การเตรียมโพแทสเซียมบนตัวรองรับ Al-SBA-15 สำหรับปฏิกิริยาทรานส์เอสเทอริฟิเคชันของน้ำมันปาล์ม

Preparation of Potassium Supported on Al-SBA-15 For Transesterification of Palm Oil

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บทคัดย่อ

แม้ว่าจะมีการศึกษามากมายเกี่ยวกับปฏิกิริยาทรานส์เอสเทอริฟิเคชันที่ใช้ตัวเร่งปฏิกิริยาวิวิธพันธ์ที่มีโพแทสเซียมอยู่บนวัสดุที่มีความพรุน แต่ผลของขนาดรูพรุนก็ยังไม่ชัดเจนนัก งานนี้จึงศึกษาการใช้วัสดุมีโซพอรัส Al-SBA-15 เป็นตัวรองรับของโพแทสเซียม จากการสังเคราะห์ด้วยวิธีไฮโดรเทอร์มัล ได้ยืนยันเฟสและสัณฐานของ Al-SBA-15 ด้วยเทคนิคการเลี้ยวเบนของรังสีเอกซ์ (XRD) และกล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน (TEM) อย่างไรก็ตาม โครงสร้างมีโซพอร์ของ Al-SBA-15 ถูกทำลายหลังจากการทำให้เอิบชุ่มด้วยสารละลายบัฟเฟอร์โพแทสเซียมอะซิเตทและการแคลไซน์ วัสดุ K/Al-SBA-15 มีความสามารถในการเร่งปฏิกิริยาทรานส์เอสเทอริฟิเคชันของน้ำมันปาล์ม โดยมีผลได้ไบโอดีเซลประมาณ 40% โดยพิจารณาจากการแยกผลิตภัณฑ์ด้วยโครมาโทกราฟีแบบแผ่นบาง (TLC) จากการที่โครงสร้าง Al-SBA-15 เกิดการพัง บทบาทของขนาดรูพรุนของตัวรองรับจึงยังคงไม่ชัดเจน

ABSTRACT

There are several studies on transesterification using heterogeneous catalysts consisting of potassium on porous materials. However, the effect of the support pore size is still not cleared. This work focuses on the application of mesoporous material, Al-SBA-15 as support for potassium. From hydrothermal synthesis, the phase of Al-SBA-15 was confirmed by X-ray diffraction (XRD) and mesoporous morphology was observed by transmission electron microscopy (TEM). However, the mesoporous structure of Al-SBA-15 collapsed after impregnation with potassium acetate buffer and calcination. In the transesterification of palm oil, K/Al-SBA-15 was an active catalyst, providing the biodiesel yield of about 40% according to the product separation by thin layer chromatography (TLC). With the collapse of Al-SBA-15, the role of the support pore size was not yet clearly identified.

คำสำคัญ: Al-SBA-15 วัสดุมีโซพอรัส โพแทสเซียม ปฏิกิริยายาทรานส์เอสเทอริฟิเคชัน ไบโอดีเซล
Keywords: SBA-15, Mesoporous material, Potassium, Transesterification, Biodiesel

INTRODUCTION

Fatty acid methyl ester (FAME), also known as biodiesel, is one of the alternative fuels that has been utilized continuously (Manaf et al., 2019). Biodiesel is produced by transesterification of triglycerides and alcohol, generally methanol, in the presence of a catalyst (Mansir et al., 2017). The common process employs a homogeneous catalyst which has to be washed out from the biodiesel product and generates a large amount of wastewater (Sharma et al., 2011). Consequently, the catalyst is not reusable. There are several studies on transesterification with heterogeneous catalysts (Sharma et al., 2011) because they are easy to separate from the biodiesel product and reusable. The catalysts commonly consist of active species supported on porous materials. For instance, Rakmae et al. (2016) prepared potassium supported on zeolite sodium Y (K/NaY) by impregnation with potassium acetate buffer with 12 wt.% potassium loading. After calcination, potassium carbonate (K_2CO_3) was generated. The K/NaY catalyst was active in transesterification of refined palm oil, producing the biodiesel yield of 72%. However, the sorption dimensionality of NaY is 0.34 nm (Baerlocher and McCusker, 2007), which is smaller than the estimated three-dimension of triglyceride, 2.4 nm (Harrison, 2007). Thus, the diffusion of triglyceride to the active sites in the pore of NaY is limited. To improve the diffusion of the reactant to the active sites, mesoporous material with pore size larger than zeolite was employed as a support in this work.

