# Single-step conversion of xylose to furfural and furfuryl alcohol on zeolite-based catalyst

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A Thesis Submitted in Partial Fulfillment of the Requirements
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# การแปลงไซโลสเป็นเฟอร์ฟิวรัลและเฟอร์ฟิวริลแอลกอฮอล์บนตัวเร่งปฏิกิริยาซีโอไลต์ในขั้นตอนเดียว

น.ส.จิราพัชร ฉัตรกวีกุล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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| By | Miss Jirapat Chatkaweekoon |
| Field of Study | Chemical Engineering |
| Thesis Advisor | Professor JOONGJAI PANPRANOT, Ph.D. |

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จิราพัชร ฉัตรกวีกุล : การแปลงไซโลสเป็นเฟอร์ฟิวรัลและเฟอร์ฟิวริลแอลกอฮอล์บนตัวเร่งปฏิกิริยาซีโอไลต์ในขั้นตอนเดียว. ( Single-step conversion of xylose to furfural and furfuryl alcohol on zeolite-based catalyst) อ.ที่ปรึกษาหลัก : ศ. ดร. จูงใจ ปั้นประณต

เฟอร์ฟิวรัลมีศักยภาพที่ใช้เป็นสารประกอบแพลตฟอร์มสำหรับการสังเคราะห์สารเคมีหลากหลายชนิดโดยเฉพาะอย่างยิ่งเฟอร์ฟิวริลแอลกอฮอล์ ซึ่งเป็นสารมัธยันตร์สำคัญที่ใช้ผลิตเป็นสารเคมีมูลค่าสูง ในงานวิจัยนี้ตัวเร่งปฏิกิริยาซีโอไลต์หลากหลายชนิดที่อยู่ในรูปแบบไฮโดรเจนถูกนำมาใช้เป็นตัวเร่งปฏิกิริยาสำหรับการแปลงไซโลสเพื่อผลิตเป็นเฟอร์ฟิวรัลและเฟอร์ฟิวริลแอลกอฮอล์ในขั้นตอนเดียว ปฏิกิริยาดำเนินการภายใต้อุณหภูมิ 130 องศาเซลเซียส ความดันไฮโดรเจน 30 บาร์ และเวลาในการทำปฏิกิริยา 2 ชั่วโมง ชนิดของไซต์กรด (ลิวอิสและบรอนสเตต) มีความสำคัญต่อการเร่งปฏิกิริยาและการกระจายตัวของผลิตภัณฑ์ ไซต์กรดบรอนสเตตส่งเสริมการเลือกเกิดเป็นเฟอร์ฟิวรัล ในขณะที่ไซต์กรดลิวอิสส่งเสริมการเกิดไฮโดรจีเนชั่นเป็นเฟอร์ฟิวริลแอลกอฮอล์หรือไซลิทอล ตัวเร่งปฏิกิริยา HY-500 ให้ค่าการแปลงของไซโลสที่สูงถึง 61.7 เปอร์เซ็นต์ และค่าการเลือกเกิดเป็นเฟอร์ฟิวรัลและเฟอร์ฟิวริลแอลกอฮอล์ที่ดีที่สุด ที่ 58.5 เปอร์เซ็นต์ และ 8.8 เปอร์เซ็นต์ตามลำดับ นอกจากนั้นโครงสร้างของตัวเร่งปฏิกิริยาซีโอไลต์ก็เป็นปัจจัยสำคัญที่ส่งผลต่อการเข้าถึงของสารตั้งต้นและผลิตภัณฑ์ภายในรูพรุนของตัวเร่งปฏิกิริยาซีโอไลต์เพื่อให้การเกิดปฏิกิริยาภายในรูพรุนทำได้ง่าย การวิเคราะห์คุณลักษณะของตัวเร่งปฏิกิริยาใช้เทคนิคการดูดซับทางกายภาพโดยโมเลกุลโพรบไนโตรเจน การเลี้ยวเบนของรังสีเอ็กซ์ กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด เอ็กเรย์ แบบเทคนิคการเรืองรังสี เครื่องวิเคราะห์โครงสร้างด้วยเทคนิคเอ็นเอ็มอาร์ การคายซับแอมโมเนียด้วยการโปรแกรมอุณหภูมิ และเทคนิคไพริดีนอินฟราเรดสเปกโตรสโกปี

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KEYWORD: One-step xylose conversion, Zeolite catalyst, Furfural, Furfuryl alcohol

Jirapat Chatkaweekoon : Single-step conversion of xylose to furfural and furfuryl alcohol on zeolite-based catalyst. Advisor: Prof. JOONGJAI PANPRANOT, Ph.D.

Furfural possesses the potential to be utilized as a platform compound for the synthesis of a wide variety of chemicals, especially furfuryl alcohol, which is an important intermediate used to produce high-value chemicals. In this research, several types of zeolite catalysts in hydrogen form are used as catalysts for conversion of xylose to produce furfural and furfuryl alcohol in one step. The reaction is carried out under 130°C, 30 bar hydrogen pressure, and 2 h reaction time. Acid site types (Lewis and Bronsted) are important for the catalysis and distribution of the product. Bronsted acid sites promote xylose dehydration to furfural production. On the other hand, Lewis acid sites promote hydrogenation to furfuryl alcohol or xylitol. The HY-500 catalyst provides high conversion of xylose at 61.7 percent and the highest selective to furfural and furfur alcohol at 58.5 percent and 8.8 percent, respectively. In addition, the structure of the zeolite catalyst is also an important factor affecting the accessibility of the reactants and products within the pores of the zeolite catalyst to facilitate the reaction within the pore. The characterization of the catalyst using $N_2$-physisorption, X-ray diffraction, SEM, XRF, $^{27}$Al and $^{29}$Si solid-state NMR, $NH_3$-TPD and pyridine infrared spectroscopy technique.

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Jirapat Chatkaweekoon

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# CHAPTER I

# INTRODUCTION

## 1.1 Introduction

In recent years, the progress in the production of green chemistry has been greatly improved to reduce the environmental problems that arise with the sustainable development of reducing and replacing fossil sources into renewable sources [1]. The challenge to convert biomass into chemicals and fuel is to control the removal of functional groups that contain oxygen. There are two ways to eliminate oxygen from biomass: dehydration and another is decarbonylation or decarboxylation. Dehydration is an interesting route as it can eliminate oxygen from biomass without reducing the carbon atoms in the raw material. In addition, there is no $CO_2$ emission which is a cause of global warming [2].

Furfural is used in a wide range of industries, not only as a solvent but also as a platform compound used for the synthesis of a wide variety of chemicals such as furfuryl alcohol and linear alkanes. Moreover, Furfural has the potential to be used for the biofuel, biochemical, and biopolymer industrial. Furfural can be used as a monomer for many types of polymers such as polyester, polyimide, and polyurethane [3-5].

Furfuryl alcohol, a high-value green chemical, was produced from furfural. It is widely used in the production of chemically stable resins, fibers, polymer and essential medicine as well as an important intermediate in the production of a valuable chemical such as levulinic acid [1, 6, 7].

Xylose has been used to produce furfural in the industrial sector by xylose dehydration using acid catalysts [8]. The most interesting catalyst among many acid catalysts is zeolite, a heterogeneous acid catalyst that has interesting properties such as large surface area, crystalline structure, uniform pore size that can adjust the acidity [9].

It also has hydrothermal stability and is easy to separate from the product [2]. It makes zeolite an acid catalyst capable of promoting dehydration of xylose without using metal [10]. Furfuryl alcohol is produced from the hydrogenation of furfural on metal catalysts, in which many studies focused on noble metal catalysts [1]. An effective catalyst, platinum, facilitates the partial hydrogenation of furfural to furfuryl alcohol [11].

In this framework, zeolites were used as catalysts to study the effect of zeolite acidity and zeolite structure such as H-ZSM-5, H-beta, HY as well as HY with hierarchical structure on the single step production of furfural and furfuryl alcohol conversion from xylose.

## 1.2 Objectives of the Research

Study the effects of zeolite structure and acidity in single-step conversion of xylose to furfural and furfuryl alcohol.

## 1.3 Scope of the Research

1.3.1 The acidity of zeolite catalysts, including HY zeolite with different Si / Al ratio from 15-500 were tested in the liquid-phase conversion of xylose in a batch reactor at constant temperature 130°C and pressure 30 bar in hydrogen for 2 h using water:2-propanol (1:1) as a solvent.

1.3.2 The zeolite structure such as H-ZSM-5, H-beta, HY zeolite with Si / Al ratio of 500 and hierarchical HY zeolite were tested in the liquid-phase conversion of xylose in a batch reactor at constant temperature 130°C and pressure 30 bar in hydrogen for 2 h using water:2-propanol (1:1) as a solvent.

1.3.3 The HY-500 catalyst was tested in the liquid-phase conversion of xylose in a batch reactor at high reaction temperature 150°C and pressure 30 bars in hydrogen for 2 h using water:2-propano (1:1) as a solvent.

1.3.4 The catalyst was tested in the liquid-phase conversion of xylose over HY-500 zeolite in a batch reactor at reaction temperature 130°C in the absence of $H_2$ pressure (30 bar $N_2$) for 2 h using water:2-propano (1:1) as a solvent.

