COMPARISON OF NaY ZEOLITE SYNTHESIZED BY MICROWAVE-ASSISTED AND CONVENTIONAL HYDROTHERMAL METHODS: PROPERTIES AND APPLICATION AS CATALYST SUPPORT IN AQUEOUS AND NON-AQUEOUS SYSTEMS

Khomsan Bunmai
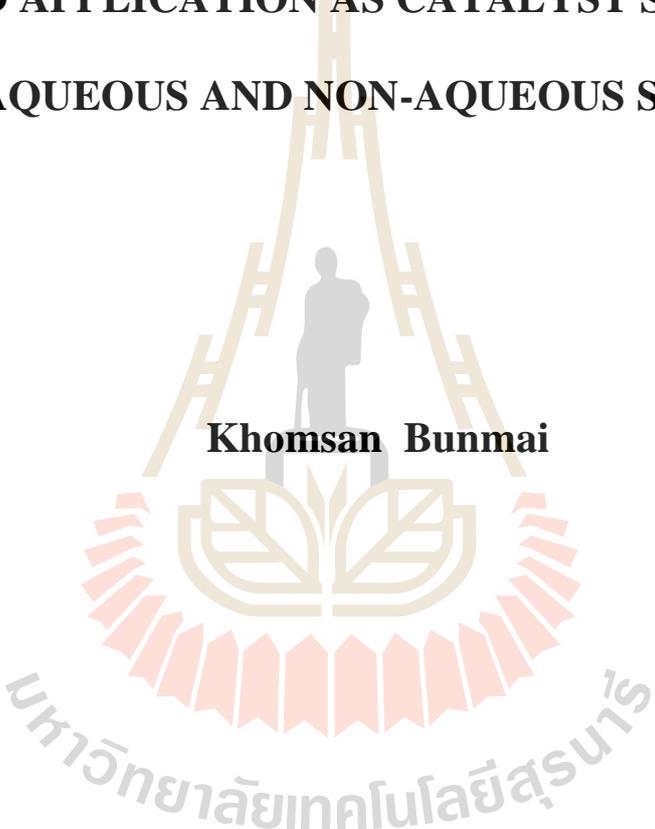
A Thesis Submitted in Partial Fulfillment of the Requirements for the

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การเปรียบเทียบซีโอไลต์โซเดียมวายจากการสังเคราะห์ด้วยวิธีไฮโดรเทอร์มอลแบบใช้ไมโครเวฟและแบบดั้งเดิม: สมบัติการใช้เป็นตัวรองรับสำหรับตัวเร่งปฏิกิริยาในระบบที่เป็นน้ำและไม่ใช่น้ำ

นายคมสันต์ บุญใหม่

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

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ปีการศึกษา 2562

COMPARISON OF NaY ZEOLITE SYNTHESIZED BY MICROWAVE-ASSISTED AND CONVENTIONAL HYDROTHERMAL METHODS: PROPERTIES AND APPLICATION AS CATALYST SUPPORT IN AQUEOUS AND NON-AQUEOUS SYSTEMS

Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master's Degree.

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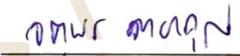
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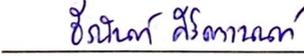
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คมสันต์ บุญใหม่ : การเปรียบเทียบซีโอไลต์โซเดียมวายจากการสังเคราะห์ด้วยวิธีไฮโดรเทอร์มอลแบบใช้ไมโครเวฟและแบบดั้งเดิม: สมบัติการใช้เป็นตัวรองรับสำหรับตัวเร่งปฏิกิริยาในระบบที่เป็นน้ำและไม่ใช่น้ำ (COMPARISON OF NAY ZEOLITE SYNTHESIZED BY MICROWAVE-ASSISTED AND CONVENTIONAL HYDROTHERMAL METHODS: PROPERTIES AND APPLICATION AS CATALYST SUPPORT IN AQUEOUS AND NON-AQUEOUS SYSTEMS) อาจารย์ที่ปรึกษา : ศาสตราจารย์ ดร.จตุพร วิทยาคุณ, 42 หน้า.

ซีโอไลต์โซเดียมวาย คือ ผลึกของอะลูมิโนซิลิเกตที่มีโครงสร้างแบบฟูจาไซต์ โดยทั่วไปแล้วสามารถนำมาประยุกต์ใช้ได้หลายอย่าง เช่น การดูดซับ การแยกสาร และ การเร่งปฏิกิริยา เป็นต้น การสังเคราะห์ซีโอไลต์โซเดียมวายโดยทั่วไปใช้วิธีการให้ความร้อนแบบดั้งเดิม ซึ่งใช้เวลานาน เพื่อลดเวลาการสังเคราะห์การให้ความร้อนโดยใช้ไมโครเวฟเป็นอีกหนึ่งทางเลือกเพราะมีอัตราการให้ความร้อนที่รวดเร็วและสม่ำเสมอ ดังนั้น เป้าหมายของงานนี้คือความเป็นไปได้ของซีโอไลต์จากวิธีการให้ความร้อนแบบดั้งเดิม (NaY-CH) กับวิธีการให้ความร้อนโดยใช้ไมโครเวฟ (NaY-MH) ในการนำไปประยุกต์ใช้เป็นตัวรองรับตัวเร่งปฏิกิริยาในระบบที่ใช้น้ำ และ ไม่ใช้น้ำ เช่น ตัวเร่งปฏิกิริยาในระบบที่เป็นน้ำ 10Mg/NaY-CH และ 10Mg/NaY-MH ที่มีแมกนีเซียม 10%โดยน้ำหนัก และในระบบไม่ใช้น้ำ 8K/NaY-CH และ 8K/NaY-MH ที่มีโพแทสเซียม 8%โดยน้ำหนัก ตัวเร่งปฏิกิริยาเตรียม โดยวิธีทำให้เอิบชุ่มด้วยแมกนีเซียมไนเตรทและโพแทสเซียมอะซิเทต และเผา หลังจากนั้นวิเคราะห์ตัวรองรับและตัวเร่งปฏิกิริยาด้วยเทคนิคหลายชนิด ได้แก่ SEM XRD FTIR *in situ* XRD และ CO_2-TPD เพื่อเข้าใจเอกลักษณ์ ลักษณะสัญฐาน หมู่ฟังก์ชัน เสถียรภาพทางความร้อน เสถียรภาพทางความร้อนในน้ำและความเป็นเบส จากการวิเคราะห์พบว่า ซีโอไลต์ที่ตกผลึกแบบไมโครเวฟที่อุณหภูมิ 100 องศาเซลเซียส เป็นเวลา 2 ชั่วโมง มีขนาดอนุภาคที่เล็กกว่าเป็น แบบสัณฐานวิทยาแปดด้านและมีความเป็นผลึกที่ต่ำกว่าซีโอไลต์ที่ตกผลึกแบบดั้งเดิม 100 องศาเซลเซียส เป็นเวลา 24 ชั่วโมง และหลังจากเติมแมกนีเซียมและโพสแทสเซียมบนซีโอไลต์ ความเป็นผลึกของซีโอไลต์ลดลงจากเดิม ยิ่งไปกว่านั้นความเป็นเบสของตัวเร่งปฏิกิริยาที่มีแมกนีเซียมหรือโพสแทสเซียมสูงกว่าของซีโอไลต์ เมื่อทดสอบการเปลี่ยนกลูโคสเป็นฟรักโตส ตัวเร่งปฏิกิริยา 10Mg/NaY-CH และ 10Mg/NaY-MH ให้ผลได้ของฟรักโตสที่ใกล้เคียงกัน คือ 28.81% และ 31.25%

อย่างไรก็ตามตัวเร่งปฏิกิริยาทั้งสองเสื่อมสภาพในการเร่งปฏิกิริยาครั้งต่อไป   และในการทดสอบปฏิกิริยาทรานส์เอสเทอริฟิเคชันของกลีเซอริล ไตรออคทาโนเอท 8K/NaY-CH และ 8K/NaY-MH ให้ผลได้ของไบโอดีเซลที่ใกล้เคียงกัน คือ 46.8% และ 43.8% เนื่องมาจากมีความเป็นเบสที่ใกล้เคียงกัน สรุปได้ว่า NaY-MH สามารถใช้แทน NaY-CH ได้ เนื่องจากมีคุณสมบัติที่คล้ายคลึงกันและใช้เวลาในการตกผลึกที่น้อยกว่า
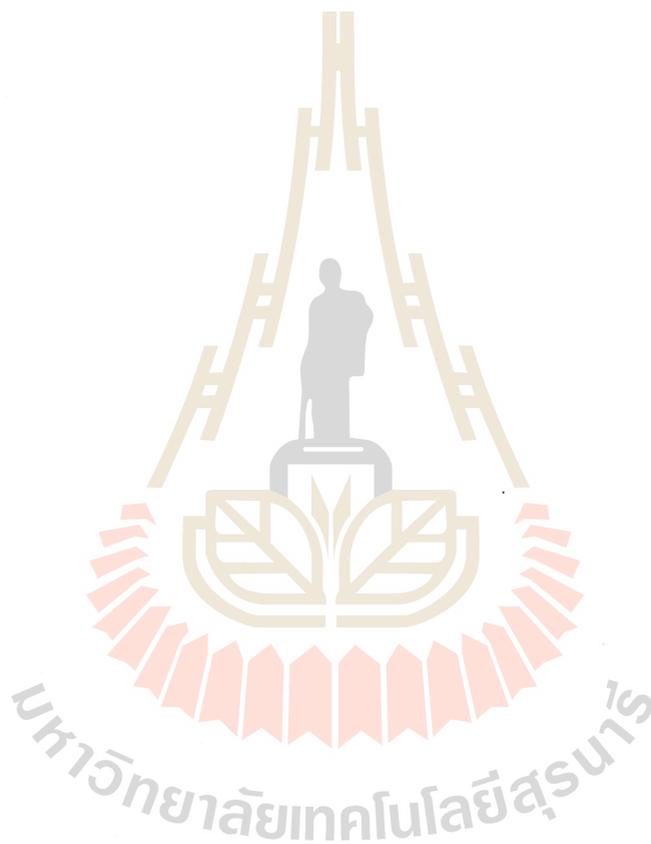
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KHOMSAN BUNMAI : COMPARISON OF NAY ZEOLITE
SYNTHESIZED BY MICROWAVE-ASSISTED AND CONVENTIONAL
HYDROTHERMAL METHODS: PROPERTIES AND APPLICATION AS
CATALYST SUPPORT IN AQUEOUS AND NON-AQUEOUS SYSTEMS.
THESIS ADVISOR : PROF. JATUPORN WITTAYAKUN, Ph.D. 42 PP.

ZEOLITE NaY/CATALYSIS/MICROWAVE-ASSISTED HYDROTHERMAL/
POTASSIUM/MAGNESIUM

Zeolite NaY is a crystalline microporous aluminosilicate material with faujasite
(FAU) structure. It has been used in many applications such as adsorption, separation,
and catalysis. Zeolite NaY is generally synthesized by a conventional hydrothermal
method (CH) which is time-consuming. To shorten the synthesis time, microwave-
assisted hydrothermal method (MH) is an alternative approach which has a fast heating
rate and homogeneous heat. although, the fast synthesis of NaY is achieved by the MH
method, the zeolite stability in the practical utilization as catalyst support or other
applications becomes a crucial concern. Therefore, this work aims to compare the
feasibility of NaY-MH with NaY-CH as base catalyst supports in the applications of
aqueous (isomerization of glucose to fructose) and non-aqueous (transesterification of
glyceryl trioctanoate) reactions. The catalysts in an aqueous system are 10Mg/NaY-MH
and 10Mg/NaY-CH with 10%wt of magnesium and those in a non-aqueous system are
8K/NaY-MH and 8K/NaY-CH with 8%wt of potassium. Those catalysts were prepared
by incipient wetness impregnation of magnesium nitrate and potassium acetate followed
by calcination. Subsequently, the supports and catalysts were characterized by various

techniques including SEM, XRD, FTIR, *in situ* XRD and CO_2-TPD to understand morphology, phase, functional groups, thermal stability, and basicity. The NaY-MH crystallized at 100 °C for 2 h has a smaller particle size and lower crystallinity than NaY-CH crystallized at 100 °C for 24 h. After loaded with magnesium and potassium, the crystallinities of the NaY-CH and the NaY-MH decrease. Moreover, the basicities of the catalysts containing either magnesium or potassium are higher than those of the bare zeolites.

