigated in a continuous flow fixed-bed reactor. The effects of operating parameters including pressures, weight hourly space velocities, and reaction temperatures on catalytic performance are investigated and described as follows:

3.2.1 Effect of pressure

The effect of pressure on the catalytic activity and product distribution of Ni-AISBA-15 catalyst is investigated at WHSV of 0.56 h⁻¹ and 275 °C. Steady state ethylene conversion is achieved around 3 h after the initial system startup in each experiment, as shown in Fig. 4. Therefore, the average conversion value after 3 h on stream is selected to

Fig. 3 **a** N₂ adsorption–desorption isotherms and **b** pore size distribution of samples

Fig. 4 Ethylene conversion as a function of time on stream at various pressures

represent the data of each experiment. According to Fig. 5, the steady state ethylene conversion, selectivity toward biojet fuel range hydrocarbons (C_{8+}) and liquid hydrocarbons yield increase with the increasing pressure from 1 to 20 bar. At 1 bar, the steady state ethylene conversion is 60 mol%. Further increasing the pressure to 10 and 20 bar, the conversions drastically increase to 92.4 and 98.4 mol%, respectively. The specific oligomerization activity, which corresponds to the numbers of mmoles of ethylene converted per gram of a catalyst and per hour, increases from 13 to 20 mmol $g^{-1} h^{-1}$ when increasing pressure from 1

to 20 bar. Such results are consistent with other studies [21, 23], that might be due to the decreasing of ethylene gas velocity at higher pressure, which is leading to higher residence times. Ethylene molecules could be further adsorbed to active sites, allowing higher conversions and activities.

Oligomerization pressure not only affects on ethylene conversion, but also the product selectivity. GC analysis results indicate that ethylene is converted into complex mixture of hydrocarbons containing olefins, paraffin, iso-paraffin, cycloparaffin, and aromatic compounds. The major component of the oligomerization products are linear and branched oligomers with even carbon numbers mainly ranging from 4 to 10 atoms, while aromatic and cyclic hydrocarbons are detected in small amount. Figure 5b shows that the product distribution shifted from lighter to heavier hydrocarbons as the pressure is increased. Product distribution at 1 ($C_4 > C_8 > C_6 > C_{10+}$), 10 ($C_6 \approx C_4 > C_8 > C_{10+}$) and 20 bar ($C_6 > C_4 \approx C_8 > C_{10+}$) are different. At 1 bar, the selectivity towards C_4 is the highest (79.4 wt%), while the selectivity toward C_{8+} is the lowest (~7.4 wt%). Such results suggest that ethylene is selectively dimerized to butene at a low pressure. As the pressure is increased, the oligomerization is directed toward the formation of C_6 and C_8 , which resulted in the increasing of C_{8+} selectivity to 20.1 and 33.8 wt% at 10 and 20 bar, respectively. Results obtained indicate that higher pressure promoted ethylene trimerization and butene dimerization. In addition, small amount of odd carbon number

Fig. 5 **a** Effect of pressure on ethylene conversion, C_{8+} selectivity and liquid hydrocarbon yield and **b** product selectivity; Condition: Ni-AISBA-15, $0.56 h^{-1}$ WHSV, and $275 ^\circ C$

products ranging from C_5 to C_9 due to cracking reactions is observed at the pressure range of 1–20 bar. However, no noticeable difference on the formation of cracked products detected when pressure is increased.