1.3.6 Characterization of the catalysts by various method including

1.3.7.1 X-ray diffraction (XRD)

1.3.7.2 Scanning electron microscope (SEM)

1.3.7.3 $N_2$ physisorption

1.3.7.4 X-Ray Fluorescence Spectrometer (XRF)

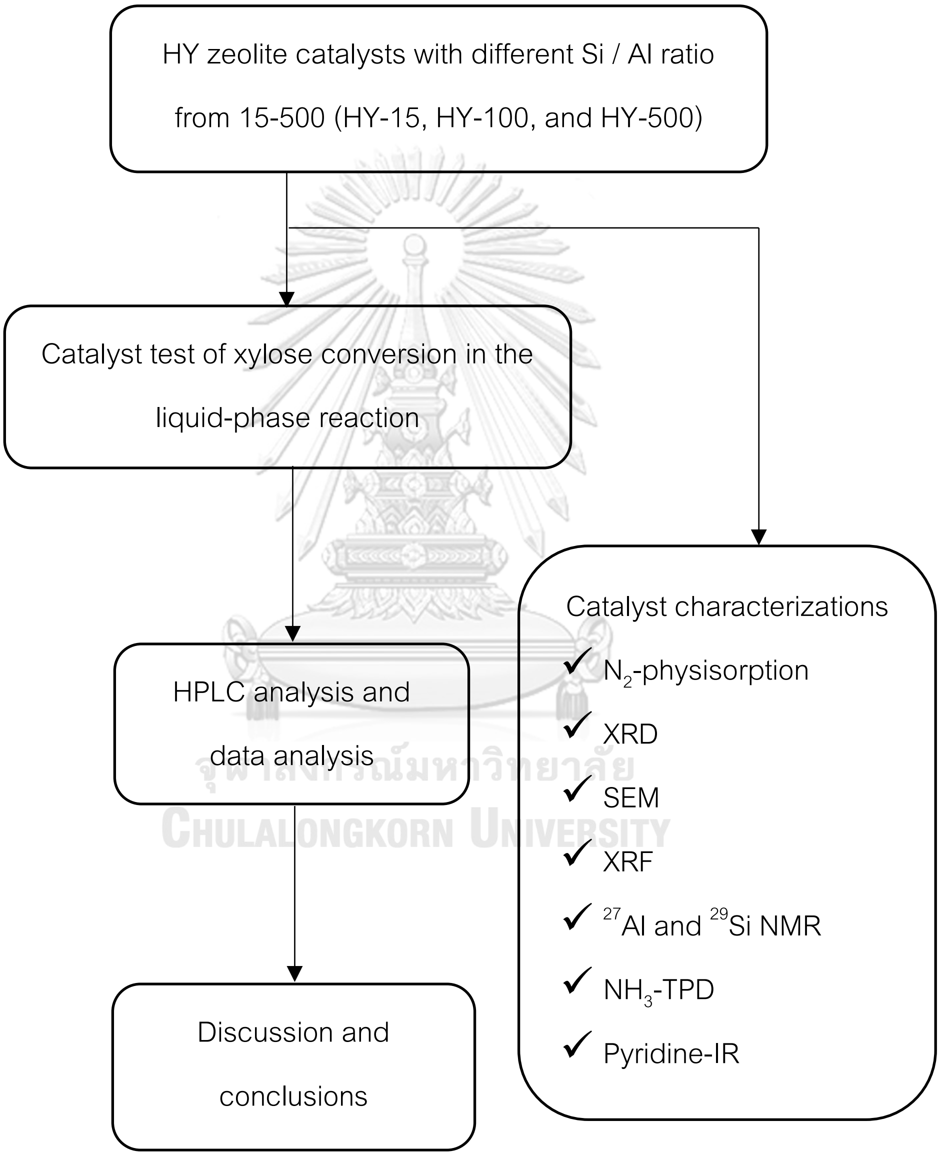
1.3.7.5 Fourier Transform Nuclear Magnetic Resonance Spectrometer (solid stated NMR)

1.3.7.4 Temperature-programmed desorption of ammonia ($NH_3$-TPD)

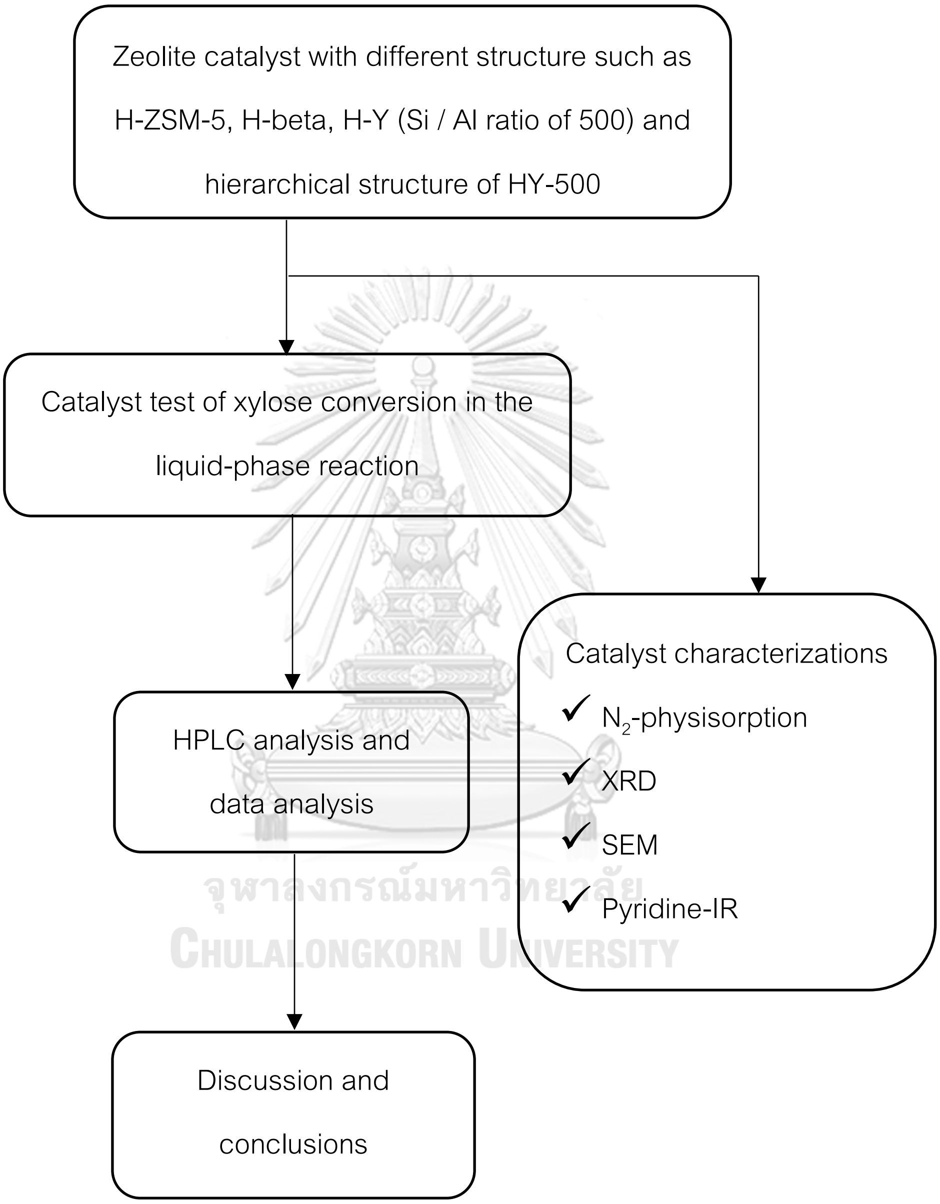
1.3.7.5 Pyridine-IR

### 1.4 Research Methodology

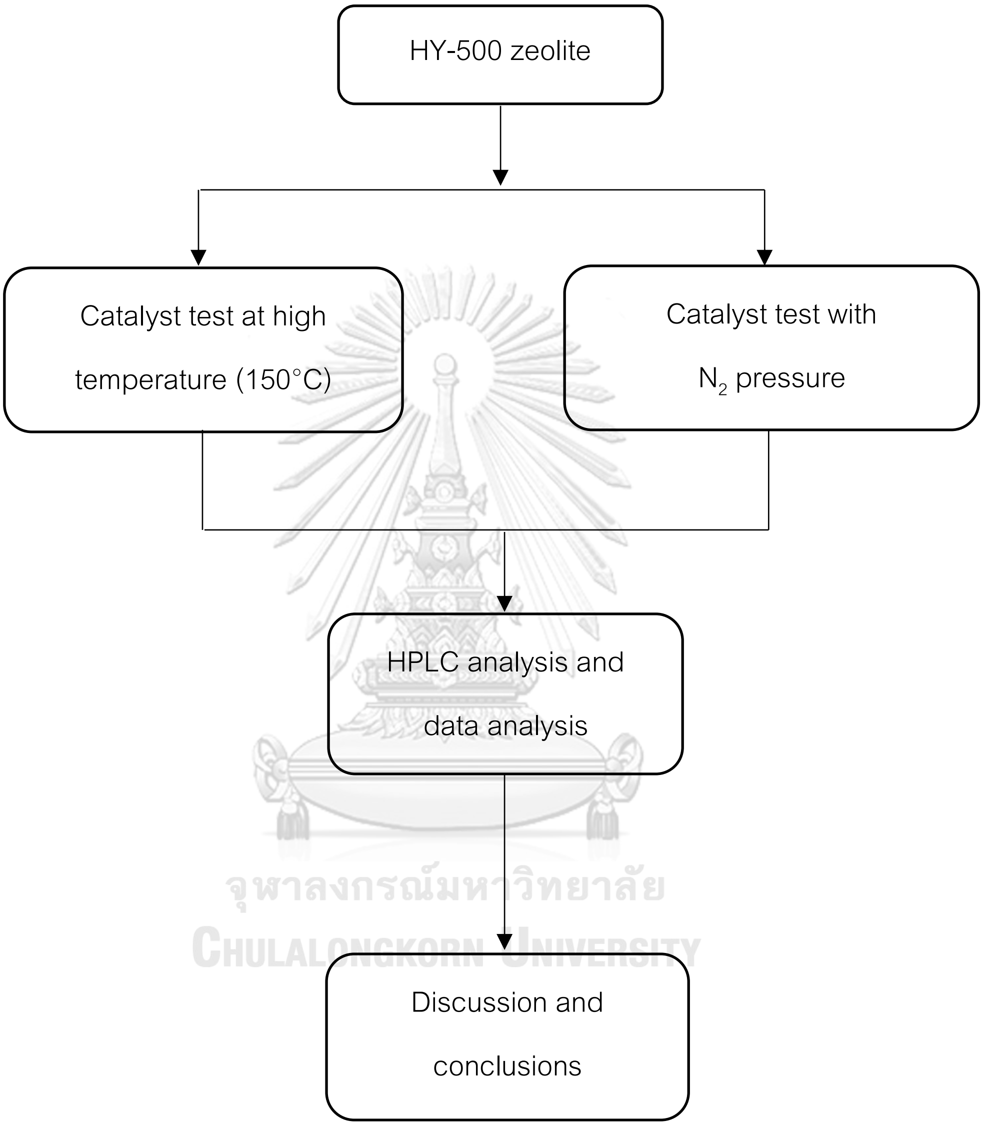
**Part I.** The investigation of the effect of acidity on HY zeolites with different Si / Al ratios from 15 to 500 by examining the characteristics and the catalytic activity for the one-step conversion of xylose to furfural and furfuryl alcohol.



**Part II.** The study of the effect of zeolite structure and its characteristics for a single-step reaction in the conversion of xylose to furfural and furfuryl alcohol.



**Past III** Study the effect of temperature and the different environment on the reaction of xylose to furfural and furfuryl alcohol in one step.