When tested in the isomerization of glucose to fructose, the 10Mg/NaY-CH and 10Mg/NaY-MH catalysts provide nearly similar fructose yields namely, 28.81% and 31.25%. However, both catalysts deactivate in the next run. In transesterification of glyceryl trioctanoate, the 8K/NaY-CH and 8K/NaY-MH give similar biodiesel yields namely, 46.8% and 43.8% due to similar basicity. In conclusion, NaY-MH is interchangeable with NaY-CH due to similar properties and shorter crystallization time.

School of Chemistry   Student's Signature_____

Academic Year 2019   Advisor's Signature_____

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Khomsan Bunmai

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CHAPTER I

INTRODUCTION

1.1 Introduction

Zeolite Y is in the faujasite family. It has a Si/Al ratio in the range of 1.5 – 8.0 and a pore diameter of 7.35 Å. Zeolite Y is widely used in various applications, such as catalysis, ion exchange and adsorption. Its wide application is owing to its high stability, crystallinity, well-defined porous structure and tunable Si/Al ratios.

Zeolite Y in sodium form (NaY) can be synthesized by a conventional hydrothermal (CH) method which is a slow process with crystallization time of 24 h or longer at 100 °C or above (Robson and Lillerud, 2001). Thus, the shorter crystallization time is desired for commercial synthesis due to energy saving. Microwave heating has been employed in the synthesis of several materials, including zeolites. Microwave provides a fast heating rate and homogeneous heat due to the interactions of the polar molecules and ions with the electromagnetic field (Le et al., 2017). Consequently, the process is quicker and consumes less energy than conventional heating (Le et al., 2019). To decrease energy consumption in the crystallization, microwave can be applied. Arafat et al. (1993) and Wu et al. (2017) have synthesized zeolite NaY by microwave-assisted hydrothermal (MH) method at 120 °C with a short crystallization time (30 s and 60 s, respectively). However, the products contained both NaY and amorphous silica phase. Thus, longer crystallization time is needed. Zhao et al. (1997) and Katsuki et al. (2001) have used the MH method

at 100 and 150 °C, respectively, with a longer crystallization time (5-240 min) to reduce the amorphous phase. Katsuki et al. (2001) have produced zeolite NaY from two-step synthesis, with aging for 8 h at room temperature and crystallization at 100 °C for 2 h. The zeolite had surface area and particle size similar to NaY from the CH method but still contained some amorphous phase. A longer aging time could improve the zeolite crystallinity. Bunmai et al. (2018) have reported that the NaY with high crystallinity is synthesized from cogon grass silica by a two-step MH method with a longer aging time (24 h) and crystallization at 100 °C for 2 h. However, the cogon grass has a low silica yield which is not a suitable silica source. Consequently, fumed silica is used in this work for the synthesis of zeolite NaY by the MH method.

The NaY from the CH method has been used as a catalyst support of active species in aqueous system. For example, Graca et al. (2017) have tested zeolite NaY from the CH method and magnesium supported on NaY (Mg/NaY) as catalysts for isomerization of glucose to fructose at 100 °C in an aqueous solution. For this purpose, the zeolite has to be stable in hydrothermal condition. To the best of my knowledge, there are few reports about application of the NaY from MH method for catalysis in the aqueous solution. Thus, the hydrothermal stability of NaY from the MH and CH methods is compared in this thesis. Then the catalytic performance of Mg/NaY-MH and Mg/NaY-CH is compared.

The NaY is also used as a catalyst support of active species in a non-aqueous system, such as potassium catalyst (K/NaY) for transesterification. Supamathanon et al. (2011) have dispersed potassium on NaY-CH by impregnation with potassium acetate buffer to produce K/NaY with potassium loading 4, 8 and 12 wt%. The zeolite structure partially collapsed after impregnation with high potassium loading. The

basicity increased with potassium loading and the obtained catalysts had high activity in transesterification of jatropha seed oil to produce biodiesel. Montalbo et al. (2013) have studied the properties of K/NaY-CH catalyst with potassium loading 9, 10, 11 and 12% and tested with the same reaction. The phase of NaY determined by XRD decreases with potassium loading. Thus, the stability of NaY upon impregnation is still questionable. To test the feasibility of NaY-MH as a catalyst support, potassium catalyst on NaY-MH and NaY-CH (K/NaY-MH and K/NaY-CH) is compared in this thesis. Hence, it is focused in this work on properties of K/NaY with potassium loading of 8 wt%. Moreover, to avoid complications in the analysis of biodiesel products, glyceryl trioctanoate which is a single-component oil, is used instead of jatropha seed oil.

1.2 Objectives

The objectives of this thesis are to compare characteristic and hydrothermal properties of zeolite NaY-MH with NaY-CH method synthesized from fumed silica, and to compare feasibility of zeolite NaY-MH with NaY-CH as a catalyst support of magnesium in glucose isomerization and for potassium in transesterification of glyceryl trioctanoate.

1.3 References

Arafat, A., Jansen, J. C., Ebaid, A. R., and Van Bekkum, H. (1993). Microwave preparation of zeolite Y and ZSM-5. **Zeolites**. 13: 162-165.

Bunmai, K., Osakoo, N., Deekamwong, K., Rongchapo, W., Keawkumay, C., Chanlek, N., Prayoonpokarach, S., and Wittayakun, J. (2018). Extraction of silica from cogon grass and utilization for synthesis of zeolite NaY by conventional and microwave-assisted hydrothermal methods. **Journal of the Taiwan Institute of Chemical Engineers**. 83: 152-158.

Graca, I., Iruretagoyena, D., and Chadwick, D. (2017). Glucose isomerisation into fructose over magnesium-impregnated NaY zeolite catalysts. **Applied Catalysis B: Environmental**. 206: 434-443.

Katsuki, H., and Furuta, S. (2001). Microwave versus conventional-hydrothermal synthesis of NaY zeolite. **Journal of Porous Materials**. 8: 5-12.

Le, T., Ju, S., Lu, L., Peng, J., Zhou, L., and Wang, S. (2017). A novel process and its mechanism for recovering alumina from diasporic bauxite. **Hydrometallurgy**. 169: 124-134.

Le, T., Wang, Q., Pan, B., Ravindra, A. V., Ju, S., and Peng, J. (2019). Process regulation of microwave intensified synthesis of Y-type zeolite. **Microporous and Mesoporous Materials**. 284: 476-485.

Montalbo, K. D., De Leon, R. L., Sophiphun, O., Manadee, S., Prayoonpokarach, S., and Wittayakun, J. (2013). Characterization and catalytic performance of potassium loaded on rice husk silica and zeolite NaY for transesterification of jatropha seed oil. **Quimica Nova**. 36(8): 1116-1120.

Robson, H., and Lillerud, K. P. (2001). **Verified Syntheses of Zeolitic Materials** (2nd ed.). 156-158. Amsterdam: Elsevier.

Supamathanon, N., Wittayakun, J., and Prayoonpokarach, S. (2011). Properties of Jatropha seed oil from Northeastern Thailand and its transesterification catalyzed by potassium supported on NaY zeolite. **Journal of Industrial and Engineering Chemistry**. 17: 182-185.

Wu, W., Shi, C., Xue, B., and Yuting, B. (2013). Microwave radiation hydrothermal synthesis and characterization of micro- and mesoporous composite molecular sieve Y/SBA-15. **Arabian Journal of Chemistry**. 10: 2773-2777.

Zhao, J. P., Cundy, C., and Dwyer, J. (1997). Synthesis of zeolites in a microwave heating environment. **Studies in Surface Science and Catalysis**. 105: 181-187.
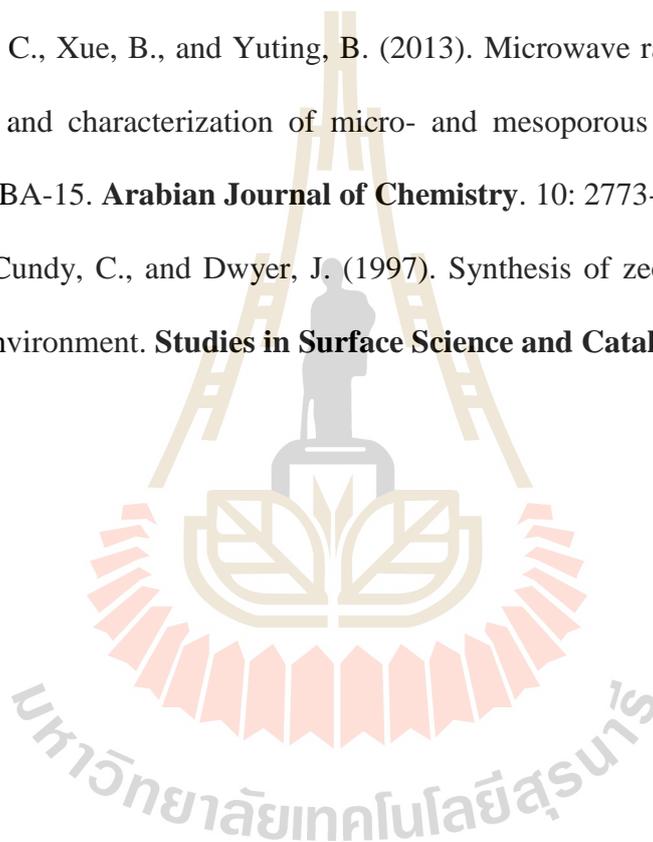
CHAPTER II

LITERATURE REVIEW

This review is divided into two parts. The first part focuses on the synthesis of zeolite NaY by conventional (CH) and microwave hydrothermal (MH) methods. The second part is about the application of zeolite NaY as catalyst supports of magnesium for glucose isomerization and of potassium for transesterification of glyceryl trioctanoate.

2.1 Background and synthesis of zeolite NaY

Zeolite NaY belongs to the faujasite (FAU) family with a framework containing double 6 rings (D6R) linked through sodalite cages (SOD) generating supercage which has a window diameter of 7.4 Å (Figure 2.1). The Si/Al ratio of NaY is typically between 1.5 and 8.0 (Ríos et al., 2012).
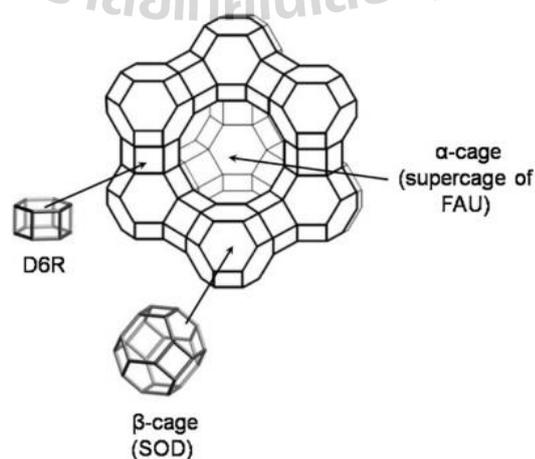
Figure 2.1 Framework structure of FAU zeolite (Ríos et al., 2012).

Zeolite NaY can be synthesized by a conventional hydrothermal (CH) method by one- or two-step methods. In the one-step method, a synthesis gel is prepared by mixing all precursor and crystallized without aging (Zhao et al., 1997). In the two-step method, a seed gel is mixed with a feed gel to produce the overall gel with molar ratio of 4.62 Na_2O: Al_2O_3: 10 SiO_2: 180 H_2O and crystallized at 100 °C for 24 h or longer (Robson and Lillerud, 2001). From CH method, the long crystallization time leads to high energy consumption. An alternative method to synthesize zeolite NaY with less energy consumption has been reported by using microwave-assisted hydrothermal (MH) method. The silica sources and synthesis conditions are summarized in Table 2.1

Table 2.1 Synthesis condition of zeolite NaY via microwave-assisted hydrothermal method.