3.2.2 Effect of WHSV

The ethylene oligomerization is carried out at different WHSVs (0.56, 1.19, 2.4 and 4.5 h^{-1}) to understand the effect of WHSV on the catalytic performance. Ethylene conversion, selectivity toward biojet fuel range hydrocarbons (C_{8+}) and liquid hydrocarbons yield are increased with the decrease of WHSV from 4.5 to 0.56 h^{-1} as shown in Fig. 6. 65.3 mol% ethylene conversion along with 28.1 wt% yield of liquid hydrocarbons and 18.9 wt% C_{8+} selectivity are observed at 4.5 h^{-1} WHSV. As the WHSV is decreased to 0.56 h^{-1} , the ethylene conversion is nearly completed (99.4 mol%). Consequently, 44.9 wt% yield of liquid hydrocarbons and double value of C_{8+} selectivity (42.3 wt%) are

obtained. The higher catalytic performance of Ni-AISBA-15 in ethylene oligomerization at lower WHSV is due to the longer residence time of reactants to contact with the catalyst, which improves oligomerization reaction [15, 17, 24].

Product distribution at 4.5 h^{-1} ($C_4 \approx C_6 > C_8$), 2.4 h^{-1} ($C_4 > C_6 > C_8 > C_{10+}$), 1.19 h^{-1} ($C_6 > C_4 > C_8 > C_{10+}$), and 0.56 h^{-1} ($C_6 > C_8 > C_4 \approx C_{10+}$), are different, as shown in Fig. 6b. The product distribution at 4.5 h^{-1} WHSV contains about 36.4 wt% C_4 , 35.6 wt% C_6 and 18.9 wt% C_8 . With the decrease of WHSV to 2.4 h^{-1} , selectivity of C_4 and C_6 drop to 32.2 wt% and 29.1 wt%, respectively. The decreasing in selectivity of C_4 and C_6 are accompanied by the increasing in selectivity of C_8 (23.3 wt%) and C_{10+} (5.9 wt%). These results suggest that the lower WHSV is in favor of obtaining high selectivity for heavier products. As the WHSV is further decreased to the ranges of 0.56–1.19 h^{-1} , product distribution changes to non-Schulz-Flory type. The selectivity toward C_4 and C_6 are decreased obviously and C_8 selectivity is slightly decreased. While C_{10+} selectivity is greatly improved to 15.4 and 17.3 wt% at 1.19 h^{-1} and 0.56 h^{-1} WHSV, respectively.

3.2.3 Effect of reaction temperature

The effect of reaction temperature is investigating for the ethylene oligomerization reaction carried out at 20 bar and WHSV of 0.56 h^{-1} , in the ranges of reaction temperature between 150 and 350 °C. As illustrated in Fig. 7, temperature had a significant effect on the ethylene conversion, product selectivity toward C_{8+} and liquid product yield. The steady state ethylene conversions are increased from 34.9 to 99.4 mol%, as the temperatures are increased from 150 to 300 °C, indicating that the reaction is accelerated by the increase of reaction temperature. However, the conversion is slightly decreased to 92.3 mol% when increasing temperature beyond 350 °C. The yield of liquid hydrocarbons product shows the same change tendency. It is highest at the value of 45.7 wt% at 275 °C and then are slightly decreased to 44.9 wt% and 35.6 wt% at 300 °C and 350 °C, respectively.

Ethylene is selectively dimerized to butene with C_4 selectivity around 91%, and Schulz-Flory type hydrocarbons distribution ($C_4 > C_6 > C_8 > C_{10+}$) is obtained at 150 °C, as shown in Fig. 7b. With further increasing temperature ranges to 250–275 °C, the oligomerization is mainly directed towards the formation of C_6 and C_8 olefins, and product distribution changed to non-Schulz-Flory type. The C_4 products are linear and C_8 products contain 84 wt% branched olefins. The C_6 products contain 57 wt% linear olefins and 43 wt% branched olefins, as shown in Table 2. Small amount of iso-paraffins, aromatics and odd number olefins are presented in oligomerization products. Such results imply that the initial product of ethylene

Fig. 6 **a** Effect of weight hourly space velocity on ethylene conversion, C_{8+} selectivity and liquid hydrocarbon yield and **b** product selectivity; Condition: Ni-AISBA-15, 300 °C and 20 bar

Fig. 7 **a** Effect of temperature on ethylene conversion, C₈₊ selectivity, liquid hydrocarbon yield and aromatic content in product and **b** product selectivity; Condition: Ni-ALSBA-15, 20 bar and 0.56 h⁻¹ WHSV

oligomerization is C₄ which could be further undergo oligomerization, leading to the formation of longer-chain olefins that becomes prominent at higher reaction temperature [12].