There are reports about potassium on mesoporous material such as MCM-41, which is an amorphous silica with uniform pore shape and size. Loading potassium on MCM-41 by using potassium acetate (Artkla et al., 2008) and potassium acetate buffer (Supamathanon, 2011) resulted in the collapse of MCM-41 structure. Despite the collapse, the K/MCM-41 catalysts could still produce FAME, but not with a complete conversion (Artkla et al., 2008; Supamathanon, 2011). Thus, it becomes the interest of this study to use other mesoporous material with better stability than MCM-41 as support for potassium. SBA-15 is silica with a hexagonal array of mesopore containing size between 2-10 nm (Alothman, 2012). With the large pore size and thicker pore wall than MCM-41, SBA-15 could be a suitable support to reduce mass transfer limitation and improve the catalytic activity of transesterification. However, SBA -15 acts as only support and does not involve in catalysis. The incorporation of Al into the SBA-15 framework generated BrØnsted and Lewis acid sites as confirmed by FTIR spectroscopy of pyridine adsorption (Li et al., 2004). Jiménez-Morales et al. (2011) reported that the acid sites could improve catalytic activity of transesterification. They suggested that the triglyceride molecules chemisorb on the Lewis acis sites, then reacted with methanol to produce FAME. Moreover, Liang et al. (2013) reported that the FAME yield of canola oil produced from Al-SBA-15 as support was four times higher than SBA-15. From the excellent catalytic performance, Al-SBA-15 was employed as the support for potassium in this work.

To study the effect of pore size of support on the catalytic performance in transesterification, Al-SBA-15 was synthesized by incorporating Al into the SBA-15 structure to generate BrØnsted and Lewis acid site. 12 wt.%. K supported on Al-SBA-15 was prepared via

incipient wetness impregnation by using potassium acetate buffer as a potassium precursor to generate K_2CO_3 as active species according to Rakmae et al. (2016). The obtained K/Al-SBA-15 was tested in transesterification of palm oil to determine its catalytic performance in biodiesel production. The performance of K/Al-SBA-15 was compared to K/NaY reported by Rakmae et al. (2016) to elaborate the effect of support pore size.

MATERIALS AND METHODS

The chemicals in the synthesis of Al-SBA -15 were poly(ethylene glycol)-block-poly(proplylene glycol)-block-poly(ethylene glycol) (Pluronic123, $M_n \sim$ 5800, Sigma-Aldrich), tetraethyl orthosilicate (98%, Sigma-Aldrich), aluminum isopropoxide (>98%, Acros Organics) and hydrochloric acid (AR grade, Sigma-Aldrich). The chemicals for the preparation of potassium acetate buffer were potassium acetate (ACS grade, Carlo Erba) and acetic acid (99.7%, RCI Labscan). The chemicals for transesterification palm oil were refined palm oil (palm olein type) and methanol (HPLC grade, Honeywell Riedel-de Haën). The chemicals for thin-layer chromatography (TLC) testing were TLC plate (Silica Gel 60 F_{254}, Merck), petroleum ether (Panreac), diethyl ether (99.7%, Panreac) and acetic acid (99.7%, RCI Labscan).

1. Synthesis of Al-SBA-15 and preparation of K/Al-SBA-15 Al-SBA-15 was synthesized by hydrothermal method with the procedure and condition from the literature (Kocík et al., 2017) with half-scale of the original synthesis. Pluronic123 (5 g) was dissolved in deionized water (75 mL) and protonated with 2 M HCl (75 mL) under stirring at 40ºC for 3 h. The solution of aluminum isopropoxide (0.417 g) in 2 M HCl (12.5 mL) and tetraethyl orthosilicate (10 g) were added dropwise to the P123 solution to obtain the gel with molar ratio of Si/Al = 25. The solution was stirred continuously at 40ºC for 24 h. Then, the solution was transferred to a Teflon-lined stainless steel autoclave, heated to 95ºC and held for 48 h. The obtained solid was separated by centrifugation washed by deionized water until the pH of the washed solution equal to the pH of deionized water (pH 5.5), dried overnight at 90ºC and calcined at 550ºC for 6 h to remove the template. The sample name was Al-SBA-15.

The K/Al-SBA-15 with 12 wt.% potassium supported on Al-SBA-15 was prepared by the procedure modified from Rakmae et al. (2016). Potassium acetate buffer, a potassium precursor was prepared by dissolving CH_3COOK (1.4230 g) in deionized water (5 mL) before adding 1 M CH_3COOH (17.5 mL), then adjusted the volume to 25 mL by deionized water. The buffer solution (6 mL) was dropped to 1 g of Al-SBA-15. The mixture was dried at 80ºC overnight, then calcined at 550ºC for 6 h.