Silica source	Synthesis route	Temperature and crystallization time	Overall gel composition aNa_2O: bAl_2O_3: $cSiO_2$: dH_2O	Characteristics of products	Reference
Fumed silica	Two steps	Heat to 120 °C in 30 s then hold at 100 °C for 10 min	3-4: 1: 8-10: 100-135	Uniform sized crystal	Arafat et al., 1993
Fumed silica	One step	150 °C for 5-20 min then at 150 °C for 5-20 min	4-7: 0-1: 10-20: 240	NaY mixed with amorphous phase	Zhao et al., 1997
Colloidal silica	Two steps	100 °C for 0.5-2 h	14: 1: 10: 800	NaY mixed with amorphous phase	Katsuki et al., 2001
Fumed silica	Two steps	Heat to 120 °C in 60 s then hold at 100 °C for 20 min	3: 1: 9: 120	NaY mixed with amorphous phase	Wu et al., 2013
Cogon grass silica	Two steps	100 °C for 2 h	4.6: 1: 10: 180	Pure NaY phase and small particle size	Bunmai et al., 2018

Arafat et al. (1993) have synthesized zeolite NaY from a two-step MH method with overall gel molar ratio 3-4 Na_2O: Al_2O_3: 8-10 SiO_2: 10-135 H_2O from fumed silica by heating to 120 °C in 30 s and holding at 100 °C for 10 min. The Si/Al ratio of the obtained zeolite was in the range of 1.5- 5.0. From scanning electron microscopy (SEM) the zeolite has uniform-sized crystals with aggregation, indicating simultaneous and abundant nucleation. The largest crystal size was 0.5 µm. The crystallinity of zeolite NaY decreased with the increasing of Si/Al ratio.

Wu et al. (2017) have synthesized zeolite NaY from a two-step MH method from the overall gel with molar ratio 3 Na_2O: Al_2O_3: 9 SiO_2: 120 H_2O. The gel was aged for 24 h and heated to 120 °C using heating power of 800 W for 1 min then heated at 100 °C using heating power of 200 W for 20 min. The results show that zeolite with uniform sized crystal aggregates with a maximum crystal size of 2 µm indicating simultaneous and abundant nucleation. The XRD pattern shows the phase of zeolite NaY and amorphous phase. It is possible to reduce the amorphous phase by increasing the crystallization time.

Zhao et al. (1997) have synthesized zeolite NaY from MH method in one step with gel molar ratio 4-7 Na_2O: 0-1 Al_2O_3: 10-20 SiO_2: 240 H_2O from fumed silica with crystallization at 150 °C. The crystallization time is varied from 5 to 20 min. The XRD patterns show that the amorphous phase decreased with the longer crystallization time. Although the crystallization time up to 120 min does not produce impurity phase, the crystallization temperature at 150 °C is higher than the IZA method. Thus, the procedure is not efficient in term of energy consumption.

Katsuki and Furuta (2001) have synthesized zeolite NaY with the overall synthesis gel molar ratio 10 Na_2O: Al_2O_3: 10 SiO_2: 800 H_2O from colloidal silica. They used two steps including aging at 25 °C for 8 h which was shorter than the IZA method, and crystallizing by the MH method at 100 °C for varied time: 0.5, 0.75, 1.0 and 2.0 h. The NaY zeolite crystallized for 2.0 h has surface area similar to the zeolite NaY from the CH method, namely, around 700 m^2/g. However, its XRD pattern still shows amorphous phase. Therefore, a further modification such as longer aging time could improve the zeolite crystallinity.

Bunmai et al. (2018) have synthesized zeolite NaY by the MH method using cogon grass silica. The overall gel has aged for 24 h and microwave-crystallized at 100 °C for 2 h. The obtained zeolite NaY had pure FAU phase with smaller particle size and a narrower size distribution than the NaY-CH. From the good quality of NaY-MH, this method is used in this study. However, cogon grass has low silica content which is not suitable for a large scale synthesis. Consequently, the silica source is changed to fumed silica which is commercially available.

2.2 Application of NaY as a catalyst support

Zeolite NaY from CH method has been used as a catalyst support for biomass conversion in aqueous solution. For example, Mg on NaY (Mg/NaY) is used in glucose conversion to fructose. To the best of my knowledge, there are no reports on utilization of NaY-MH for the same application. Thus, the feasibility of NaY-MH should be compared with NaY-CH. For such application, information about the hydrothermal stability of NaY-MH in hot water is important. Moreover, zeolite NaY-CH has been used as a support for potassium catalysts in transesterification

which is a non-aqueous system to produce biodiesel. Therefore, it is interesting to compare feasibility of NaY-MH with NaY-CH in the application in the nonaqueous system.

2.2.1 Hydrothermal stability of zeolite NaY

Ravenelle et al. (2011) have studied the hydrothermal stability of commercial HY (in proton form presumably from the CH method) with the various Si/Al ratios. The zeolite was mixed with water in an autoclave and heated at 150 and 200 °C for various time. When the HY with Si/Al ratio of 41 was heated at 200 °C, the crystallinity decreased with the longer heating time. In contrast, the HY with Si/Al ratio of 14 shows the better hydrothermal stability. Lutz et al. (2005) have compared hydrothermal stability of HY with NaY (presumably from the CH method, Si/Al ratio 2.4) in the temperature range of 130 - 240 °C under saturated pressure for 72 h. The NaY was stable at all temperatures whereas HY collapsed at 130 °C.

From the literature above, NaY-CH has hydrothermal stability in the isomerization of glucose in aqueous solution. However, there are no reports on hydrothermal stability of NaY-MH under these conditions. Therefore, the hydrothermal stability of zeolite NaY-CH and NaY-MH should be compared before using them as catalyst support in aqueous systems.

2.2.2 Application of NaY as a support for magnesium catalyst (Mg/NaY) for glucose isomerization to fructose (aqueous solution)

Moreau et al. (2000) have compared catalytic performance of NaA, NaX and NaY for the glucose isomerization to fructose in water at 95 °C and nitrogen pressure of 8 bar. The glucose conversion is in the order: NaA (26%) > NaX (20%) > NaY (9%) and the fructose selectivity is in the order: NaX (86%) > NaA (72%) >

NaY (62%). However, NaY is the most stable one due to the least cation leaching. Thus, it is a good choice as a support. Graca et al. (2017) have tested the performance of Mg/NaY catalysts for the glucose isomerization to fructose in water solvent at 100 °C under an inert atmosphere for 2 h under a continuous stirring. From 10%Mg/NaY, the glucose conversion is 45% and the fructose yield is 32%. Graca et al. (2018) have studied the effect of desilication on the performance of a different NaOH concentrations (0.01 - 0.2 M) of alkali-treated NaY zeolites impregnated with 5 wt.% of magnesium. They have tested the performance of Mg/treated-NaY for glucose isomerisation into fructose in water solvent at 100 °C under an inert atmosphere for 2 h under a continuous stirring. They have found that the glucose conversion gradually increases with the degree of desilication. From this literature NaY from the CH method is a good support but there are no reports on the use of NaY from the MH method in the same application. Therefore, NaY-MH and NaY-CH is compared as a support for Mg for glucose isomerization to fructose.

2.2.3 Application of NaY as a support for potassium catalyst (K/NaY) for transesterification (non-aqueous solution)

Supamathanon et al. (2011) have prepared K/NaY by impregnation with potassium loading 4, 8 and 12 wt.%. Potassium acetate buffer solution is employed in order to prevent the collapse of the zeolite framework. The prepared catalysts are applied in the transesterification of Jatropha seed oil. The catalyst with K loading of 12 wt.% provided high biodiesel yield of 73.4% under the reaction temperature of 65 °C in 3 h.

Montalbo et al. (2013) have studied transesterification of Jatropha seed oil and using K/NaY catalysts prepared by the same method with potassium loading 9,

10, 11, and 12 wt.%. They have found that the catalyst basicity increases with K loading but after impregnation the structure of zeolite NaY partially collapsed. The optimum catalyst with K loading of 11 wt.% provids high biodiesel yield of 77.9% under the reaction temperature of 65 °C in 3 h. However, the structure of NaY seems to collapse when the K loading increased. From literature review up to April 2020, there are no reports on the comparison between the K/NaY-CH and K/NaY-MH for transesterification. So, the potassium catalyst on NaY-CH and NaY-MH is compared in this work. In the preliminary results both 12K/NaY-MH and 12K/NaY-CH collapse after calcination. To make the comparison possible NaY-MH and NaY-CH, a lower potassium loading 8 wt.% is employed in this work. However, the analysis of biodiesel is complicated because there are many components in the oil ranging from C_{12} to C_{18}. To avoid complication, glyceryl trioctanoate is used instead of the jatropha seed oil.

2.3 References

Arafat, A., Jansen, J. C., Ebaid, A. R., and Van Bekkum, H. (1993). Microwave preparation of zeolite Y and ZSM-5. **Zeolites**. 13: 162-165.

Bunmai, K., Osakoo, N., Deekamwong, K., Rongchapo, W., Keawkumay, C., Chanlek, N., Prayoonpokarach, S., and Wittayakun, J. (2018). Extraction of silica from cogon grass and utilization for synthesis of zeolite NaY by conventional and microwave-assisted hydrothermal methods. **Journal of the Taiwan Institute of Chemical Engineers**. 83: 152-158.

Robson, H., and Lillerud, K. P. (2001). **Verified Syntheses of Zeolitic Materials** (2nd ed.). 156-158. Amsterdam: Elsevier.

Graca, I., Bacariza, M. C., Fernandes, A., and Chadwick, D. (2018). Desilicated NaY zeolites impregnated with magnesium as catalysts for glucose isomerisation into fructose. **Applied Catalysis B: Environmental**. 224: 660-670.

Graca, I., Iruretagoyena, D., and Chadwick, D. (2017). Glucose isomerisation into fructose over magnesium-impregnated NaY zeolite catalysts. **Applied Catalysis B: Environmental**. 206: 434-443.

Katsuki, H., and Furuta, S. (2001). Microwave versus conventional-hydrothermal synthesis of NaY zeolite. **Journal of Porous Materials**. 8: 5-12.

Lut, W., Toufar, H., and Kurzhals, R. (2005). Investigation and Modeling of the Hydrothermal Stability of Technically Relevant Zeolites. **Springer**. 11: 405-413.

Montalbo, K. D., De Leon, R. L., Sophiphun, O., Manadee, S., Prayoonpokarach, S., and Wittayakun, J. (2013). Characterization and catalytic performance of potassium loaded on rice husk silica and zeolite NaY for transesterification of jatropha seed oil. **Quimica Nova**. 36(8): 1116-1120.

Moreau, C., Durand, R., Roux, A., and Tichit, D. (2000). Isomerization of glucose into fructose in the presence of cation-exchanged zeolites and hydrotalcites. **Applied Catalysis A: General**. 193: 257-264.

Ravenelle, R. M., Schüler, F., D'Amico, A., Danilina, N., van Bokhoven, J. A., Lercher, J. A., Jones, C. W., and Sievers, C. (2010). Stability of zeolites in hot liquid water. **The Journal of Physical Chemistry C**. 114: 19582-19595.

Rios, C. A. R., Oviedo, J. A. V., Henao, J. A. M., and Macias, M. A. L. (2012). A NaY zeolite synthesized from Colombian industrial coal by-products: Potential catalytic applications. **Catalysis Today**. 190: 61-67.

Supamathanon, N., Wittayakun, J., and Prayoonpokarach, S. (2011). Properties of Jatropha seed oil from Northeastern Thailand and its transesterification catalyzed by potassium supported on NaY zeolite. **Journal of Industrial and Engineering Chemistry**. 17: 182-185.

Wu, W., Shi, C., Xue, B., and Yuting, B. (2013). Microwave radiation hydrothermal synthesis and characterization of micro- and mesoporous composite molecular sieve Y/SBA-15. **Arabian Journal of Chemistry**. 10: 2773-2777.