Various distinct reactions may occur during the ethylene oligomerization, depending on both the nature of

the active sites in the catalyst and the reaction parameters. A possible reaction pathway which contributes to the oligomerization of ethylene over Ni-based catalyst is given in Scheme 1. The initial oligomerization of ethylene proceeds by the insertion of two molecules of ethylene into a nickel ion leading to the formation of a metallacyclopentane intermediate which could release 1-butene through hydride transfer [14]. The primary 1-butene product undergoes further oligomerization with ethylene molecules, yielding mainly medium-chain linear olefins. The formation of longer-chain or higher branched olefins could be obtained by co-oligomerization reactions of C₄ and C₆ olefins on an acid site via a cationic mechanism. This reaction is known to be favored with high density of acid sites, and high reaction temperature [25]. As shown in Scheme 2, branched 2-ethylene-1-butene occurs from 1-butene and ethylene on the Ni site through an alkyl metallacyclopentane intermediate and further converts to 3-methyl-2-pentene over the acid sites. The acid site could also catalyze isomerization of the primary product leading to the formation of internal double-bond olefins.

Product selectivity toward C₈₊ is increased from 3.2 to 46.8 wt% as the temperature is increased from 150 to 350 °C. However, the increase of reaction temperature ranges to 300–350 °C, induces the formation of aromatic hydrocarbons. This is probably due to the aromatization reaction at acid site of catalyst at high temperatures. It is important to be noticed that neither the high aromatic contents nor a complete lack of aromatics in jet fuel are desirable. However, the proportion of aromatics in liquid product obtained at 350 °C is as high as 39 wt%, i.e. equivalent to 29 wt% in total product when considering the composition of gaseous and liquid products together, which is in excess of the ideal aromatic contents of biojet fuel [2].

Additionally, the selectivity towards odd-numbered carbon products is increased with temperature. This phenomenon is attributed to the increasing rate of cracking and disproportionation reactions with temperatures, which results in unstable hydrocarbons species that could

Table 2 C₄, C₆ and C₈ isomers over Ni-ALSBA-15, Condition: 275 °C, 20 bar and 0.56 h⁻¹

C ₄ (wt%)		C ₆ (wt%)		C ₈ (wt%)	
Linear	Branch	Linear	Branch	Linear	Branch
98	2	57	43	84	16

Scheme 1 The reaction mechanism for linear ethylene oligomerization process [14]

Scheme 2 The reaction mechanism for branched ethylene oligomerization process [14]

be further reacted to form coke [24]. The high amount of both C_{8+} hydrocarbons and aromatic compounds, and high cracking products contents could be the cause of more pore blockages, and leading to lower ethylene

conversion at a high temperature as observe at 350 °C. These findings are consistent with previously observed from studies, where a bimodal distribution for optimal ethylene conversion as a function of temperature for the

ethylene oligomerization is reported. The higher temperature increases the conversion until coke covers much of the surface and further increases in temperature no longer increases the conversion [2, 24].

3.2.4 Catalyst stability and reusability

Catalyst stability over long periods of operation is also a critical factor. Therefore, time on stream of the catalyst is carried out for 96 h in order to observe the stability of the catalyst. The reaction condition at 275 °C, 20 bar and 0.56 h⁻¹ WHSV is chosen for the stability test. Products obtained are determined by GC instrument every hour of the reaction and results are shown in Fig. 8. Ni-AISBA-15 catalyst performs an initial activity around 93–95 mol% ethylene conversion at 4–6 h on stream, and then is gradually decreased to 84 mol% and 70 mol% after 48 and 96 h on stream, respectively, with a deactivation rate of 2.8×10^{-3} h⁻¹. However, the catalyst maintains a high selectivity toward C₈₊ in the ranges of 35–40% with non-Schulz-Flory type hydrocarbons distribution up to 72 h time on stream. The loss in catalytic performance is most likely caused by carbon depositions on the catalyst commonly found in the ethylene oligomerization over Ni-based catalysts.