# CHAPTER II

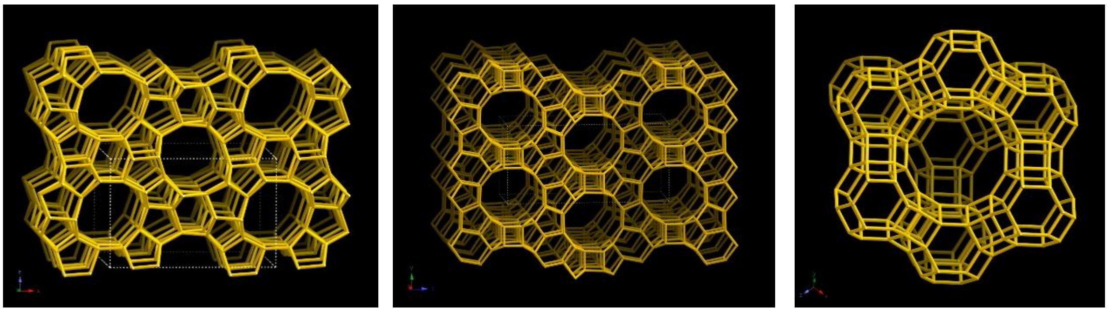
# BACKGROUND AND LITERATURE REVIEW

## 2.1 Dehydration Reactions

In chemical reactions, dehydration reaction is a chemical reaction between two compounds that involves the loss of water molecules from the substrate. In general, the dehydration reaction begins with a single molecule and creates a new molecule along with the water molecule. These reactions occur frequently in organic chemistry [12].

## 2.2 Zeolite support catalyst

Zeolite is a very stable compound that can provide good resistance to experimental conditions. Their high melting and boiling points make them stable under high temperature conditions. In addition, zeolites are resistant to high pressure and organic/inorganic solvents. Although zeolite catalysts are used extensively, their role in catalysts in the industrial sector is increasing, especially because of their shape selection and acidity/basicity properties. It is then used in petroleum refineries and petrochemical plants as a catalyst [13]. The three-dimensional structure of the zeolite is shown in **Figure 1**. The channel structure presents in **Figure 1 (a)** and **Figure 1 (b)** for H-ZSM-5 (5.1 × 5.5 Å ↔ 5.3 × 5.6 Å) and H-β (6.6 × 6.7 Å ↔ 5.1 × 5.6 Å), respectively. H-Y Faujasite system (7.4 Å for all directions) and cavity presence of approximately 13 Å as shown in in **Figure 1 (c)** [2, 14, 15].



(a) MFI (ZSM-5): <010> (b) BEA (beta): <100> (c) FAU (Faujasite): <111>

Figure 1 zeolite framework : (a) ZSM-5, (b) beta and (c) Y zeolite

### 2.3 Dehydration of xylose to furfural

Furfural is a versatile chemical platform for producing value-added chemicals. For example, pharmaceutical intermediates, fuel additives, solvents, including the synthesis of a variety of chemicals such as furfuryl alcohol. Furfural production through the dehydration of xylose by heterogeneous catalysts is described as follows: The reaction mechanism generally relies on the acidity of the Brønsted catalyst. The formation of xylulose, isomerization of xylose, is produced while modified by using Lewis acid site. The presence of Lewis acid sites shows the reaction pathway to the xylose-xylose-furfural route. The active catalyst for promoting the dehydration reaction of xylose to furfural should have both the acidity of both Lewis and the Brønsted sites [16].

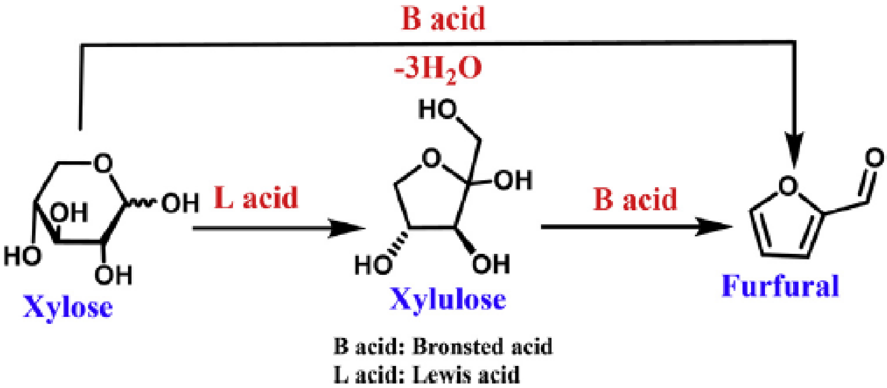


Figure 2 Schematic of furfural production route from xylose

**Table 1** Summary of the research of xylose dehydration to the furfural hydrogenation on various catalysts under different reaction condition

| Researcher | Studies | Catalyst and preparation method | Reaction condition | Results |
|---|---|---|---|---|
| Kim, S.B., et al. (2011) [14] | Dehydration of D-xylose to furfural over a variety of H-zeolites with the various $SiO_2$/Al2$O_3$ molar ratios in several solvent systems including water, DMSO, and water/toluene. | H-ferrierite,<br>H-β,<br>H-ZSM-5,<br>H-Y,<br>H-mordenite,<br>$SiO_2/Al_2O_3$,<br>γ-$Al_2O_3$ | 0.20 M D-xylose,<br>30 ml of solvent (water, DMSO, and water/toluene (3:7 by volume));<br>T = 140°C, reaction time = 4 h | - D-xylose conversion and furfural yield decreases with increasing $SiO_2/Al_2O_3$ molar ratio of H-zeolite.<br>- The highest furfural selectivity found in H-β in water and water/toluene<br>- The highest furfural selectivity found in H-mordenite in DMSO |
| Choudhary, V. et al. (2012) [3] | Studied Lewis and Brønsted acid catalysts for the conversion of xylose to furfural | Lewis acid, $CrCl_3$<br>Brønsted acid, HCl | T = 378 - 418 K<br>(105 - 145°C)<br>Solvent = water, | The optimum conditions which lead to the maximum furfural yield, 76% yield of furfural, appear in the combination of Lewis and |

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| | | | water:toluene (1:1)<br>Reaction time = 2 - 8 h | Brønsted acid catalysts when using the water-toluene biphasic system at 413 K for 120 min |
| You, S.J. (2014) [17] | Studied on the improvement of catalytic activity by dealumination or desilication H-ZSM-5 for D-xylose dehydration | - H-ZSM-5<br>- Acid treatment; H-ZSM-5 was treated with 1–3 M of HCl at 90°C for 24 h.<br>- Alkaline treatment; H-ZSM-5 was treated with 0.2–0.6 M of NaOH at 65°C for 2 h. Filtration, washing and drying<br>at 120°C. Ion-exchange solid in 0.1 M of | 0.20 M D-xylose,<br>30 mL of water, catalyst weight = 0.30 g, reaction temperature = 170°C,<br>reaction time = 1 h. | - D-xylose conversion is slightly less for dealuminated H-ZSM-5, but similar conversion for desilicated H-ZSM-5 when compared to the parent catalyst H-ZSM-5<br>- The dealuminated H-ZSM-5 demonstrates the highest furfural selectivity |

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| | | $NH_4NO_3$ to converted Na-form into the H-form and calcination<br>in air at 600 "C | | |
| García-Sancho, C. et al. (2014) [4] | Studied the different types of support niobia catalysts by testing in the dehydration of xylose to furfural | The different amounts of $Nb_2O_5$ (4, 12 and 20 wt%) was impregned onto the different support (MCM-41, SBA-15, $SiO_2$, $\gamma$-$Al_2O_3$) by incipient wetness impregnation method | T = 160°C<br>P = 15 bar $N_2$<br>Solvent = water:toluene (1:1)<br>Reaction time = 24 h | - $Nb_2O_5$ content at 12 wt% increases furfural selectivity<br>- Maximum conversion and furfural selections after 24 h (84% and 93% respectively) were found for SBA-12Nb catalysts at 160°C in water/toluene<br>- The use of toluene as a co-solvent improves the furfural selectivity when compared to using |

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| | | | | only water as a solvent. |
| Mishra, R. K. et al. (2019) [18] | Studied the catalytic performance of Zn doped CuO NPs compared with ZnO NPs, ZnO bulk, CuO NPs and CuO bulk catalysts to test the dehydration reaction of xylose to furfural | Zn doped CuO nanoparticles (NPs), ZnO NPs and CuO NPs were prepared by a sonochemical method | Catalyt to reactant ratio (wt%/wt%) = 1:50, 1:10, 1:5<br>Solvent = water<br>T = 80, 150, 180°C<br>Reaction time = 2,4,8,12 h | Zn doped CuO NP with a catalyst to xylose ratio 1:5 enhances the catalytic activity and allows the conversion of xylose to a complete furfural at 86% furfural yield under the optimum temperature of 150 °C within 12 hours without other by-products. |
| Tran, T. T. V. et al. (2019) [19] | Studied the selective dehydration of xylose to furfural using a sulfonic acid-functionalized mesoporous | 0.1-$SO_3H$-KIT-6,<br>0.2-$SO_3H$-KIT-6,<br>0.3-$SO_3H$-KIT-6 were prepared by a co- | T = 130-170°C<br>Solvent = water:toluene (1:1)<br>Reaction time = 1-3 h | The suitable catalyst is 0.2-$SO_3H$-KIT-6 which gives both high activity and furfural selectivity more than 94% at 170°C for 2 h |

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| | silica KIT-6 type catalyst in a water/toluene biphasic system | condensation reaction | | |

Kim, S.B., et al. (2011) [14] studied the various $SiO_2/Al2O_3$ molar ratios of H-zeolite, including H-ferrierite, H-β, H-ZSM-5, HY, and H-mordenite in different solvents such as water, dimethyl sulfoxide (DMSO) and water/toluene for the conversion of xylose in a liquid phase to furfural production. Increasing of $SiO_2/Al_2O_3$ molar ratio of H-zeolite, D-xylose conversion and furfural yield are decreased regardless of the solvent type. In the solvent system, D-xylose conversion and furfural selectivity decreased in the following order. water/toluene> DMSO> water. The highest furfural selectivity found in H-β while water and water/toluene are used as a solvent. In opposite, DMSO showed the highest furfural selectivity, when H-mordenite is used as a catalyst.

Choudhary, V. et al. (2012) [3] studied Lewis and Brønsted acid catalysts for the conversion of xylose to furfural. Lewis acid, $CrCl_3$, is used to xylose isomerization to xylose, and Brønsted acid, HCl, is used for furfural production from xylulose dehydration. The furfural yield is improved when the combination of Lewis and Brønsted acid is used. In a biphasic system for the combination of catalysts functionalities, 76% furfural yield is obtained at low temperature and short time (413 K and 120 min, respectively). In this work indicate that the pathway of xylose conversion to furfural is changed in the presence of the combined Lewis and Brønsted acids compared to the reaction in only Brønsted acids.