2. Characterization The synthesized Al-SBA-15 and K/Al-SBA-15 were analyzed by X-ray diffraction on a Bruker D8 Advance with monochromatic light source Cu Kα (wavelength 1.5418 Å). The sample was analyzed at 2θ = 0.5-10 degree by using scan speed 1.0 s/step and increment 1.0 s/step and scan speed 0.5 s/step.

Morphology of Al-SBA-15 and K/Al-SBA-15 were studied by transmission electron microscopy (FEI Tecnai G^2) at electron acceleration voltage 200 kV. The sample was dispersed in ethanol and then sonicated for 5 min. The mixture was dropped on the carbon-coated copper grid for the measurement.

3. Catalytic testing on transesterification of palm oil K/Al-SBA-15 was tested for transesterification of palm oil with the procedure from Rakmae et al. (2016) in a round bottom flask equipped with a water-cooled condenser. The refined palm oil (5 g) was stirred at 250 rpm and heated to 60ºC. Then, methanol (2.9 g)

and catalyst (0.2 g) was added in the oil. The mixture was stirred at 60°C for 3 h. The mixture was hot filtered (Whatman No. 5) to separate the catalyst from the solution. The remaining methanol in the filtrate was removed by a rotary evaporator at 50°C. Then, the solution was transferred into a separatory funnel and left to separate into two layers: palm oil and fatty acid methyl ester in the upper layer and glycerol in the bottom layer. The upper layer solution was spotted on the TLC plate for the preliminary result of catalytic activity by using a solution of petroleum ether/diethyl ether/glacial acetic acid (volume ratio of 85:15:1) as the mobile phase (Supamathanon et al., 2011).

RESULTS AND DISCUSSION

1. Preparation of K/Al-SBA-15

Figure 1 shows the XRD patterns of Al-SBA-15 and K/Al-SBA-15. The pattern of Al-SBA-15 consists of peaks at 0.9°, 1.5°, 1.7°, 2.3° and 2.6° attributing to (100), (110), (200) (210) and (300) planes, respectively. The peaks correspond to P6mm hexagonal symmetry (Zhao et al., 1998), similar to that of siliceous SBA-15. The results also agree well with the reference synthesis of SBA-15 (Kocík et al.,2017), confirming that the synthesis of Al-SBA-15 with half-scale was successful.

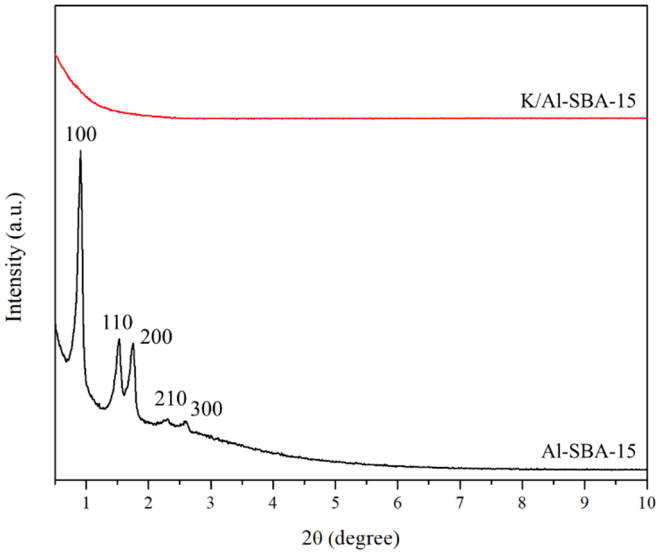

Figure 1. XRD patterns of Al-SBA-15 and K/Al-SBA-15 prepared with potassium acetate buffer.

In contrast, the XRD pattern of K/Al-SBA-15 does not show the characteristic peaks of SBA-15, indicating that the structure collapsed after calcination. There are similar reports about the collapse of potassium-loaded mesoporous silica, namely, potassium loaded on MCM-41 with potassium acetate (Artkla et al., 2008) and potassium acetate buffer (Supamathanon, 2011). The collapse of Al-SBA-15 is similar to MCM-41, probably because they both composed of silica as the main composition.

Figure 2a and b show the TEM images of Al-SBA-15 exhibiting the array of long rods with a width of about 3.3 nm. Figure 2c shows the hexagonal arrangement of pores with a pore diameter of about 10 nm and wall thickness 4 nm. The wall thickness of synthesized Al-SBA-15 is close to that of SBA-15 which around 3-5 nm (Zhao et al.,1998) and is also the same thickness as Al-SBA-15 reported from Li et al. (2004) and Li et al. (2010).