The reusability of Ni-AISBA-15 is also investigated for two cycles using identical reaction conditions of 275 °C, 20 bar and 0.56 h⁻¹ WHSV. Practically, deactivated catalyst due to coke formation, could be regenerated by calcination. Therefore, the spent catalyst is regenerated by oxidizing under an air flow at 550 °C for 8 h. The regenerated catalyst exhibits good activity with slightly decreasing in ethylene conversion (93 mol%) but

slightly increasing C₈₊ selectivity (34.2 wt%) compares to the fresh catalyst (95 mol% and 32.4 wt%). The lower catalytic performance of regenerated catalyst might be attributed to both the presence and amount of coke deposition. Consequently, the higher calcination temperature may be required to complete the removal of deposited coke.

3.2.5 Comparison of platelet and conventional Ni-AISBA-15 catalysts

To compare the catalytic performance of platelet structure Ni-AISBA-15 catalyst (denoted as p-Ni-AISBA-15) with conventional rod-like Ni-AISBA-15 catalysts (denoted as c-Ni-AISBA-15) previously reported in the literatures [17, 26], the turnover frequency (TOF) is evaluated. TOF (h⁻¹) is calculated by the number of ethylene molecules converted per moles of Ni site per unit time, by considering each Ni atom as a single accessible active site. As shown in Table 3, TOF value of p-Ni-AISBA-15 is 53 h⁻¹, which is higher than that of c-Ni-AISBA-15 catalysts (35–41 h⁻¹). Moreover, similar values of ethylene conversion and C₈₊ selectivity could be achieved over p-Ni-AISBA-15 when operating at higher value of WHSV, suggesting that the platelet structure catalyst has a higher production rate. Overall, p-Ni-AISBA-15 shows the higher catalytic performance in ethylene oligomerization reaction than c-Ni-AISBA-15 catalyst, which could be attributed to the faster molecular diffusion and more accessible of Ni active sites to the reactants inside the short channel of platelet structure catalyst, than the conventional material.

Fig. 8 **a** Ethylene conversion and C₈₊ selectivity as a function of TOS and **b** product selectivity

Table 3 Comparison of the catalytic performance in ethylene oligomerization of platelet Ni-AlSBA-15 in the present work with those of previously reported conventional Ni-AlSBA-15 catalysts

Catalyst	Optimum reaction condition		Ethylene conversion (mol%)	S_{C_8+} (wt%)	TOF (h^{-1})	References
	WHSV (h^{-1})	T ($^{\circ}C$)				
p-Ni-AlSBA-15	0.56	300	99	42	53	Present study
c-Ni-AlSBA-15	0.375	200	99	47	41	[17]
c-Ni-AlSBA-15	0.375	200	96	31	35	[26]

4 Conclusions

Platelet Ni-AlSBA-15 catalysts prepared for the present study could be utilized for the oligomerization of ethylene to produce jet fuel ranged hydrocarbons. The reaction conditions had great effect on the catalytic performance and product distributions. The formation of C_{8+} hydrocarbons was favored at high temperature, high pressure and low WHSV. The optimum reaction conditions for oligomerization of ethylene over Ni-AlSBA-15 catalysts were as follows: reaction temperature range of 275–300 $^{\circ}C$, reaction pressure 20 bar and WHSV 0.56 h^{-1} . Under the optimized reaction conditions, approximately 98–99 mol% ethylene conversion with non-Schulz-Flory type hydrocarbons distribution was obtained. The selectivity to C_{8+} and liquid yield were 34–42 wt%, and 45–46 wt%, respectively. Moreover, the catalyst exhibited high stability of the activity during long-term experiment.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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