You, S.J. (2014) [17] suggested that the conversion of D-xylose increases with increasing zeolite channels, but H-ZSM-5 has a channel size similar to the furfural molecule, resulting in the highest furfural selectivity. To improve the catalytic activity, H-

ZSM-5 was dealuminated or desilicated with an aqueous solution of HCl or NaOH, respectively. After the dealuminated H-ZSM-5, the total amount of acid sites slightly decreased. On the other hand, the desilicated H-ZSM-5 significantly decreased. The dealuminated H-ZSM-5 has slightly less D-xylose conversion, desilicated H-ZSM-5 with mesopores represents a similar D-xylose conversion when compared to the parent H-ZSM-5 catalyst. In a similar conversion, furfural selectivity increases with enhancing dealumination in H-ZSM-5 zeolite.

García-Sancho, C. et al. (2014) [4] studied the different types of support $Nb_2O_5$ catalysts by testing in the dehydration of xylose to furfural for explaining the effects of different supports. The amount of $Nb_2O_5$ that is loaded and the influence of the monophasic water and biphasic water/toluene system. that the amount of $Nb_2O_5$ that is loaded has almost no effect on the dehydration activity of xylose, but the 12 wt.% of $Nb_2O_5$ shows a higher furfural selectivity. The SBA-12Nb catalysts were confirmed to have a highest conversion of xylose up to 84% and 93% for furfural selectivity in a water/toluene at 160°C for 24 h. Comparison of systems that are monophasic water and biphasic water/toluene, although it rarely affects the xylose dehydration activity. When toluene is used as a co-solvent in the reaction, the selectivity of furfural is improved.

Mishra, R. K. et al. (2019) [18] studied the catalytic performance of Zn doped CuO NPs compared with ZnO NPs, ZnO bulk, CuO NPs and CuO bulk catalysts to test the dehydration reaction of xylose to furfural. The Zn doped CuO catalyst shows improved activity and selectivity compared to the CuO and ZnO catalysts. The synthesized Zn doped CuO nanoparticles (NPs) have a large surface area which enhances the catalytic activity and allows to completely convert the xylose to furfural at 150°C in 12 hours without the side product. Furfural yield is as high as 86 mol% compared to the catalysts ZnO NPs, ZnO, CuO NPs and CuO, which 45 mol% furfural yields.

Tran, T. T. V. et al. (2019) [19] Studied the selective dehydration of xylose to furfural using a sulfonic acid-functionalized mesoporous silica KIT-6 type catalyst in a water/toluene biphasic system. The sulfonic acid-functionalized KIT-6 mesoporous silica was prepared with different molar ratio (0.1-$SO_3H$-KIT-6, 0.2-$SO_3H$-KIT-6, and 0.3-$SO_3H$-KIT-6) by a co-condensation reaction. The 0.2-$SO_3H$-KIT-6 provides high xylose conversion and the highest selectivity of furfural in the dehydration reaction of the xylose. In addition, the three-dimension structure of KIT-6 mesoporous silica is an important factor that can overcome the limitation of pore diffusion, both the reactant and the products that occur in dehydration reaction.

## 2.4 Conversion of xylose to furfuryl alcohol in single-step reaction

The production of furfuryl alcohol from biomass is carried out in two steps. The dehydration of xylose to furfural occurs on the acid catalyst. Then, furfuryl alcohol is subsequently produced from furfural hydrogenation on metal catalysts. This alcohol is caused by the selective hydrogenation of the C = O bond of the furfural molecule. The co-existence of the acid site and the metal site can promote the production of furfuryl alcohol from xylose in one step [1, 8].

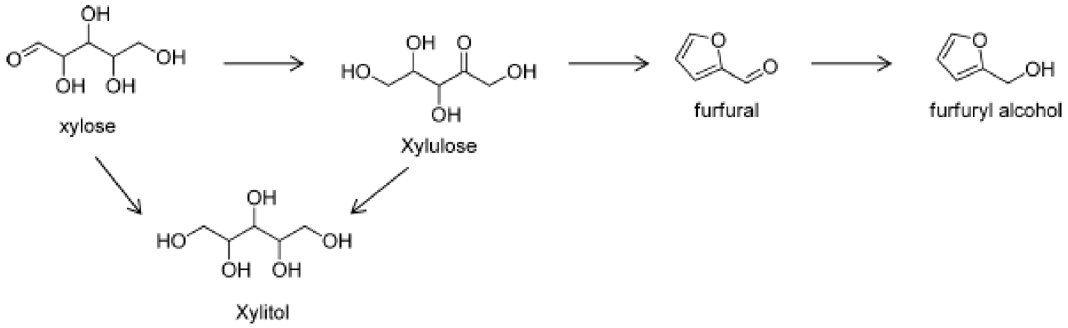


**Figure 3** Schematic of xylose conversion to furfuryl alcohol

**Table 2** Summary of the research of xylose conversion to furfuryl alcohol in single-step reaction on various catalysts under different reaction condition

| Researcher | Studies | Catalyst and preparation method | Reaction condition | Results |
|---|---|---|---|---|
| Perez, R. F. et al (2014) [20] | Studied the dual catalyst system composed of $Pt/SiO_2$ and sulfated $ZrO_2$ as metal and acid catalysts in | $SiO_2$,<br>$ZrO_2$-$SO_4$,<br>$Pt/SiO_2$,<br>$SiO_2$+ ZrO2-$SO_4$,<br>$Pt/SiO_2$+ ZrO2-$SO_4$<br>-$Pt/SiO_2$ was obtained by | T = 110-170°C<br>P = 30 bar $H_2$<br>Solvent = $H_2O$:2-propanol at | - Furfural and furfural alcohol are more balanced at 130 ° C<br>- Furfural alcohol selectivity of up to 50% can be |

| | | | | |
|---|---|---|---|---|
| | one-pot production of furfuryl alcohol from xylose | incipient wetness impregnation method, calcined at 500°C for 4 h under synthetic air and reduced at 500°C for 1 h<br>- $SiO_2$ or $Pt/SiO_2$ was mixed with ZrO2-$SO_4$ in the reactor (physical mixture) | 1:0, 1:1, 1:2 and 1:3<br>Reaction time = 6 h | achieved at the ratio $H_2O$ - 2-propanol at 1: 3. |
| Paulino, P. N. et al (2017) [10] | Studied dehydration and transfer hydrogenation tandem reactions of xylose to furfuryl alcohol in water/isopropanol were performed on zeolites catalysts (MFI, FAU and BEA). | ZSM-5, USY and beta-type zeolite | T = 130°C<br>P = 30 bar $N_2$<br>Catalyst = 0.25 g<br>Solvent = $H_2O$:2-propanol (IPA) 1:0.007, 1:1, 0.0026:1<br>Reaction time = 6 h | - The large amount of water (water:IPA 1: 0.007) inhibit the catalytic activity of the catalyst<br>- The large amount of IPA (water:IPA 0.0026: 1), the catalytic activity of the catalyst was improved.<br>- The highest selectivity of |

| | | | | |
|---|---|---|---|---|
| | | | | 75% was accomplished on zeolite beta |
| Canhaci, S. J. et al (2017) [8] | Studied the conversion of xylose to furfuryl alcohol in one step over Pt catalysts supported on ordered mesoporous SBA-15 bearing $SO_3H$ acid groups. | Pt/SBA-15, Pt/SBA-15-$SO_3H$ (12), Pt/SBA-15-$SO_3H$ (20), Pt/SBA-15-$SO_3H$ (28), were obtained by incipient wetness impregnation method<br>- Calcined in a synthetic air (20 vol%$O_2$/$N_2$) for 4 h at 200°C<br>- Reduced for 1 h under $H_2$ stream at 200°C | T = 130°C<br>P = 30 bar $H_2$<br>Solvent =$H_2O$:2-propanol (1:1)<br>Reaction time = 6 h | - The unmodified Pt/SBA-15 catalyst contains xylitol as the main product (selectivity of 45%)<br>- Modification by grafting organosulfonic groups on catalyst surface successfully resulted in 83-87% furfuryl alcohol selectivity in direct xylose conversion. |
| Perez, R. F et al (2017) [1] | Studied Pt/$ZrO_2$-$SO_4$ catalysts with different acid/metal ratios were prepared | Pt/$ZrO_2$-$SO_4$ was prepared by incipient wetness impregnation method to | T = 130°C<br>P = 30 bar $H_2$<br>Solvent =$H_2O$:2- | Pt/$ZrO_2$-$SO_4$ catalyst with acid/metal ratio of 142 promote one-step xylose |

| | | | | |
|---|---|---|---|---|
| | and investigated in the xylose conversion | obtained 1 wt.% Pt<br>- Calcined in a synthetic air for 4 h at 500°C | propanol (1:1)<br>Reaction time = 6 h<br>- $Pt/ZrO_2$-$SO_4$ catalyst with acid/metal ratio of 69, 142 and 532 | conversion to furfuryl alcohol |
| Perez, R. F et al (2018) [6] | Studied of 1D multiwalled carbon nanotubes (MWCNT) supported noble metal catalysts (Pt, Pd, Ru, Rh and Au) to evaluate the xylose conversion reaction | - Nanocyl 3100 was reflux with nitric acid at 130°C for 3 h to obtained MWCNT.<br>- 1 wt.% of noble metal (Pt, Pd, Ru, Rh) is impregnated onto the MWCNT by incipient wetness impregnation method, thermal treated at 200°C | T = 130°C<br>P = 30 bar $H_2$<br>Solvent =$H_2O$:2-propanol (1:1)<br>Reaction time = 6 h | The main product formed on noble metals is xylitol. The most active metal, Ru, can promote xylose direct hydrogenation to 85% yield of xylitol. Furfuryl alcohol tends to be found in metal catalysts, Pd and Rh. |

| | | | | |
|---|---|---|---|---|
| | | for 1 h under $N_2$ and reduced at 100°C for 3 h under $H_2$<br>- Au/MWCNT was prepared by colloidal method, calcined at 350°C for 1 h and reduced at 350°C for 3 h | | |
| Deng, T. Et al (2020) [7] | Studied the appropriate conditions for one-pot cascade conversion of xylose to furfuryl alcohol using bifunctional Cu/SBA-15-$SO_3H$ catalyst | - A series of sulfonic acid functionalized SBA-15 carriers was synthesized by the co-condensation method<br>- Cu/SBA-15 was obtained by impregnation process | T = 110-160°C<br>P = 1-5 MPa $H_2$<br>Solvent = $H_2O$: n-butanol<br>Reaction time = 6 h | - A bifunctional Cu/SBA-15-$SO_3H$ catalyst shown high yield up to 62.6%<br>- The optimized conditions of 140 °C, 4 MPa, and for 6 h in a biphasic water/n-butanol solvent |

Perez, R. F. et al (2014) [20] studied one-pot production of furfuryl alcohol from xylose using the dual catalyst system composed of $Pt/SiO_2$ and sulfated $ZrO_2$ as metal and acid catalysts. From the result, the optimum temperature that balances between furfural and furfural alcohol is 130°C. The presence of both acid and metal sites is essential to promote the dehydration of xylose to furfural and its hydrogenation to furfuryl alcohol. The selectivity to furfuryl alcohol is highly dependent on solvents, which can inhibit the formation of polymers to a certain extent.