Zhao, J. P., Cundy, C., and Dwyer, J. (1997). Synthesis of zeolites in a microwave heating environment. **Studies in Surface Science and Catalysis**. 105: 181-187.
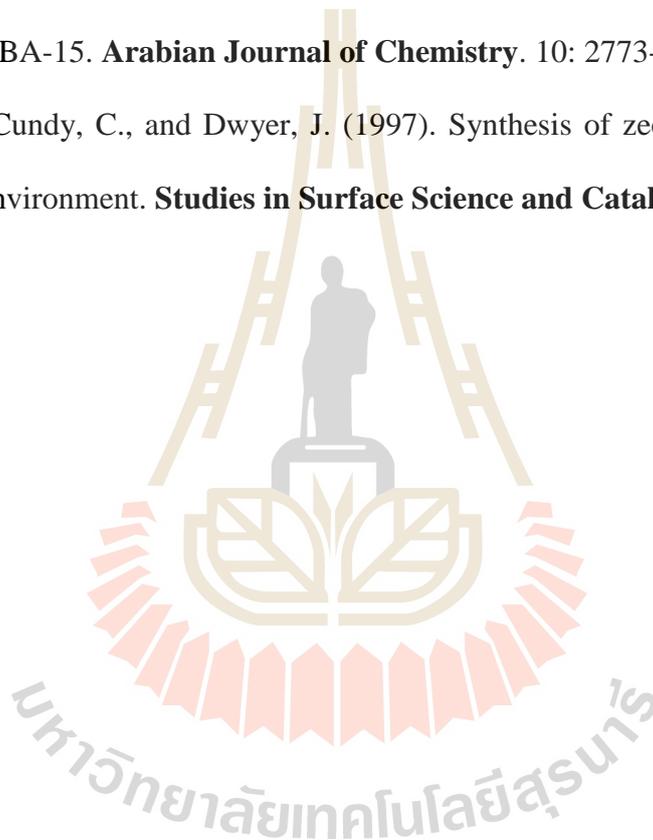
CHAPTER III

EXPERIMENTAL

3.1 Chemicals

Chemicals used in this research are listed in Table 3.1.

Table 3.1 Chemicals used in this research.

Chemicals	Phase	Formula	Content (%)	Suppliers
Sodium aluminate	Solid	$NaAlO_2$	56.0	Riedel-de Haën
Sodium hydroxide	Solid	$NaOH$	98	Carlo Erba
Fumed silica	Solid	SiO_2	99.8	Sigma-Aldrich
Potassium acetate	Solid	CH_3COOK	99.0	Carlo Erba
Potassium chloride	Solid	KCl	99.5	Carlo Erba
Acetic acid	Liquid	CH_3COOH	99.7	RCI Labscan Limited
Glyceryl trioctanoate	Liquid	$CH_3(CH_2)_6[COOCH_2]_2$ $CHOCO(CH_2)_6CH_3$	99.0	Sigma-Aldrich
Magnesium nitrate hexahydrate	Solid	$Mg(NO_3)_2 \cdot 6H_2O$	99.0	Sigma-Aldrich
Glucose	Solid	$C_6H_{12}O_6$	99.5	Sigma-Aldrich

3.2 Zeolite NaY synthesis and characterization

The zeolite NaY was synthesized with a modified procedure from Robson and Lillerud (2001). First, a Na_2SiO_3 solution was prepared by dissolving 14.35 g of fumed silica in NaOH solution (5.74 g of NaOH and 29.90 g of DI water). Then, a seed gel with a molar ratio of 4.62 Na_2O: Al_2O_3: 10SiO_2: 180H_2O was prepared as follows. NaOH 0.32 g was dissolved in 1.59 g of DI water in a PE bottle, then, $NaAlO_2$ anhydrous 0.18 g was added to the NaOH solution. The mixture was stirred for 10 min untill the solution was clear before adding 1.82 g Na_2SiO_3 solution to the solution of $NaAlO_2$. The mixture was stirred for 10 min, capped, and aged at room temperature for 24 h. Then, a feedstock gel with molar ratio 4.30 Na_2O: Al_2O_3: 10 SiO_2: 180 H_2O was prepared with similar procedure to that of the seed gel, except that it was used immediately without aging. NaOH 0.03 g was dissolved in DI water 21.05 g in PE bottle, then, $NaAlO_2$ 2.11 g will be added, stirred for 10 min and Na_2SiO_3 solution 22.90 g was added to the $NaAlO_2$ solution. Finally, the feedstock gel was slowly added into the seed gel under stirring. The mixture was stirred for 20 min, capped, and aged at room temperature for 24 h. Then it was transferred into a Teflon-lined autoclave 250 mL and crystallized at 100 °C for 24 h for the CH method and 100 °C for 2 h for the MH method (Microwave heating, Anton Paar - Multiwave 3000). After the crystallization, the samples were cooled down to room temperature. The solid product was separated by centrifugation, washed thoroughly with DI water until the pH was equal to pH of the DI water and dried at 110 °C.

Phase of zeolite sample was studied by XRD (Bruker D8 ADVANCE) with a Cu Kα radiation (λ = 1.5418 Å) operated at voltage and current of 40 kV and 40 mA with a step size of 0.02° and speed of 0.2 s/step. Functional groups of zeolite samples were

studied by FTIR (Bruker Tensor 27) using Attenuated Total Reflectance (ATR) mode with resolution at 4 cm^{-1} and number of scans at 64. Morphology of the zeolite sample was studied by SEM (Auriga Carl Zeiss) and the sample powder was spread on a layer of carbon tape adhered on a metal stub and then coated by gold under an argon atmosphere for a 30 min. Thermal stability of zeolite NaY was evaluated by a thermogravimetric analysis (TGA, Mettler TGA/DSC1). The samples were heated from room temperature to 1050 °C under a flow of nitrogen gas rate of 50 mL/min with a heating rate of 10 °C/min. The basicity of the NaY was determined by CO_2-TPD in a Belcat-B equipped with a thermal conductivity detector (TCD). The samples of approximately 50 mg was loaded into a U-shaped quartz tube supported by quartz wool and pretreated at 500 °C under He gas flow with a rate of 50 mL/min for 180 min in order to eliminate physisorbed species. After it was cooled down to 70 °C, an introduced gas mixture of CO_2/He with a flow rate of 50 mL/min was allowed into the sample cell for 30 min. Then, it was purged with He for 10 min, heated up to 100 °C with a heating rate of 10 °C/min and held for 1 h. Afterward, the CO_2-TPD process was performed from 100 °C to 800 °C with a heating rate of 10 °C/min.

3.3 Hydrothermal stability of zeolite NaY

Hydrothermal stability of NaY-MH and NaY-CH were studied by the method from Ravenelle et al. (2011). The stability was studied by adding 1 g of zeolite to 100 mL of DI water in a Teflon-lined autoclave 250 mL and heat at 150 °C for 6 h. After that, the samples were cooled down to room temperature. The zeolite was separated by centrifugation, washed thoroughly with DI water and dried at 90 °C for 12 h. Phase

and morphologies of treated zeolite was studied by XRD and SEM with similar procedures to that in section 3.1

3.4 Preparation, characterization and testing of Mg/NaY-MH and Mg/NaY-CH catalysts in glucose isomerzation

Catalyst containing 10 wt.% magnesium on the zeolite NaY-CH and NaY-MH (10Mg/ NaY-CH and 10Mg/ NaY-MH) were prepared by incipient wetness impregnation according to Graca et al. (2017). The zeolite was dried in an oven 100 °C. An aqueous solution of the magnesium nitrate with a water volume close to that of the zeolite pores was added dropwise to the zeolite. After that, samples were dried in an oven overnight at 100 °C and calcined at 500 °C. Phase and functional groups of catalyst was studied by XRD with similar procedures to that in section 3.1

The catalytic testing in glucose isomerization procedure was done according to Graca et al. (2017). Glucose 1.0 g, catalyst 0.2 g and deionization water 10 mL were poured into a 50 mL three-necked round bottom flask equipped with a condenser. Then, the mixture was purged with continuous flow of nitrogen at atmospheric pressure and heated up to 100 °C for 2 h under continuous stirring. After the reaction, the round bottom flask was cooled down and the liquid was separated from the catalyst by filtration. The liquid part was diluted with deionized water and analyzed by ion chromatography (IC, Dionex, ICS 3000) using an electrochemical detector (ECD) and CarboPac PA1 column. The mobile phase was used a 10 mM NaOH at a flow rate of 1.0 mL/min and injection volume was 25 µL. The fructose yield was calculated by equation 1. The spent catalysts were washed with deionized water and dried at 105 °C overnight and used in the following run. The weight of spent catalyst

10Mg/NaY-CH and 10Mg/NaY-MH after being filtered and washed from the first run were 0.1956 g and 0.1944 g, respectively and from the second run were 0.1920 g and 0.1889 g, respectively and from the third run were 0.1894 g and 0.1864 g, respectively.

$$\text{Yield} = \frac{mole\ of\ fructose\ produced}{mole\ of\ fructose\ produced\ theoretically} \times 100 \qquad (1)$$

3.5 Preparation, characterization and testing of K/NaY-MH and K/NaY-MH in transesterification

The catalysts containing potassium supported on the faujasite zeolite were prepared by the method modified from Montalbo et al. (2013). In catalyst preparation, the NaY-MH and NaY-CH zeolites were dried in a vacuum oven at 120 °C for 2 h. Potassium acetate buffer solution was prepared by mixing of potassium acetate 2.45 g with potassium chloride 0.2 g in 25 mL of 1 M acetic acid solution. For a wet impregnation step, the buffer solution of 1.00 mL was added dropwise to 0.5 g of the zeolite to produce a slurry, sonicated for 10 min, dried in a vacuum oven at 100 °C for 6 h and calcined at 550 °C for 3 h with a heating rate of 2 °C/ min. Phase, functional groups and basicity of the catalysts were studied by XRD, *in situ* XRD and CO_2-TPD with similar procedures to that in section 3.1

In catalyst testing, the catalyst of 0.3 g was dried at 90 °C overnight and methanol of 2.9 g was stirred at 65 °C in a 50 mL three-necked round bottom flask equipped with a condenser. The glyceryl trioctanoate of 5.0 g was slowly added and further stirred for 3 h. After the reaction, the mixture was cooled to room temperature and the

catalyst was separated from the product mixture using filtration. The liquid phase was allowed to separate into two layers. The biodiesel in the top layer was collected and the remaining methanol was removed using an oven at 55 °C for 10 min. The obtained biodiesel product 20 µL was mixed with 80 µL internal standard (C-17) and diluted with 3900 µL hexane. The biodiesel yield was determined by a gas chromatograph (Agilent Technologies, 7890A) equipped with a flame ionization detector (FID) and 100 m SUPELCO, SPTM-2560 fused silica capillary column with 0.25 mm id and 0.20 μm film thickness. The program was used with an initial temperature at 70 °C for 4 min. Then, the column temperature was heated up to 175 °C with a rate of 13 °C/min and held for 10 min. Finally, the final temperature was increased to 240 °C with a rate of 5 °C/min and held for 5 min. The biodiesel yield was calculated by equation 2.

$$\text{Yield} = \frac{mole\ of\ methyl\ ester\ produced}{mole\ of\ methyl\ ester\ produced\ theoretically} \times 100 \qquad (2)$$

3.6 References

Graca, I., Iruretagoyena, D., and Chadwick, D. (2017). Glucose isomerisation into fructose over magnesium-impregnated NaY zeolite catalysts. **Applied Catalysis B: Environmental**. 206: 434-443.

Ravenelle, R. M., Schüler, F., D'Amico, A., Danilina, N., van Bokhoven, J. A., Lercher, J. A., Jones, C. W., and Sievers, C. (2010). Stability of zeolites in hot liquid water. **The Journal of Physical Chemistry C**. 114: 19582-19595.