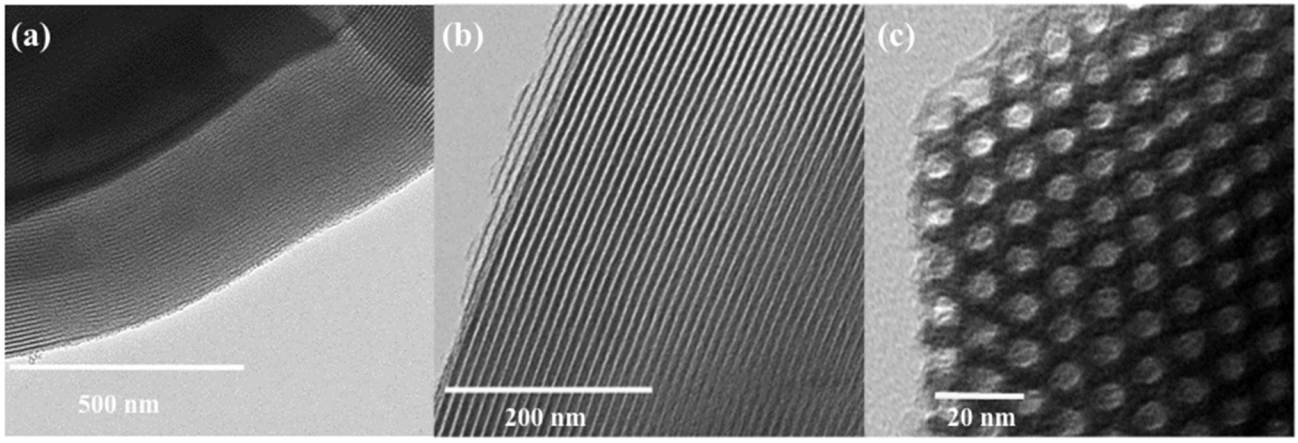

Figure 2 TEM image of (a) and (b) Al-SBA-15 rods and (c) Al-SBA-15 pores.

Figure 3a-c shows the TEM images of K/Al-SBA-15 indicating that the rods (figure 3a-b) and pores (figure 3c) of Al-SBA-15 collapsed. However, there are still pores and channels inside the particles. The TEM images of K/Al-SBA-15 are consistent with the XRD result. From the literature, SBA-15 loaded with ZrO_2 by impregnation with potassium nitrate (Liu et al., 2013) also collapsed after calcination. Moreover, the TEM image of K/ZrO_2-SBA-15 is similar to that of K/Al-SBA-15. The TEM image suggests that the destruction of siliceous framework leads to the same morphology.

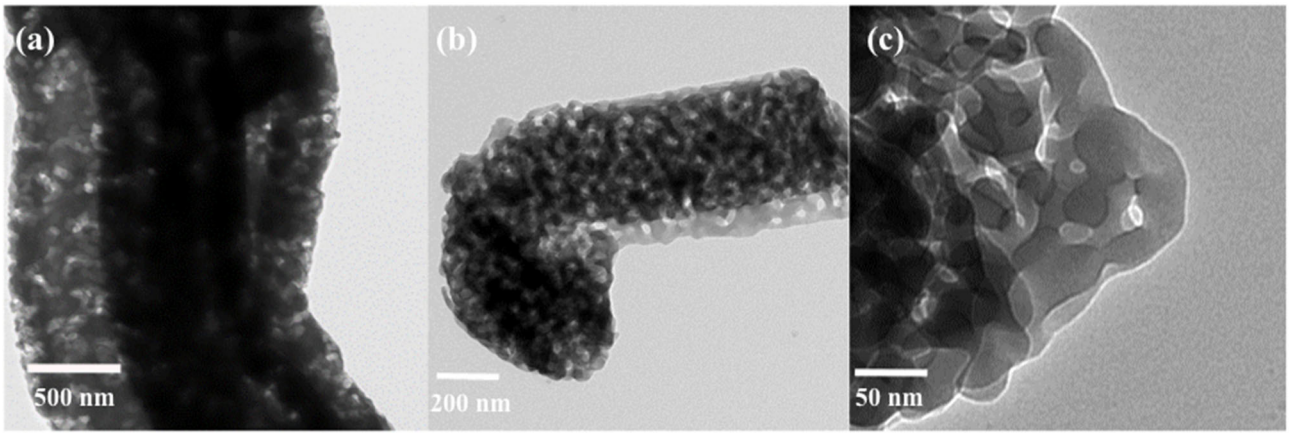

Figure 3 TEM image of K/Al-SBA-15 prepared with potassium acetate buffer.