Paulino, P. N. et al (2017) [10] studied dehydration and transfer hydrogenation tandem reactions of xylose to furfuryl alcohol in water/isopropanol were performed on zeolites catalysts (MFI, FAU and BEA). Zeolites, MFI, FAU and BEA can catalyze dehydration reactions and transfer hydrogenation reactions through direct conversion of xylose and highly selective to furfuryl alcohol on metal-free catalysts under mild conditions and without hydrogen molecules. This remarkable performance relates to the configuration of the tetrahedral Al-centers framework, which is determined by the Al-O-Si bonding distance and the BEA zeolite topology.

Canhaci, S. J. et al (2017) [8] studied the conversion of xylose to furfuryl alcohol in one step over Pt catalysts supported on ordered mesoporous SBA-15 bearing $SO_3H$ acid groups. Furfuryl alcohol can be produced directly from the xylose in a one-step process using bifunctional metal/acid catalysts. The presence of the surface site of the $SO_3H$ acid plays a role in the conversion of xylose. In addition, the improved product distribution with an acidic surface also inhibits the hydrogenation of xylose into xylitol.

Perez, R. F et al (2017) [1] studied $Pt/ZrO_2-SO_4$ catalysts with different acid/metal ratios were prepared and investigated in the xylose conversion. The distribution of products in the single-step xylose conversion to furfuryl alcohol depends on the balance between acids and metal sites. When the acid/metal ratio increased from 69 to 142, xylitol, a side product, was suppressed. Increasing the density of surface acid sites (acid/metal = 532), xylulose will be produced.

Perez, R. F et al (2018) [6] studied the cooperative role between metal and acidic sites of 1D multiwalled carbon nanotubes (MWCNT) supported noble metal catalysts (Pt, Pd, Ru, Rh and Au) to evaluate the xylose conversion reaction. From all the samples studied after 6 h, the activity order of the metal is as follows: Ru>> Pd> Pt> Rh～Au. Xylitol is the main product that occurs on the metal site in the direct reaction of the hydrogenation of xylose. Furfuryl alcohol is the second major product which is produced when the surface of the acidic site is on MWCNT. The co-existence of both the acidic site and the metal site can promote the reaction from xylose to furfuryl alcohol in one step.

Deng, T. Et al (2020) [7] studied the appropriate conditions for one-pot cascade conversion of xylose to furfuryl alcohol using bifunctional Cu/SBA-15-$SO_3H$ catalyst. The reaction temperature, hydrogen pressure and solvent system were optimized. Form the result, Cu/SBA-15-$SO_3H$ catalyst shown 62.6% yield of furfuryl alcohol at optimized conditions of 140°C, 4 MPa, and for 6 h in a biphasic water/n-butanol solvent. The further hydrogenation to 2-methyl furan was obtained at high reaction temperature, while the high hydrogen pressure led to the hydrogenation reaction to xylitol. The coexistence of acidic sites-$SO_3H$ and Cu sites, maintained balanced, affects the catalytic conversion. Excessive acidic sites and large pores can promote xylose conversion, although yield of furfuryl alcohol was low.

From the studied of all literature review above found that xylose conversion and furfural selectivity depended on

1. Surface acidity
2. Structure properties

# CHAPTER III

# MATERIALS AND METHODS

This chapter explains the experimental details of this work, including zeolite catalysts and materials, characterization of catalysts, catalytic activity for the conversion of xylose to furfuryl alcohol.

## 3.1 Zeolite catalysts

The zeolite catalysts used in the catalytic performance were shown in **Table 3**. Many types of zeolite including, H-ZSM-5 (Si / Al = 19, Riogen), $NH_4$-$\beta$ (Si / Al = 27, TOSOH), H-Y (Si / Al = 15, 100 and 500, Sasol) were purchased. To replace the $NH_4$-form zeolite with H-form, $NH_4$-$\beta$ is then calcined in the air at 350 °C for 3 h. The hierarchical structure is described elsewhere [21]. Briefly described, HY-500 is dissolved in a 3 M sodium bicarbonate solution. The mixture is continuously stirred at 75°C for 2 h under the stirrer speed of 400 rpm. Filtration of the solution and washed with deionized water until the solution is neutral after that, dried the precipitate in the oven. Following, suspension of the sample in 1 M ammonium chloride solution to exchange $Na^+$ with $NH_4^+$ for 3 times. Filtration and washing the sample with deionized water until the solution is neutral and then dried the sample overnight and further calcined in the air.

**Table 3** Zeolite catalysts

| Chemicals | Suppliers |
|---|---|
| H-ZSM-5 | Riogen |
| $NH_4$Beta | TOSOH |
| HY-15 | Sasol |
| HY-100 | Sasol |
| HY-500 | Sasol |

## 3.2 Catalyst Characterization

### 3.2.1 X-ray diffraction (XRD)

The X-ray diffraction (XRD) patterns were obtained by using X-ray diffractometer (Bruker D8 Advance) with Cu K$\alpha$ irradiation from 20° to 80° in the 2$\theta$ range at scan speed 0.5 sec/step. The crystallinity was calculated based on the sum of peak intensities.

### 3.2.2 $N_2$-physisorption

$N_2$ adsorption-desorption isotherms measured at -196°C in a Micrometrics ASAP 2020 instrument. It is used to determine the BET surface area and using BJH method to calculate pore volume and pore diameters. To obtain the micropore surface area and micropore volume, the t-plot method was applied.

### 3.2.3 Temperature-programmed desorption of ammonia ($NH_3$-TPD)

Temperature-programmed desorption of ammonia ($NH_3$-TPD) is used to determine the total acidity of the catalyst in a Micromeritics ChemiSorb 2750 with ChemiSoftTPx software. The 0.1 g sample was loaded into the quartz U-tube reactor. Elimination of the adsorbed water and organic by pretreated the catalyst in helium at 600°C and then exposed to the sample with 3 vol.% $NH_3$ / He at 550°C. The temperature at 280°C is used as a criterion for classification of weak acid sites and strong acid sites, where temperatures below 280°C are classified as weak acid sites and at temperatures above 280°C are classified as strong acid sites [9].

### 3.2.4 Scanning electron microscope (SEM)

The morphology of the zeolite catalyst is obtained from scanning electron microscopy (SEM).

### 3.2.5 Pyridine-IR

Infrared spectroscopy using pyridine as probe molecule was used to assess acidity. Catalyst was pretreated to remove water molecules at 200°C for 1 hour. After that, the sample was cooled to 40°C and pyridine was adsorbed for 30 minutes and desorbed for 1 h. The spectra were recorded on Bruker EQUINOX 55.

### 3.2.6 X-Ray Fluorescence Spectrometer (XRF)

X-Ray Fluorescence Spectrometry (XRF) is a technique for analyzing elements. To determine the type and amount of elements in a sample with a BRUKER S8 TIGER.

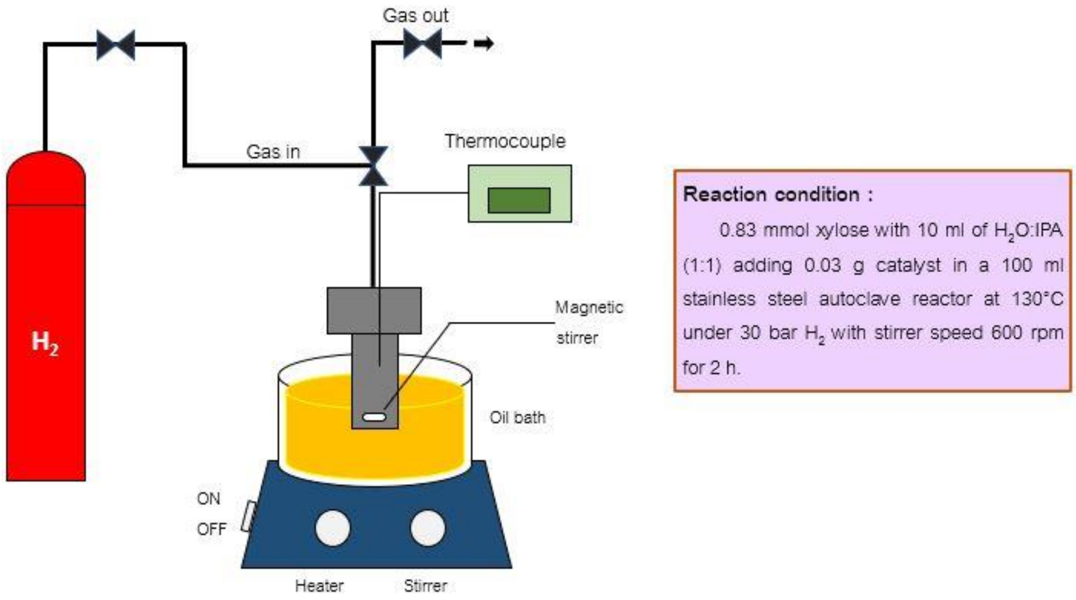
### 3.2.7 Fourier Transform Nuclear Magnetic Resonance Spectrometer 400 MHz. (Solid)

$^{27}$Al and $^{29}$Si solid-state NMRs were used to study the chemical environment of Al and Si for zeolite catalysts. Fourier Transform Nuclear Magnetic Resonance Spectrometer technique 400 MHz. (Solid) - NMR 400 MHz. was analyzed by BRUKER AVANCE III HD / Ascend 400 WB

## 3.3 Catalytic performance

The liquid phase of xylose dehydration to furfural was tested by dissolving xylose 0.83 mmol with 10 ml of water and isopropanol ($H_2O$: IPA = 1:1) being used as a solvent and adding 0.03 g catalyst in a 100 mL stainless steel autoclave reactor (JASCO, Tokyo, Japan). The reactor, after purged by $H_2$ gas 3 times to remove the air inside, was heated to 130°C and a total pressure of 30 bar $H_2$ throughout the experiment with stirrer speed 600 rpm for 2 h. After the end of the reaction, the reactor was cooled by ice until the temperature lower than room temperature.