Robson, H., and Lillerud, K. P. (2001). **Verified Syntheses of Zeolitic Materials** (2nd ed.). 156-158. Amsterdam: Elsevier.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of zeolite NaY

4.1.1 Phase analysis by X-ray diffraction XRD

XRD patterns of NaY-CH and NaY-MH are displayed in Figure 4.1a. Both samples show characteristic peaks of NaY (Robson and Lillerud., 2001.). The peaks from NaY-CH have stronger intensities than those from NaY-MH indicating the higher crystallinity. Peaks of other phases are not observed indicating that a pure phase of NaY is obtained from both syntheses. In comparison with the previous work, Bunmai et al. (2018) have synthesized zeolite NaY from cogon grass silica (purity 99.34 wt%) by CH and MH methods and crystallized at 100 °C for 24 and 2 h, respectively. The obtained NaY-MH has pure NaY phase with small particle size but NaY-CH contains zeolite NaP. Different zeolite properties could be from the different silica source. Hamilton et al. (1996) have compared the purity of the silica source in the synthesis of zeolite sodium X (NaX). The low purity of silica source results in the impurity phase in NaX.
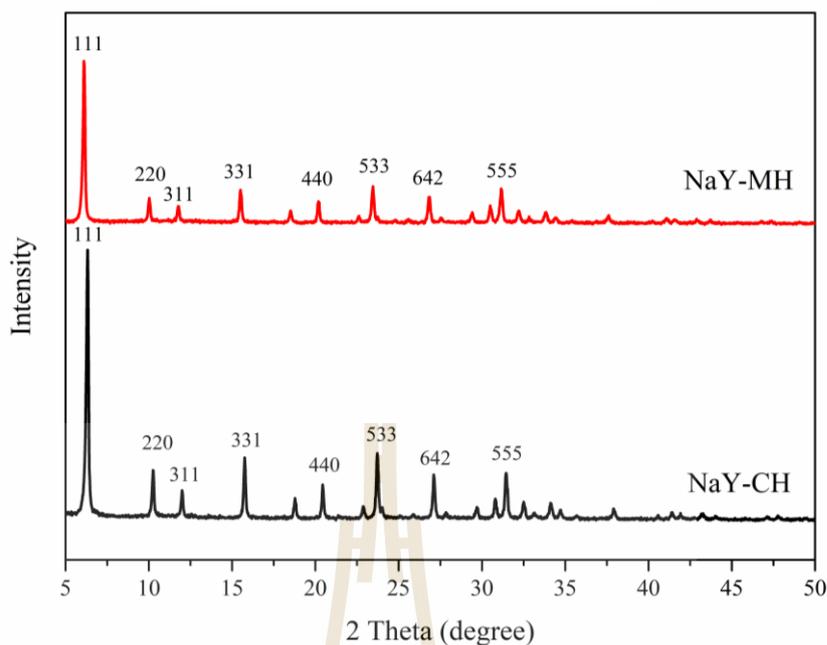
Figure 4.1 XRD pattern of zeolite NaY from conventional and microwave hydrothermal methods (NaY-CH and NaY-MH, respectively).

4.1.2 Functional groups analysis by Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of NaY-CH and NaY-MH are presented in Figure 4.2. The band at 979 cm^{-1} is assigned to T–O (T= Al, Si) asymmetric stretching. The bands at 663 cm^{-1} correspond to symmetric stretching mode of TO$_4$ tetrahedral groups in double 4 member rings in the zeolite structure. The bands in the range of 500–600 cm^{-1}, referring to double ring stretching in the zeolite framework is observed in the zeolite that contained the double 4 and double 6-rings (AlO$_6$) (Salama et al., 2016). Moreover, the bands at 1652 cm^{-1} is ascribed to the stretching vibrations of –OH groups adsorbed on the surface of the zeolite. The band at 752 cm^{-1} is attributed to the external linkages which are structure sensitive. The band at 460 cm^{-1} was

attributed to T-O bending (Ríos et al., 2012). These vibration bands are characteristic of NaY. Furthermore, the asymmetric stretching band of NaY-CH and NaY-MH samples represent in the region of 979 cm^{-1} shift to lower wavenumbers (1005 cm^{-1}) indicating the lower Si/Al ratio (2.43), consistent with the literature (Chandrasekhar et al., 2004). This result suggests that the zeolite NaY sample synthesized from fumed silica has a Si/Al ratio lower than 2.43. The exact Si/Al ratio of the NaY-CH and NaY-MH samples determined by EDS-SEM technique are 2.15 and 2.11, respectively.
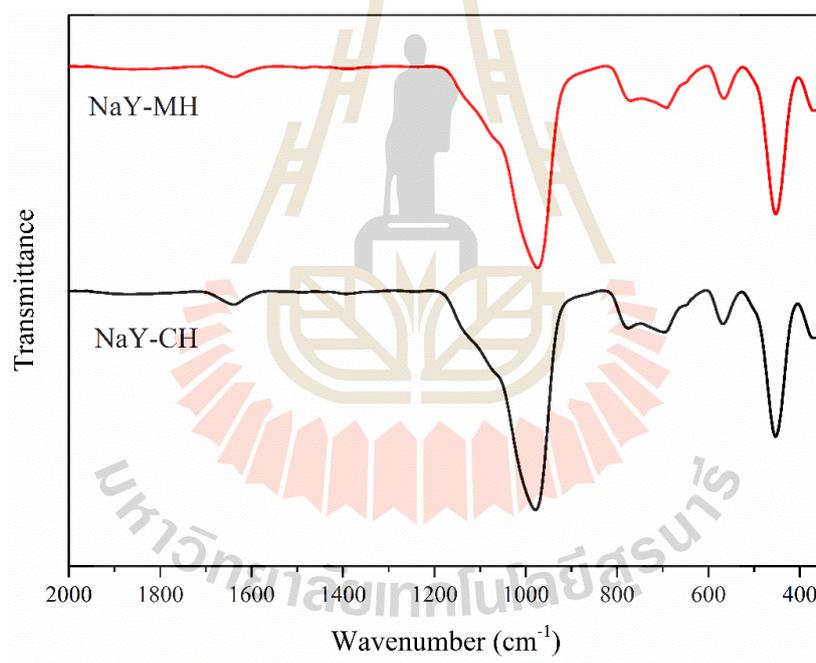
Figure 4.2 FTIR spectra of zeolite NaY from conventional and microwave hydrothermal methods (NaY-CH and NaY-MH, respectively).

4.1.3 Morphology analysis by Scanning electron microscopy (SEM)

Images of the zeolite NaY obtained from SEM are shown in Figure 4.3. The particle size of NaY-CH and NaY-MH are around 400-500 nm. The average crystal size from CH is larger than MH method. The crystals of NaY-MH have octahedral and a well-defined shape with smooth surface. Furthermore, NaY-MH has higher crystallinity and uniform crystal size than CH method. Bunmai et al. (2018) have reported that zeolite NaY from cogon grass has polycrystals with an octahedral shape. Particle size distribution of NaY-MH shows the highest count at 250 nm. The average crystal size from CH is larger than MH method (72 and 44 nm, respectively). The smaller size from NaY-MH could be contributed to the faster heating rate from microwave which leads to a quicker formation and more number of nuclei.
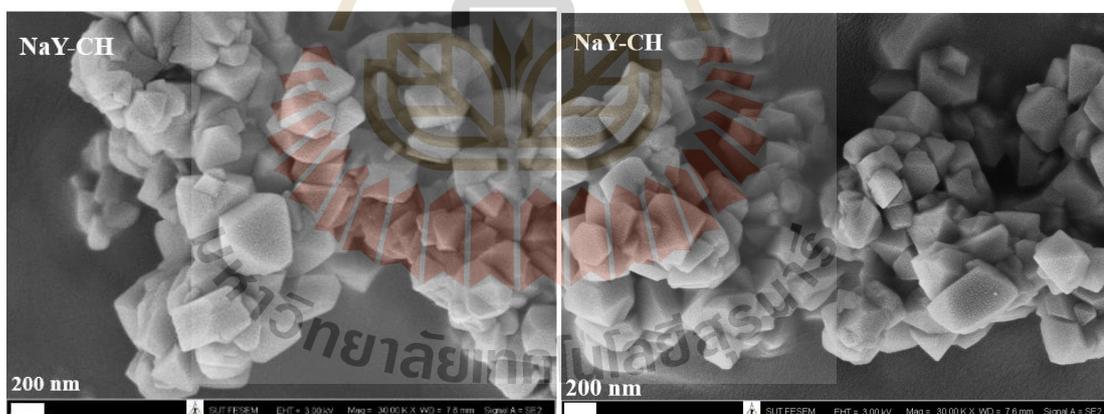
Figure 4.3 SEM images of zeolite NaY from conventional and microwave methods
(NaY-CH and NaY-MH, respectively).
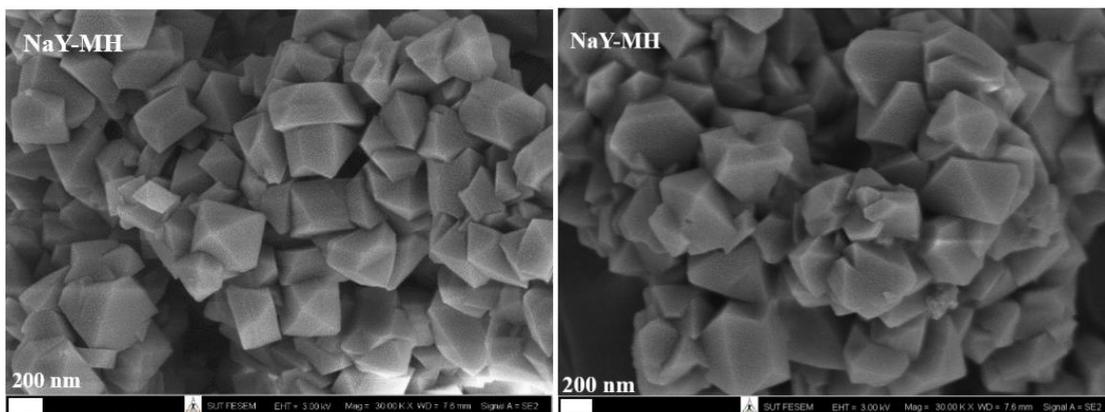
Figure 4.3 SEM images of zeolite NaY from conventional and microwave methods (NaY-CH and NaY-MH, respectively) (continued).

4.1.4 Thermal stability by thermogravimetric analysis (TGA)

The thermograms of zeolite NaY is presented in Figure 4.4. The total weight losses from NaY-CH and NaY-MH methods are 23-26.5%. The weight loss of zeolite NaY occurs from 35 to 300 °C relating to the loss of water molecules located in the zeolite cavities. In comparison, NaY-MH shows more weight loss than NaY-CH. This is due to the more hydrophilicity of NaY-MH. The Si/Al ratio of NaY-MH is 2.11 whereas that of NaY-CH is 2.15. The higher Al content results in the more hydrophilicity. This corresponds to a coordination of four water molecules to each proton associated with tetrahedrally coordinated aluminum in the zeolite (Ng and Mintova, 2008).
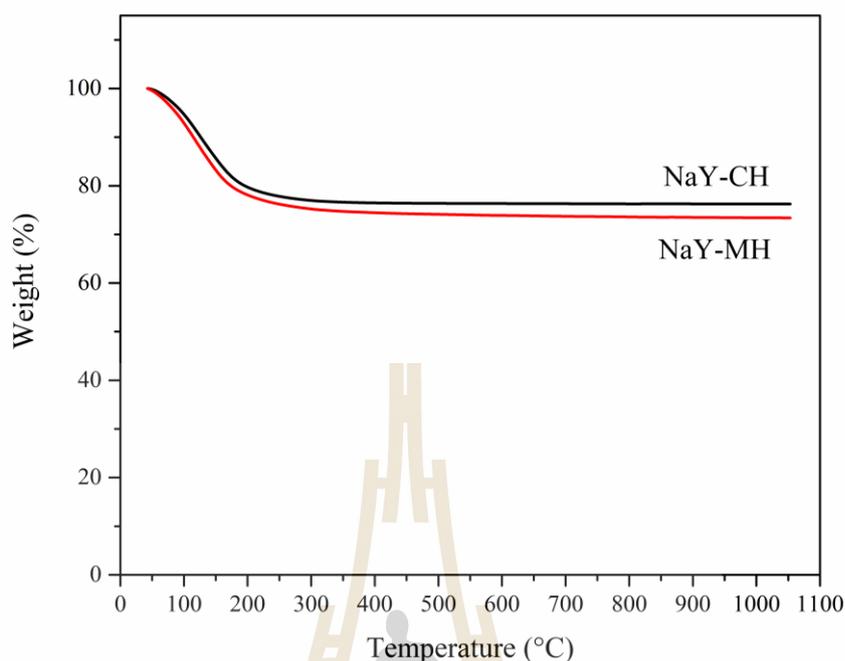
Figure 4.4 Thermograms of zeolite NaY from conventional and microwave methods

(NaY-CH and NaY-MH, respectively).