Moreover, Sun et al. (2008) prepared various catalysts by impregnation of nitrate salts of alkali metal including $NaNO_3$, KNO_3 and $CsNO_3$ into SBA-15, and then calcination at 550°C to convert the nitrate salts to oxide. As a result, the structure of SBA-15 impregnated with alkali precursors collapsed after calcination. They suggested that the mobility in terms of the diffusion of the metal oxide into the pore of silica occurs at high temperatures and accelerates the reaction between basic oxide and silica support, which leads to the destruction of support. The mobility of metal oxide improves rapidly with its Tammann temperature, defined as half of the melting point. The Tammann temperatures of alkali metal oxides are less than 430°C and lower the calcined temperature. As a result, they are active or high diffusion into the pore of silica.

Potassium carbonate, the active species for this work, has melting point at 899ºC (Haynes et al., 2015) so that its Tammann temperature is 444.5ºC which is lower than the calcination temperature. Thus, potassium carbonate can diffuse well into the pore of Al-SBA-15 resulting in the destruction of Al-SBA-15.

2. Catalytic testing in transesterification for biodiesel production

The K/Al-SBA-15 was tested in the transesterification of palm oil. The palm oil as a reactant and the upper layer product was spotted on the TLC plate. The results are shown in figure 4. The separation of the product indicates that the palm oil converted to fatty acid methyl ester around 40% estimated from the spots. The conversion can be estimated from the spot of TLC with the value close to that determined from Gas-chromatography (Manadee et al., 2017). Despite the collapse of Al-SBA-15, the K/Al-SBA-15 could still catalyze the reaction and produce methyl ester. Therefore, the result suggests that triglyceride molecules reacted with the active sites although the structure collapsed, confirming that the catalyst contained acid-base property. The main active sites might be potassium in the external surface area of catalyst.

For Al-incorporated sites, it might be difficult to access, due to the collapse of structure. The conversion from K/Al-SBA-15 is lower than that from K/NaY, which gave the biodiesel yield 72.4% (Rakmae et al., 2016). The weaker performance of K/Al-SBA-15 may result from the collapse of the support structure.

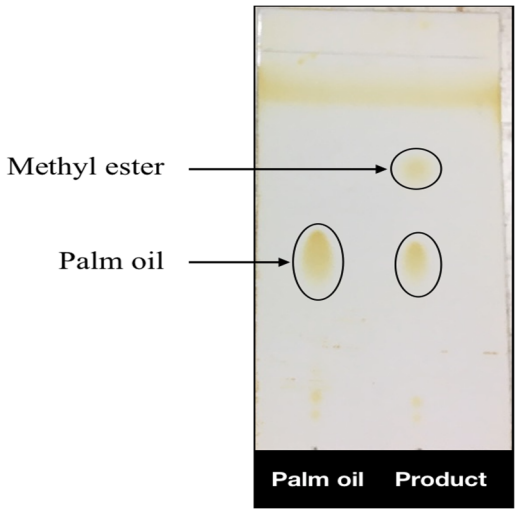

Figure 4 TLC results of upper layer biodiesel produced over 12wt.% K/Al-SBA-15.

There are similar reports on the performance of potassium on mesoporous silica. Supamethanon (2011) prepared K/MCM-41 with 8wt.% of potassium from potassium acetate buffer and tested on transesterification of extracted Jatropha seed oil. The catalyst gave the FAME yield of about 70%, also estimated form the TLC plate despite the collapse of MCM-41 structure. Artkla et al. (2008) studied the catalytic activity of potassium acetate on MCM-41 and rice husk silica calcined at 500ºC on transesterification of palm oil. The catalytic performance of K/MCM-41 with partial collapse structure is remarkably better than K/SiO_2 due to the remaining mesoporous structure and the larger surface area. Those studies suggest that the mesoporous structure and surface area are essential for catalytic performance.

From this work, K/Al-SBA-15 was proposed to improve the diffusion of triglyceride. However, the role of support can not be identified due to the structure collapse. Therefore, there is still a need for mesoporous materials with a structure that does not collapse after impregnation with potassium.

CONCLUSIONS

Al-SBA-15 with Si/Al ratio 25 was synthesized as support for potassium. The success of the synthesis was confirmed by XRD and TEM. However, the structure collapses after potassium loading and calcination to produce K/Al-SBA-15. Despite the collapse, K/Al-SBA-15 was active in transesterification of palm oil to produce biodiesel with a yield of about 40% according to the product separation by TLC.

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