Samples were collected to separate the liquid product from the catalyst and then analyzed with two detectors of high performance liquid chromatography (HPLC), the refractive index (RI) detector and ultra violet/visible (UV) detector, with Aminex HPX-87H (300 × 7.8 mm) column at column temperature of 65°C and using 5 mM $H_2SO_4$ with a flow rate of 0.6 ml/min as a mobile phase for analysis in xylose, xylulose and xylitol. Analysis of furfural and furfuryl alcohol, 14% of acetonitrile HPLC grade and 86% of 0.01 N phosphoric acid are used as a mobile phase at a column temperature of 35°C at a flow rate of 0.4 ml/min at 215 nm. Schematic of the xylose conversion to furfural and furfuryl alcohol in the liquid-phase reaction, chemicals used in the liquid-phase reaction and the operating conditions of high-performance liquid chromatography (HPLC) were shown in **Figure 4**, **Table 4**, **Table 5** and **Table 6**, respectively.



**Reaction condition :**

0.83 mmol xylose with 10 ml of $H_2O$:IPA (1:1) adding 0.03 g catalyst in a 100 ml stainless steel autoclave reactor at 130°C under 30 bar $H_2$ with stirrer speed 600 rpm for 2 h.

**Figure 4** Schematic of the xylose conversion in the liquid-phase reaction

**Table 4** Chemicals used in the liquid-phase reaction

| Chemicals | Formula | Suppliers |
|---|---|---|
| D-(+)-Xylose (≥99%) | $C_5H_{10}O_5$ | Sigma-aldrich |
| D-Xylulose (≥98%) | $C_5H_{10}O_5$ | Sigma-aldrich |
| Xylitol (≥99%) | $C_5H_{12}O_5$ | Sigma-aldrich |
| Furfural (99%) | $C_5H_4O_2$ | Sigma-aldrich |
| Furfuryl alcohol (98%) | $C_5H_6O_2$ | Aldrich |
| 2-propaol | $C_3H_8O$ | EMSURE® |

**Table 5** The operating conditions of high-performance liquid chromatography (HPLC) for specification for the sugar products

| high-performance liquid chromatography (HPLC, Shimadzu 20A) | Conditions |
|---|---|
| Detector | Refractive index (RI) |
| Column | Aminex HPX-87H (300 × 7.8 mm) |
| Mobile phase | 5 mM $H_2SO_4$ |
| Column temperature | 65°C |
| Time analysis | 60 min |

**Table 6** The operating conditions of high-performance liquid chromatography (HPLC) for the examination of furfural and furfuryl alcohol

| high-performance liquid chromatography (HPLC, Shimadzu 20A) | Conditions |
|---|---|
| Detector | Ultra violet/Visible (UV) |
| Column | Aminex HPX-87H (300 × 7.8 mm) |
| Mobile phase | 14% Acetonitrile (HPLC grade) – 86% 0.01 N phosphoric acid |
| Column temperature | 35 °C |
| Wavelength | 215 nm |
| Time analysis | 60 min |

# CHAPTER IV

# RESULTS AND DISCUSSION

This chapter describes the catalytic characteristics and properties of zeolite catalysts on the reaction of the conversion of xylose to furfural and furfuryl alcohol in one step. The results and discussion are divided into three parts. In the first part, the investigation of the effect of the zeolite acidity on the characteristics and catalytic properties. Subsequently, the effect of the zeolite structure on the characteristics and catalytic properties was investigated. Finally, investigated the effect of temperature and different environment on the catalytic activity in the conversion of xylose to furfural and furfural alcohol. The catalysts were characterized by X-ray diffraction (XRD), nitrogen ($N_2$) physisorption, scanning electron microscope (SEM), X-Ray Fluorescence Spectrometer (XRF), Fourier Transform Nuclear Magnetic Resonance Spectrometer (solid stated NMR), pyridine-IR technique and ammonia temperature program desorption ($NH_3$-TPD).

**Part I.** The investigation of the effect of acidity on HY zeolites with different Si / Al ratios from 15 to 500 by examining the characteristics and the catalytic activity for the one-step conversion of xylose to furfural and furfuryl alcohol.

## 4.1 Characterization of HY zeolite with different Si/Al ratio from 15 to 500

### 4.1.1 X-ray diffraction (XRD)

The peak characteristics and the crystallinity of zeolite in the form of hydrogen (or protons) were analyzed using the XRD technique as shown in **Figure 5**. The XRD patterns of the catalyst were measured at diffraction angles from 20° to 80°. The XRD pattern of HY zeolite with different Si/Al ratios from 15 to 500 showed diffraction peaks at 20.6°, 23.1°, 24.0°, 26.1°, 27.4°, 30.1°, 31.2°, 31.8°, 32.9°, 34.6° and 35.2° [22]. In addition, the crystallinity of HY zeolite was determined based on the sum of peak intensities in the range of 20°-35° and summarized in **Table 7**. It is indicated that the HY-100 contained the least crystallinity (94%), while the crystallinity of HY-15 and HY-100 were similar at 100% and 101%, respectively.

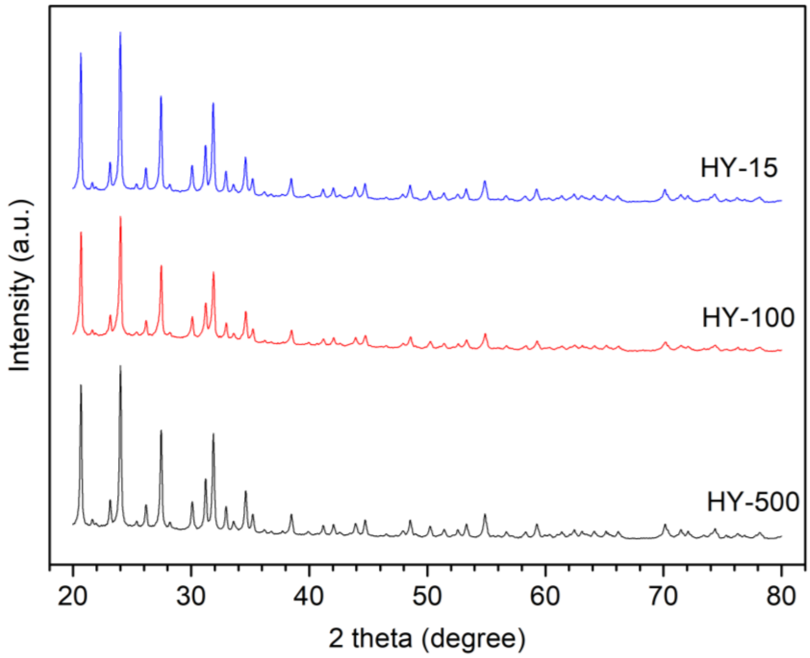


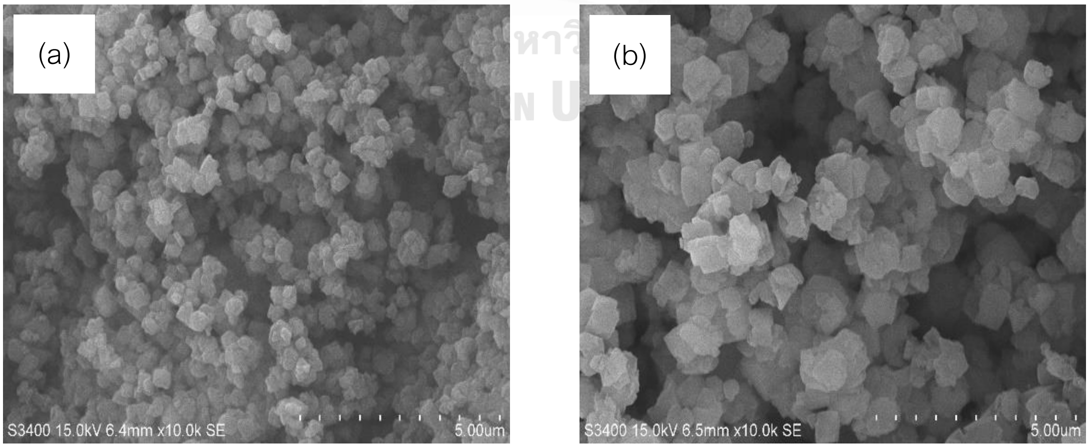
**Figure 5** XRD patterns of HY zeolite catalysts with different Si/Al ratio from 15 to 500

**Table 7** Crystallinity of HY zeolite catalysts

| Catalysts | Crystallinity (%) |
|---|---|
| HY-15 | 100 |
| HY-100 | 94 |
| HY-500 | 101 |

### 4.1.2 Scanning electron microscope (SEM)

The SEM images of Y zeolites are shown in **Figure 6**. All catalyst morphology is characterized by a similar cluster of crystals, but the particle size of HY-100 is significantly larger than HY-15 and HY-500, shown in Figure 5 (a) - (c). The particle size distributions of the zeolite Y catalysts with different Si/Al ratios are shown in Figure 5 (d). It can be seen that HY-15 and HY-500 had a narrow particle size distribution, while HY-100 had a wide size distribution than the others. **Table 8** shows the average particle size of the HY zeolite catalyst. The average diameter of HY-15 and HY-500 were small, approximately 350 nm and 390 nm respectively, while HY-100 was larger with a size of approximately 550 nm.