4.1.5 Basicity analysis by CO_2 temperature-programmed desorption (CO_2-TPD)

CO$_2$-TPD profiles reflecting the basicity of zeolite NaY-CH and NaY-MH are shown in Figure 4.5. The desorption of CO_2 from zeolite NaY-CH and NaY-MH contains only one peak at low temperature (200-400 °C) corresponding to weak basic sites (Rakmae et al., 2016). Their basicities are 0.173 and 0.179 mmol/g. It is noticeable that the desorption peak of CO_2-TPD of NaY-MH has slightly more intense than that of NaY-CH. The result could be from the lower Si/Al ratio in the zeolite structure, 2.15 for NaY-CH Vs 2.11 for NaY-MH, respectively. The higher Al content in NaY-MH could imply the greater amount of Na^+, a charge balancing which results

in the more basic sites. This remark is consistent with the report of Sápi et al. (2019) that the desorption peak of CO_2-TPD from the larger Al content in ZSM-5 is stronger than that from the lower Al content.   However, the basicity of NaY-MH is relatively similar to that of NaY-CH. So, the MH method can replace of the CH method for the preparation of NaY zeolite.
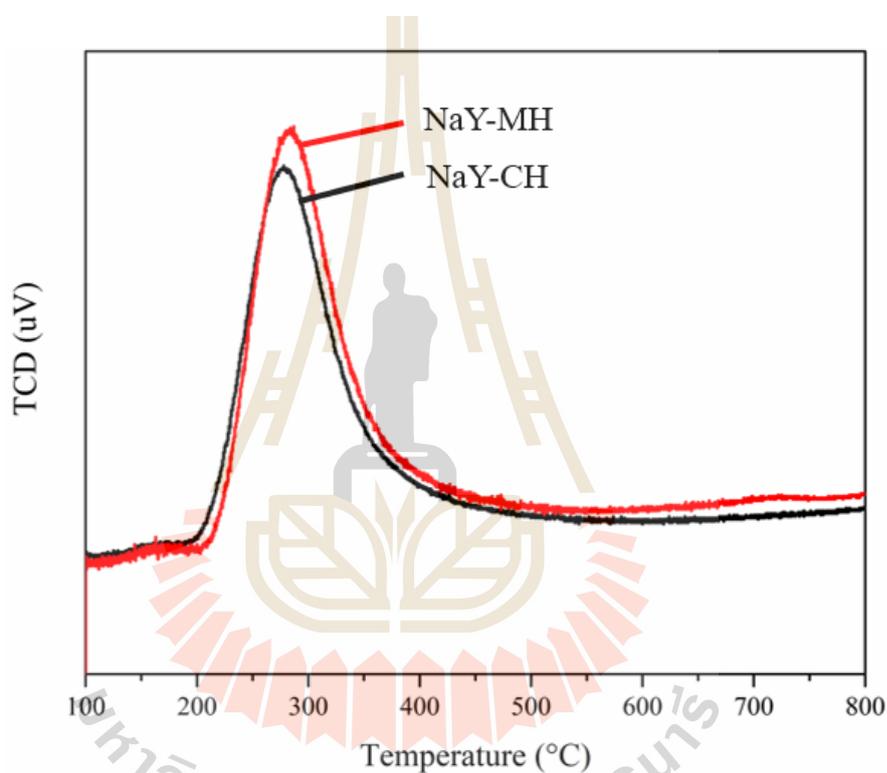
Figure 4.5 CO_2-TPD profiles of NaY-CH and NaY-MH.

4.2 Hydrothermal stability of zeolite NaY

4.2.1 Phase analysis by XRD

XRD patterns of NaY-CH and NaY-MH after hydrothermal stability testing at 150 °C for 6 h is displayed in Figure 4.6. The characteristic diffraction pattern of zeolite NaY is still observed in all samples indicating that structure dose not collapse. However, the intensity of NaY-MH after hydrothermal stability testing slightly decreases (6%) but that of NaY-MH is decreased more (38%). This indicates that hydrothermal stability of NaY synthesized from MH is higher than that from CH method.
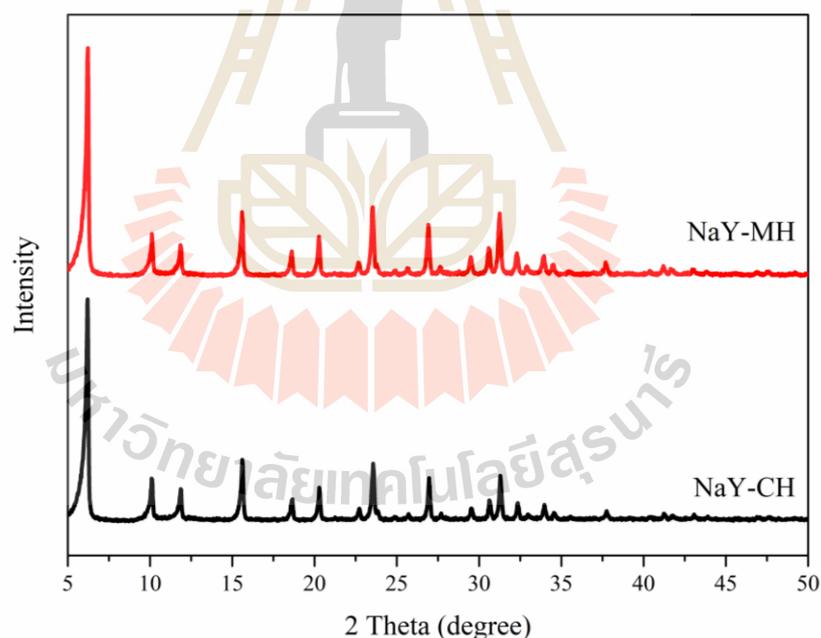
Figure 4.6 XRD pattern of zeolite NaY-CH and NaY-MH after hydrothermal stability testing at 150 °C for 6 h.

4.2.2 Morphology study by SEM

SEM images of the zeolite NaY-CH and NaY-MH after hydrothermal stability testing at 150 °C for 6 h is displayed in Figure 4.7. The treated NaY from CH and MH method is not collapsed. The particle size of treated NaY-CH and treated NaY-MH are around 200-400 nm. The slightly change in particle sizes and morphologies is observed for treated NaY-MH as compared to the untreated NaY-MH. In contrast, the treated NaY-CH has cracks on the surface and the slight changes in crystal shape. Therefore, the hydrothermal stability of NaY-MH is better than that of NaY-CH. The zeolite NaY from MH and CH method can be used as a catalyst support in aqueous systems.
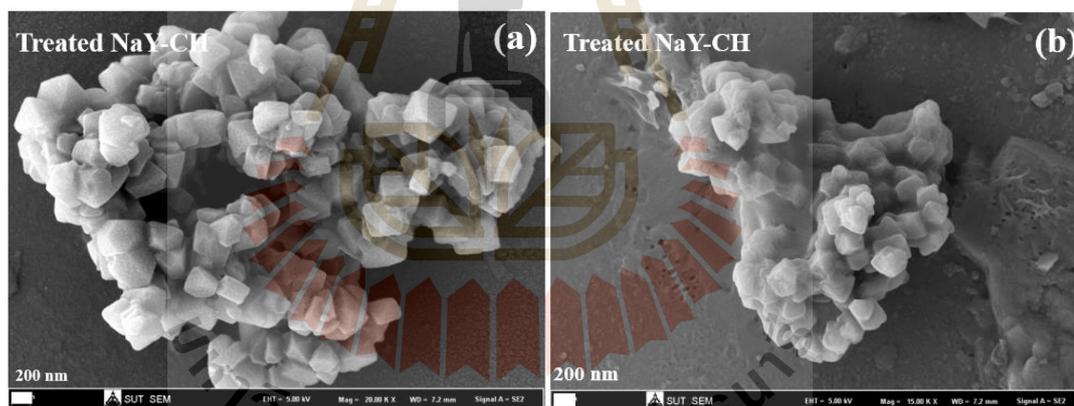
Figure 4.7 SEM images of zeolite NaY from conventional (a,b) and microwave method (c,d) after hydrothermal testing (treated NaY-CH and treated NaY-MH, respectively)
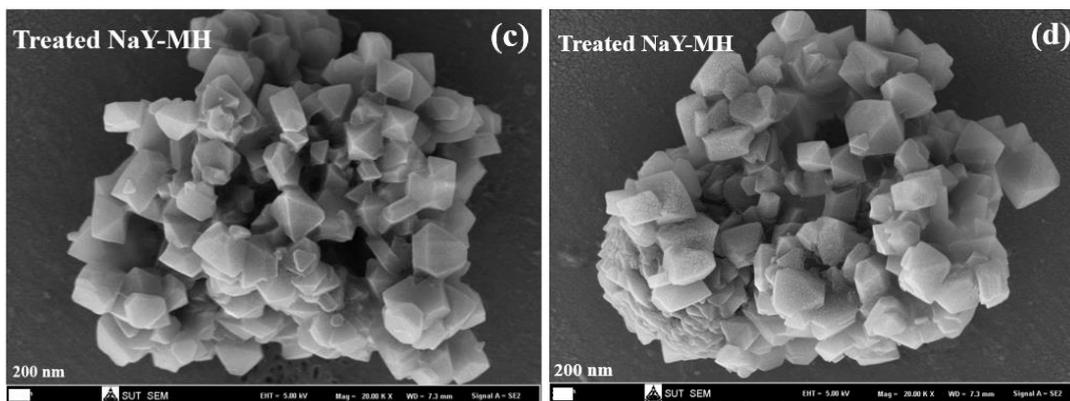
Figure 4.7 SEM images of zeolite NaY from conventional (a,b) and microwave method (c,d) after hydrothermal testing (treated NaY-CH and treated NaY-MH, respectively) (continued).

4.3 Characterization of Mg/NaY-CH and Mg/NaY-MH

XRD patterns of 10MgNaY-CH and 10Mg/NaY-MH are shown in Figure 4.8. The characteristic peaks of the zeolite NaY are still observed in both catalysts after the impregnation with Mg and calcination indicating that zeolite NaY does not collapse. The phase of MgO is not observed indicating amorphous phase or very small size (Graca et al., 2018). The intensities of the peaks of 10MgNaY-CH are similar to those of 10MgNaY-MH catalyst indicating similar crystallinity.
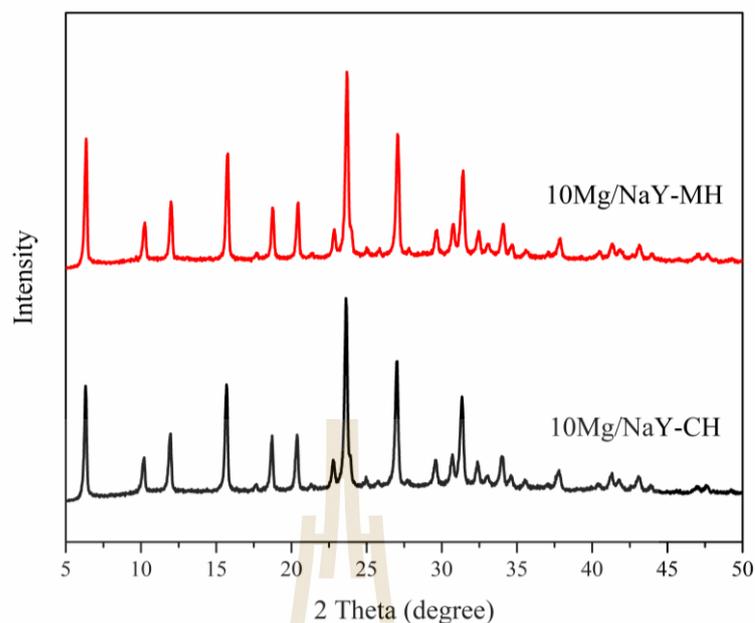
Figure 4.8 XRD pattern of 10Mg/ NaY-CH and 10Mg/ NaY-MH after calcined at 500 °C.