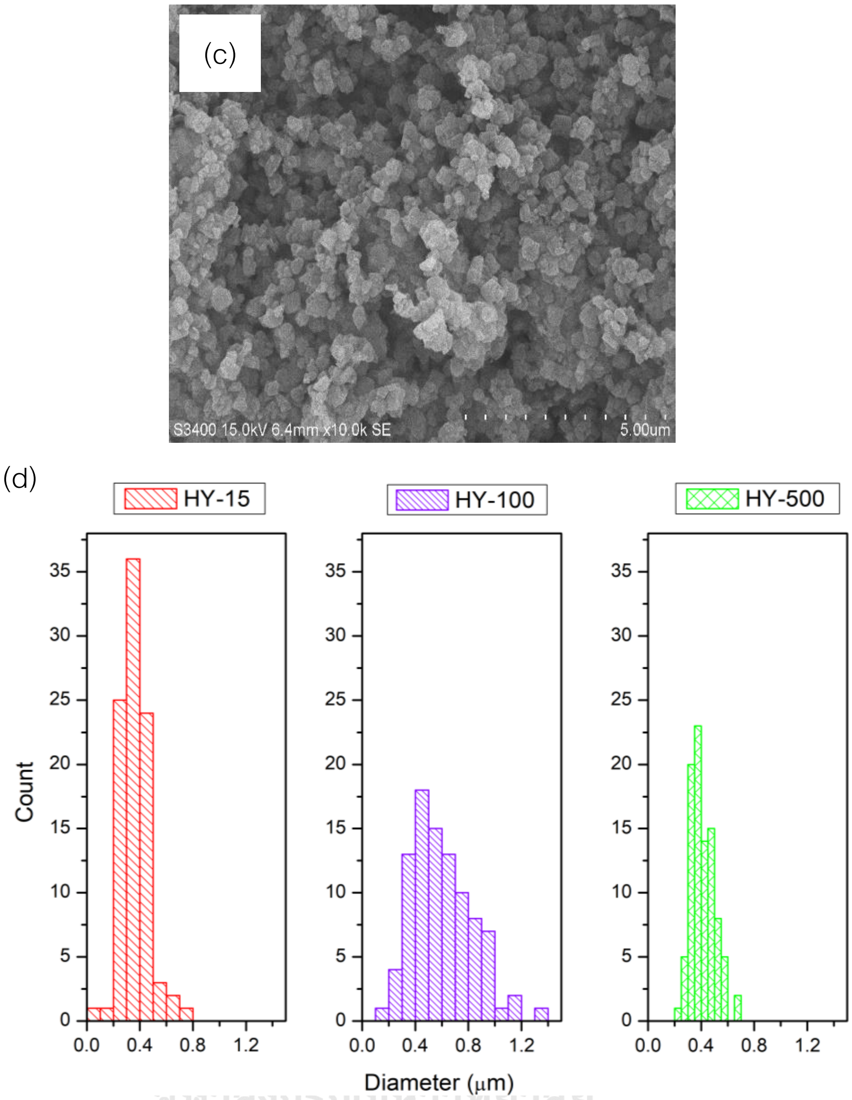


**Figure 6** SEM images of the HY zeolite catalysts: (a) HY-15, (b) HY-100, (c) HY-500 and (d) particle size distribution of HY zeolite catalysts

**Table 8** Average diameter of HY zeolite catalysts

| Catalysts | Average diameter (nm) |
|---|---|
| HY-15 | 350 |
| HY-100 | 552 |
| HY-500 | 391 |

### 4.1.3 Nitrogen ($N_2$) physisorption

$N_2$ adsorption and desorption isotherms of all the zeolite Y catalysts are demonstrated in **Figure 7**. From isotherm, HY-15 and HY-500 show a microporous structure. For the HY-100, there is a noticeable hysteresis loop, which represents isotherm type I + IV, indicating a micro and mesopore structure. The textural properties of all the catalysts are shown in **Table 9**. Si / Al ratio obtained from the XRF technique, showing less Si / Al ratio than specified from the commercial catalyst, possibly a loss in the zeolite synthesis process. The external surface area and the total surface area of the zeolite Y catalyst increased with higher Si / Al ratio. In addition, the micropore volume and average pore volume were larger according to the Si / Al ratio for the HY-15 and HY-500. While HY-100 had the smallest micropore volume, its average pore volume was the largest.

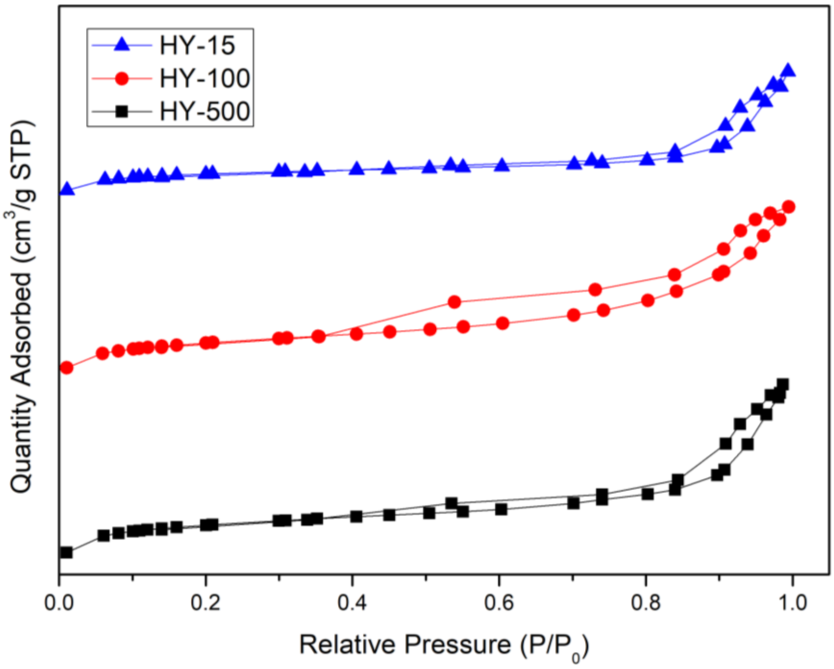


**Figure 7** $N_2$ adsorption and desorption isotherm of zeolite catalysts

**Table 9** The textural properties of all catalysts

| Catalysts | Si/Al [a] | Specific Surface area ($m^2/g$) | | Micropore volume ($cm^3/g$) [b] | Average Pore volume ($cm^3/g$) [c] |
|---|---|---|---|---|---|
| | | External surface area [b] | Total surface area | | |
| HY-15 | 7.8 | 72 | 514 | 0.206 | 0.171 |
| HY-100 | 56.2 | 126 | 539 | 0.191 | 0.263 |
| HY-500 | 366.9 | 130 | 652 | 0.243 | 0.252 |

[a] Data were obtained using XRF

[b] Data were obtained using the t-plot method from $N_2$ physisorption data

[c] Determined from the Barret-Joyner (BJH) desorption method

### 4.1.4 $^{27}$Al solid stated NMR spectra

$^{27}$Al NMR spectra of zeolite Y at various Si / Al ratios describe the chemical environment of the Al species as shown in **Figure 8**. A chemical shift approximately 60 ppm is associated with tetrahedrally Al coordinated, a Framework Al species in zeolite catalyst. The signal of chemical shift 30 ppm indicates pentahedral Al coordinated, including distorted tetrahedrally Al coordinated. The peak at chemical shift 0 ppm is octahedral Al coordinated [17, 23]. The reduced amount of Al in zeolite results in a decrease in the intense peak. **Table 10** showed relative Al species in HY zeolite. Integration of peak $Al^{IV}$ coordinated to obtain framework Al content and extra-framework Al (EFAl) content by the quantity between integrated peak $Al^{V}$ and $Al^{VI}$ coordinated. The lower Al content in zeolites results in reduced Framework Al and EFAl species.

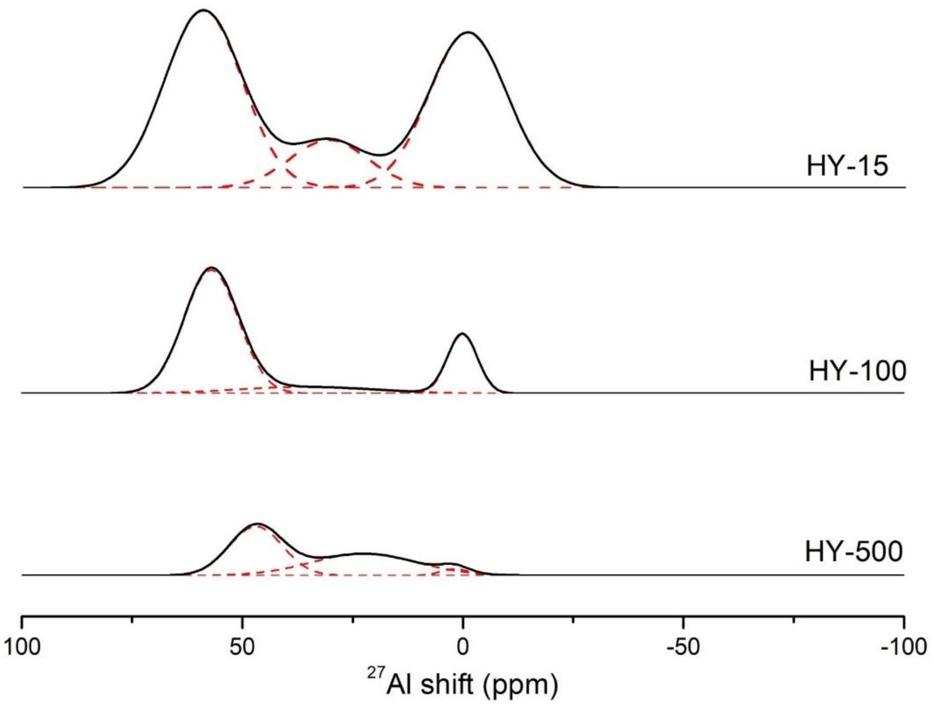


**Figure 8** Deconvolution of solid state $^{27}$Al NMR spectra for HY zeolite catalysts

**Table 10** Relative Al species of HY zeolites

| Catalysts | Framework Al content (%) | $Al^{V}$ | $Al^{VI}$ | EFAl (%) |
|---|---|---|---|---|
| HY-15 | 47 | 13 | 40 | 53 |
| HY-100 | 71 | 10 | 19 | 29 |
| HY-500 | 51 | 45 | 4 | 49 |

### 4.1.5 $^{29}$Si solid stated NMR spectra

The chemical environment of Si atoms was investigated by $^{29}$Si solid-state NMR as shown in **Figure 9**. The chemical shift ~-93 ppm shows the position of Si(2Al), when Si(nAl) means Si atoms in $Si(OSi)_{4-n}(OAl)_n$ units [17, 23], where a large peak is observed in HY-15, corresponding to the large Al content. HY-100 and HY-500 show a high Si(1Al) position at chemical shift -100 ppm. In addition to showing Si(2Al) position, it is also related to terminal silanol group [21, 24], where HY-15 may be obtained either the Si(1Al) or the terminal silanol group, but in the event of a smaller Al content, this signal was significantly higher. For HY-100 and 500, this position is expected to be more related to the terminal silanol group. The chemical shift of -112 ppm indicates Si(0Al), a tetrahedral Si framework of zeolite, is amorphous silica, which is abundant in HY-100, resulting in less crystallinity.