4.4 Catalytic performance for isomerization of glucose to fructose

The fructose yield from isomerization of glucose catalyzed by 10Mg/ NaY-CH and 10Mg/ NaY-MH were determined by IC. The results after glucose isomerization to fructose for 3 h at 100 °C on these catalysts are shown in Figure 4.9. The highest fructose yield of 10Mg/ NaY-MH is 31.25% and 10Mg/ NaY-CH is 28.81%. The fructose yields from 10Mg/ NaY-MH and 10Mg/ NaY-CH decrease similar in the second and third runs. The similar performance indicates that zeolite NaY-MH can replace NaY-CH. Graca et al. (2017) have reported that 10Mg/NaY gives fructose yield of 32.4% but high Mg leaching and coke in zeolite NaY pore. The low fructose yield may be due to incomplete glucose conversion. This result is consistent with the report by Takasaki (1967). Therefore, zeolite NaY from MH method is be used as a support similarly to NaY from CH.
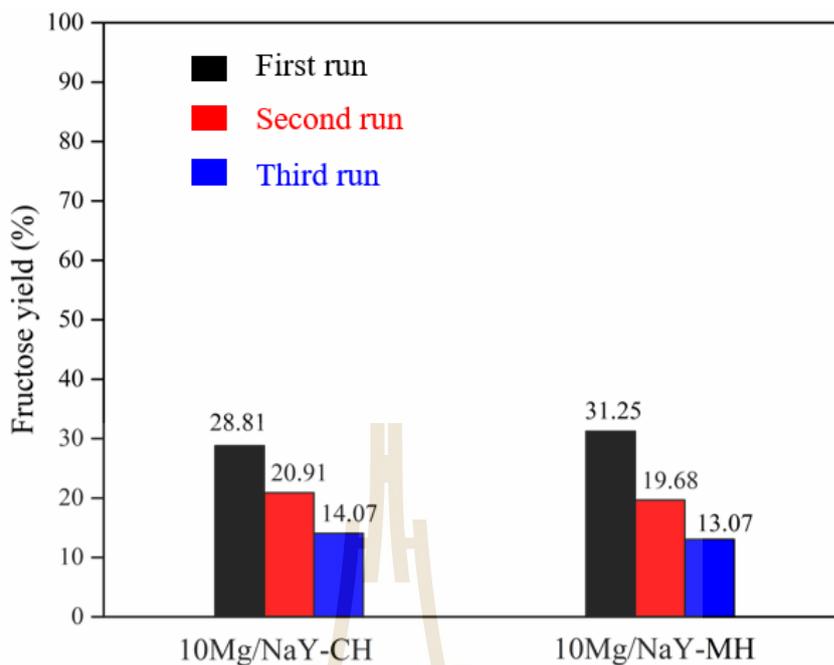
Figure 4.9 Fructose yields from glucose isomerization on 10Mg/NaY-CH and 10Mg/NaY-MH.

4.5 Characterization of 8K/NaY-CH and 8K/NaY-MH

4.5.1 Phase analysis by XRD

XRD patterns of calcine 8K/NaY-CH and 8K/NaY-MH are shown in Figure 4.10. All patterns from both methods consist of characteristic peaks of NaY indicating that the structure of zeolite NaY is retained after impregnation and calcination. Moreover, the peaks corresponding to potassium phases are not observed implying a good dispersion on the support (Rakmae et al., 2016). However, the intensity of zeolite peaks decreases, probably from hydrolysis of Si–O–Al bonds during the thermal treatment of the zeolite which is catalyzed by potassium species (Montalbo et al., 2013).
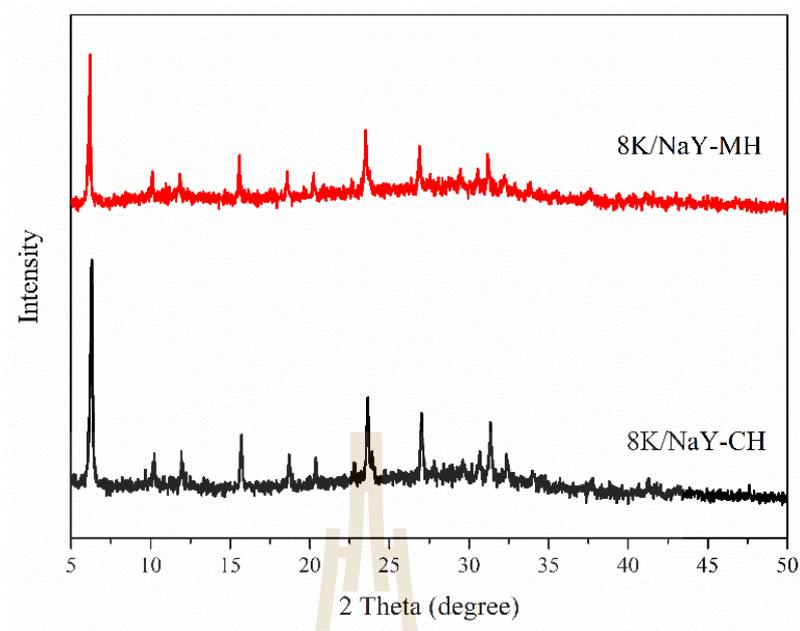
Figure 4.10 XRD patterns of 8K/NaY-CH and 8K/NaY-MH after calcined at 550 °C.

4.5.2 Thermal analysis by *in situ* XRD

In situ XRD analysis of 8K/ NaY-CH and 8K/ NaY-MH are shown in Figure 4.11. 8K/ NaY-MH and 8KNaY-CH samples retain their NaY characteristic diffraction peaks up to 750 °C and 700 °C, respectively. The crystal structure of both samples was stable at relatively high temperature. 8KNaY-MH is collapsed at higher temperature (800 °C) indicating that the NaY-MH has stronger support. After high temperature (800-900 °C) catalyst melt, then the peak of holder is observed (2Θ = 26°, 30°, 40° and 46°). The results demonstrate that NaY-MH can be used in applications under high temperature.
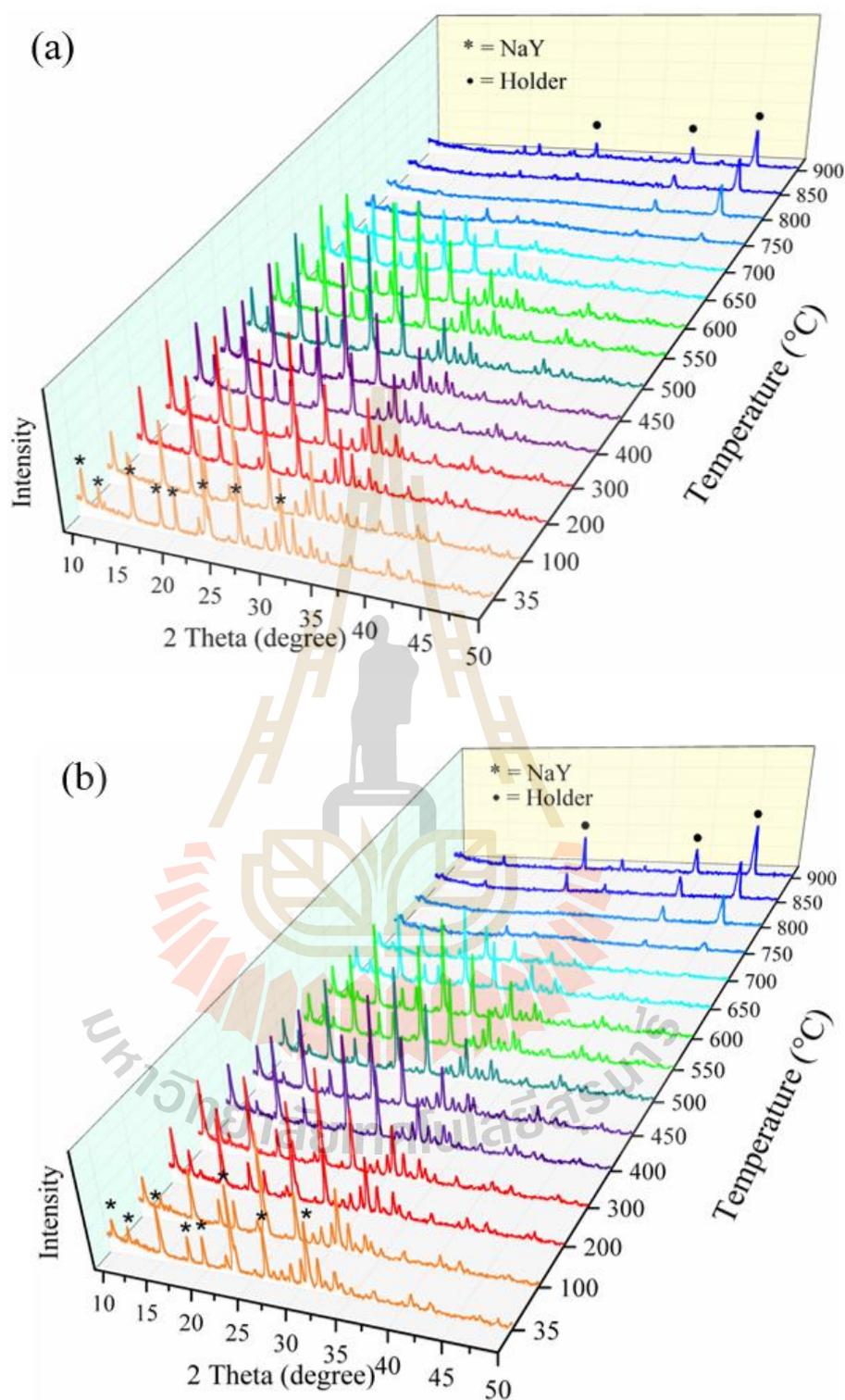
Figure 4.11 (a) *in situ* XRD pattern of 8K/ NaY-MH (b) *in situ* XRD pattern of

8K/NaY-CH.

4.5.3 Basicity analysis by CO_2-TPD

CO_2-TPD profiles reflecting the basicity of catalyst (8K/ NaY-CH and 8K/ NaY-MH) after impregnation are shown in Figure 4.12. The desorption peaks from 8K/ NaY-CH and 8K/ NaY-MH consist of two peaks at the low and high temperature, 100-350 °C and 550–750 °C, respectively. Those peaks correspond to a weak (0.120 and 0.083 mmol/ g) and a strong basic site (0.121 and 0.123 mmol/ g) (Montalbo et al., 2013). The basicity of zeolite NaY and catalysts are show in Table 1. It is remarkable that the desorption peak at low temperature of 8K/NaY-MH has weaker intensity than that of 8K/NaY-CH in spite of the presence of a stronger peak in the bare support (NaY-MH) seen in Figure 4.5. The consequence may be the result of the lower Si/Al ratio in the zeolite structure leading to the more ion-exchange capacity during impregnation of potassium precursor. When K^+ species could well exchange with the Na^+ on zeolite, the surface O^{2-} ions of framework zeolite are more abundant leading to the more strength of basic sites (Intarapong et al., 2013 and Li et al., 2014). This assumption agrees well with the larger and higher desorption peak at high temperature corresponding to the strong basic site on 8K/NaY-MH. Therefore, from the result mentioned above, the MH method can used to replace CH method. In addition, Rakmae et al. (2016) have prepared K/NaY-CH by impregnation with potassium loading 12 wt.%. The 12K/NaY shows peaks in three regions corresponding to weak, medium and strong basic sites. Therefore, the addition of potassium loading increases the basic site of catalyst.
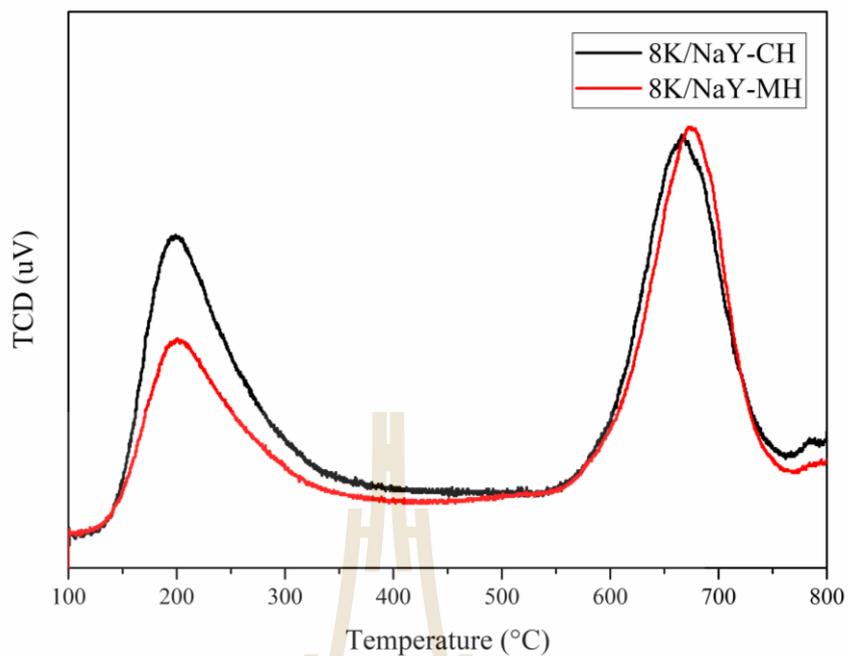
Figure 4.12 CO$_2$-TPD profiles of 8K/NaY-CH and 8K/NaY-MH catalysts.

Table 4.1 basicity of all samples determine by CO$_2$-TPD.

Samples	Basicity	
	Weak (mmol/g)	Strong (mmol/g)
NaY-CH	0.179	-
NaY-MH	0.173	-
8K/NaY-CH	0.120	0.121
8K/NaY-MH	0.083	0.123

4.6 Catalytic performance for tranwserterification reaction

The biodiesel yield from 8K/NaY-CH and 8K/NaY-MH were determined by GC. The results after transesterification of glyceryl trioctanoate for 3 h at 65 °C on these catalysts are shown in Figure 4.13. The biodiesel yield from 8K/NaY-MH is 43.8% slightly different with 8K/NaY-CH (46.8%). Noiroj et al. (2009) have reported 8KOH/NaY catalyst for transesterification of palm oil at 60 °C for 3 h. The biodiesel yield from 8KOH/NaY is 75% but this work focus on feasibility of NaY-MH with NaY-CH support in application. Therefore, the NaY from MH method is a good support for transesterification. This result indicated that the catalysts prepared from 8K/NaY-MH can be used to replace those from 8K/NaY-CH.
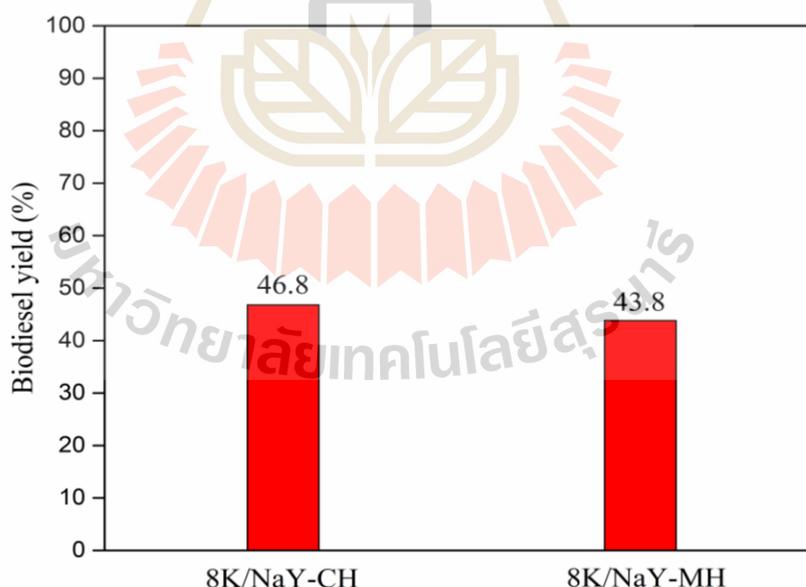
Figure 4.13 Catalytic performance of the 8K/NaY-CH and 8K/NaY-MH via transesterification.

4.7 References

Bunmai, K., Osakoo, N., Deekamwong, K., Rongchapo, W., Keawkumay, C., Chanlek, N., Prayoonpokarach, S., and Wittayakun, J. (2018). Extraction of silica from cogon grass and utilization for synthesis of zeolite NaY by conventional and microwave-assisted hydrothermal methods. **Journal of the Taiwan Institute of Chemical Engineers**. 83: 152-158.

Chandrasekhar, S., and Pramada, P. N. (2004) Kaolin-based zeolite Y, a precursor for cordierite ceramics. **Applied Clay Science**. 27: 187-198.

Graca, I., Iruretagoyena, D., and Chadwick, D. (2017). Glucose isomerisation into fructose over magnesium-impregnated NaY zeolite catalysts. **Applied Catalysis B: Environmental**. 206: 434-443.

Hamiton, K. E., Coker, E. N., Sacco, A., Dixon, A. G., and Thompson, R. W. (1993). The effects of the silica source on the crystallization of zeolite NaX. **Zeolites**. 13(8): 645-653.

Intaraponga, P., Iangthanarata, S., Phanthonga, P., Luengnaruemitchaia, A., and Jai-Inc, S. (2013). Activity and basic properties of KOH/mordenite for transesterification of palm oil. **Journal of Energy Chemistry**. 22: 690-700.

Li, Q., Wang, X., Xin, Y., Zhang, Z., Zhang, Y., Hao, C., Meng, M., Zheng, L., and Zheng, L. (2014). A unified intermediate and mechanism for soot combustion on potassium supported oxides. **Scientific Reports**. 4: 4725.

Montalbo, K. D., De Leon, R. L., Sophiphun, O., Manadee, S., Prayoonpokarach, S., and Wittayakun, J. (2013). Characterization and catalytic performance of potassium loaded on rice husk silica and zeolite NaY for transesterification of jatropha seed oil. **Quimiza Nova**. 36(8): 1116-1120.

Ng, E. P., and Mintova, M. (2008). Nanoporous materials with enhanced hydrophilicity and high water sorption capacity. **Microporous and Mesoporous Materials**. 114: 1-26.

Noiroj, K., Intarapong, P., Luengnaruemitchai, A., and Jai-In, S. (2009). A comparative study of KOH/Al_2O_3 and KOH/NaY catalysts for biodiesel production via transesterification from palm oil. **Renewable Energy**. 34: 1145-1150.

Rakmae, S., Keawkumay, C., Osakoo, N., Montalbo, K. D., de Leon, R. L., Kidkhunthod, P., Chanlek, N., Roessner, F., Prayoonpokarach, S., and Wittayakun, J. (2016). Realization of active species in potassium catalysts on zeolite NaY prepared by ultrasound-assisted impregnation with acetate buffer and improved performance in transesterification of palm oil. **Fuel**. 184: 512-517.

Rios, C. A. R., Oviedo, J. A. V., Henao, J. A. M., and Macias, M. A. L. (2012). A NaY zeolite synthesized from Colombian industrial coal by-products: Potential catalytic applications. **Catalysis Today**. 190: 61-67.

Ronson, H., and Lillerud, K. P. (2001). **Verified Syntheses of Zeolitic Materials** (2nd ed.). 156-158. Amsterdam: Elsevier.

Salama, T. M., Ali, I. O., Gumaa, H. A., Lateef, M. A., and Bakr, M. F. (2016). Novel synthesis of NaY zeolite from rice husk silica: Modification with ZnO and ZnS for Antibacterial Application. **Chemical Sciences Journal**. 7(1): 118-126.

Sápi, A., Kashaboina, U., Ábrahámné, K. B., Gómez-Pérez, J. F., Szenti, I., Halasi, H., Kiss, J., Nagy, B., Varga, T., Kukovecz, A., and Kónya, Z. (2019). Synergetic of Pt Nanoparticles and H-ZSM-5 Zeolites for Efficient CO_2 Activation: Role of Interfacial Sites in High Activity. **Frontiers in Materials**. 127.

Takasaki, Y. (1967). Kinetic and Equilibrium Studies on d-Glucosed-Fructose Isomerization Catalyzed by Glucose Isomerase from Streptomyces sp. **Agricultural and Biological Chemistry**. 31(3): 309-313.
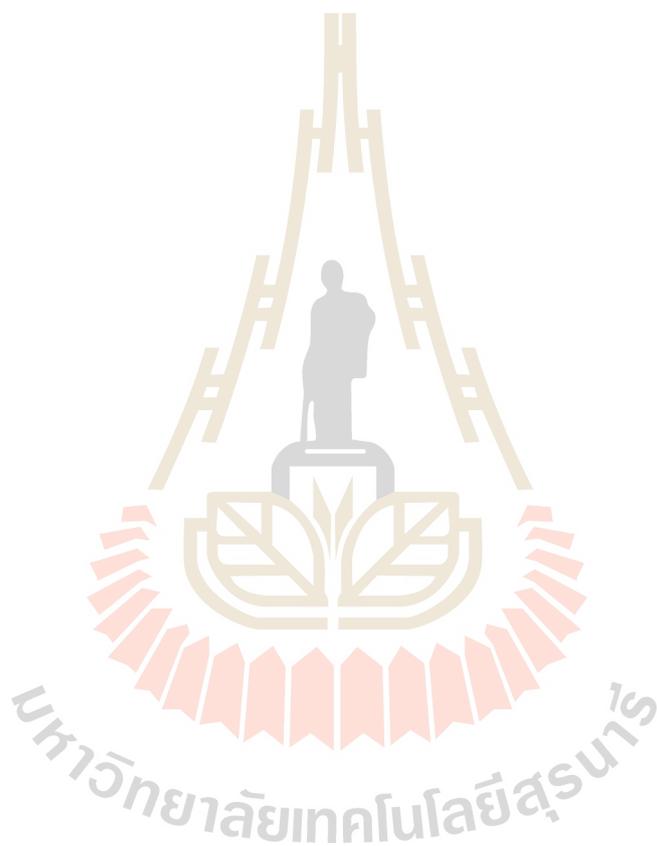
CHAPTER VI

CONCLUSIONS

The pure phase of NaY is synthesized successfully by the conventional hydrothermal (CH) at 100 °C for 24 h and microwave-assisted hydrothermal (MH) methods at 100 °C for 2 h from fumed silica. The NaY-MH has a smaller particle size and lower crystallinity than NaY-CH. The basicity of NaY-MH and NaY-CH is similar. When loaded with magnesium and potassium, the basicity is higher than the bare zeolites. The hydrothermal stability of NaY- MH method is greater than that of NaY-CH.

For the glucose isomerization to fructose, the 10Mg/NaY-CH and 10Mg/NaY-MH catalysts give the fructose yields of 28.81% and 31.25%. Meanwhile, transesterification of glyceryl trioctanoate, the 8K/NaY-CH and 8K/NaY-MH give the biodiesel yields of 46.8% and 43.8%. The catalysts in aqueous system and non-aqueous show similar performance. Thus, it can be announced that the NaY-MH has a potential to be used as a catalyst support both in aqueous and non-aqueous reaction systems instead of NaY-CH in terms of interchangeability.

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2. **Bunmai, K**., Osakoo, N., Deekamwong, K., Kosri, C., Khemthong, P., and Wittayakun, J. (2020). Fast synthesis of zeolite NaP by crystallizing the NaY gel under microwave irradiation. Materials Letters. 272: 127845