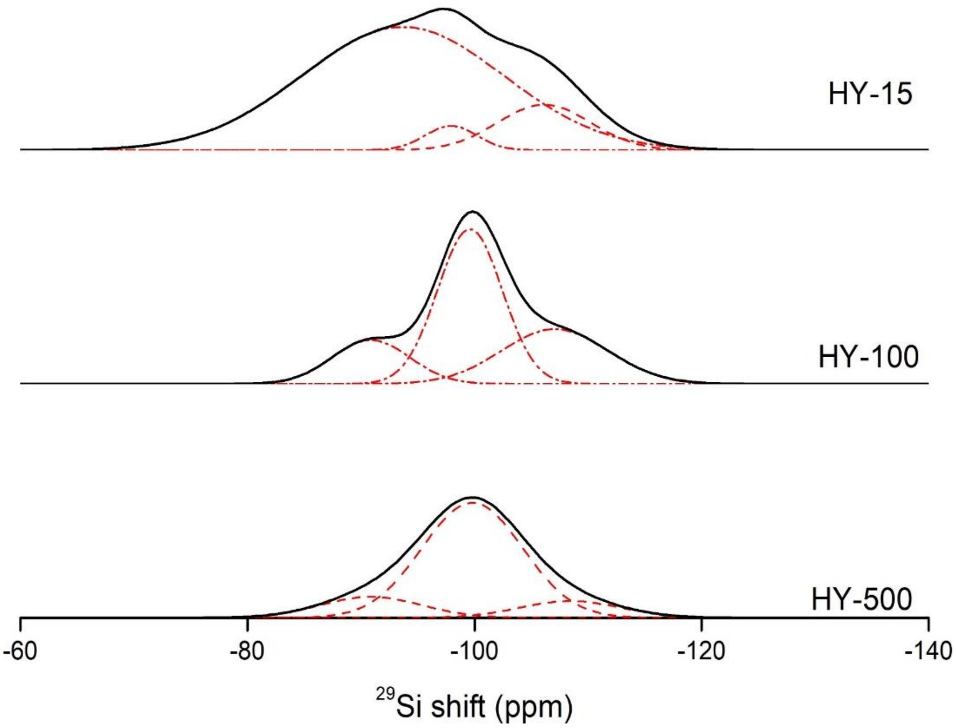


**Figure 9** Deconvolution of solid state $^{29}$Si NMR spectra for HY zeolite catalysts.

4.1.6 Ammonia temperature program desorption (NH$_3$-TPD)

The total acidity including acid strengths obtained from NH$_3$-TPD techniques is shown in **Table 11**. The total acidity and acid strengths of the Y type zeolite showed an opposite trend to the increasing Si / Al ratio. HY-15 had higher amounts and strengths of acids than HY-100 and HY-500, respectively, in relation to lower aluminum content.

### 4.1.7 Pyridine-IR technique

Brønsted and Lewis acid site were obtained from pyridine-IR techniques, represented by B / L ratio as shown in **Table 11**. It is established that B / L ratio decreased with increasing Si / Al ratio, which is similar to the results of $NH_3$-TPD except the one containing Si / Al = 100, due probably to the low crystallinity as seen from the XRD results.

**Table 11** The acidity of HY zeolite catalysts

| Catalyst | Total acidity[a] ($\mu$mol $NH_3/g_{cat}$) | Acid strength ($\mu$mol $NH_3/g_{cat}$) | | B/L[b] |
|---|---|---|---|---|
| | | Weak acid sites[a] | Strong acid sites[a] | |
| HY-15 | 1294 | 781 | 513 | 1.53 |
| HY-100 | 654 | 245 | 409 | 0.40 |
| HY-500 | 183 | 49 | 134 | 1.01 |

[a] Determined by $NH_3$-TPD technique

[b] Determined from pyridine-IR

## 4.2 Catalytic activity for xylose conversion to furfural and furfuryl alcohol over HY zeolite catalysts in single step

The catalytic performances of zeolite Y with various Si/Al ratios are shown in **Table 12**. The HY-15 zeolite exhibited 66.9% conversion, which is the highest conversion followed by HY-500, HY-100, and amberlyst-15, respectively. The amount of total acid rarely affected the catalytic activity catalysts for xylose conversion. It can be seen from the HY-500 that, although having the lowest total acidity, the catalytic activity is close to that of the HY-15 with the highest acidity. Although total acidity does not affect activity, but not for the acid type (Lewis and Bronsted acid site), xylose conversion correlates with the B / L ratio. The high B / L ratio improves the catalytic activity. From the distribution of the products, furfural was found to be the main product for HY-15 and HY-500 catalysts. Furfuryl alcohol was also detected as a product, which is occurred by furfural hydrogenation. The amberlyst-15 catalyst produced the main product as furfural and no furfuryl alcohol was detected due to the fact that amberlyst-15 contains only Bronsted acid site. According to Weingarten, R. et al., homogeneous Brønsted, HCl, and Lewis acids, $Yb(OTf)_3$, were used for xylose dehydration reactions in the aqueous phase. HCl exhibited a significantly higher furfural selectivity compared to $Yb(OTf)_3$. The nature of the acid site can significantly affect the production of furfural, with Brønsted acid sites preferring to be able to electively produce more furfural than Lewis acid sites Again, these results were consistent with heterogeneous catalysts, i.e. $\gamma$-$Al_2O_3$, $WO_X$ / $ZrO_2$, $SiO_2$-$Al_2O_3$, HY and Zr-P. These results concluded that a high ratio of Brønsted to Lewis was required to receive high furfural selectivity for heterogeneous and homogeneous catalysts [25]. The xylose was directly converted to furfural without the Lewis acid site. However, the existence of the Lewis acid site in the zeolite structure, was found to promote the formation of furfural hydrogenation to furfuryl alcohol, as confirmed by the results of HY-15 and HY-500. The amberlyst-15 that does not possess any Lewis acid produced only furfural from xylose. Only the HY-100 catalyst performed the hydrogenation of xylose to xylitol. It is possible that it has some certain structure or the type of Lewis acid sites that promoted the formation of xylose hydrogenation that were different from the HY-15 and HY-500. From the acidic properties of HY zeolite, The HY-100 had the lowest B / L ratio as seen in Table 11.

**Table 12** Catalytic conversion of xylose to furfural and furfuryl alcohol using HY zeolite catalysts

| Catalysts | Si/Al | Xylose Conversion | Selectivity (%) | | | | | Carbon balance |
|---|---|---|---|---|---|---|---|---|
| | | | Xylu [a] | Xyl [b] | FUR [c] | FFA [d] | Other | |
| HY-15 | 15 | 66.9 | 0 | 0 | 55.0 | 5.2 | 39.8 | 60.2 |
| HY-100 | 100 | 18.9 | 0 | 67.9 | 18.1 | 0 | 14.0 | 86.0 |
| HY-500 | 500 | 61.7 | 0 | 0 | 58.5 | 8.8 | 32.6 | 67.4 |
| Amberlyst-15 | - | 24.2 | 0 | 0 | 89.4 | 0 | 10.6 | 89.4 |

Reaction conditions: Temperature = 130°C, Pressure = 30 bar $H_2$, 10 ml of water:iso-propanol (1:1) as a solvent and reaction time = 2 h

[a] Selectivity of xylulose (Xylu)

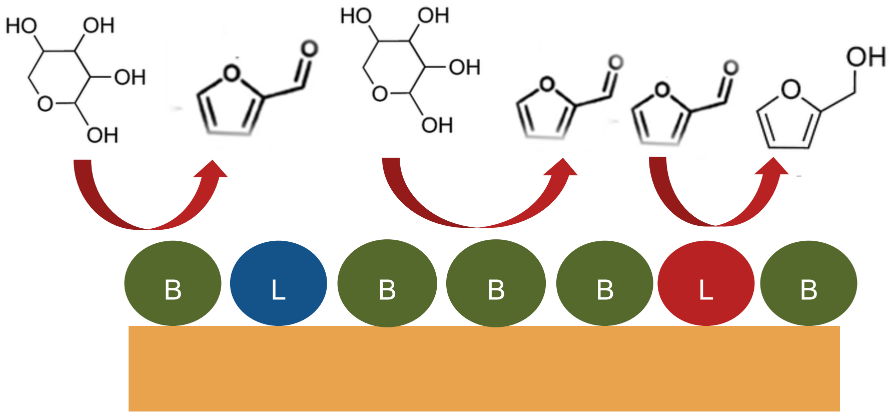
[b] Selectivity of xylitol (Xyl)

[a] Selectivity of furfural (FUR)

[b] Selectivity of furfuryl alcohol (FFA)

### 4.3 Probability of xylose conversion to furfural and furfuryl alcohol over HY-15 and HY-500 catalysts

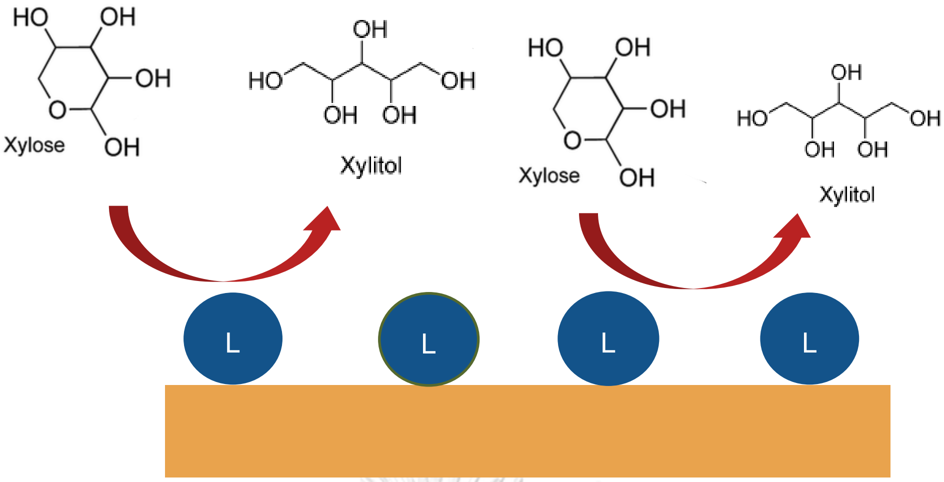
Probability of xylose conversion to furfural and furfuryl alcohol over HY-15 and HY-500 zeolite catalyst is shown in **Scheme 1**. Reaction tests showed that furfural and furfuryl alcohol were detected. These catalysts were expected to contain Brønsted and Lewis acid sites, where Lewis acid sites were possible from both the EFAl and terminal silanol group that was characterized with $^{27}$Al and $^{29}$Si NMR, respectively. When the reaction occurs, the xylose is dehydrated on the Bronsted acid site of the catalyst surface, furfural is produced. The high B / L ratio is expected to contain a high amount of Brønsted acid site, which is resulting in furfural is the main product. Some of the furfural, formed by dehydration of the sugar, can undergo a hydrogenation reaction to obtain furfuryl alcohol.



Scheme 10 Probability of xylose conversion to furfural and furfuryl alcohol over HY-15 and HY-500 catalyst

### 4.4 Probability of xylose conversion to furfural and furfuryl alcohol over HY-100 catalyst

Probability of xylose conversion to furfural and furfuryl alcohol over HY-100 zeolite catalyst is shown in **Scheme 2**. Lewis acid site is the predominant active site for HY-100, despite the amount of EFAl less than HY-15 and HY-500, according to the pyridine-IR technique, this catalyst may rarely contain Bronsted acid sites due to its lower B / L ratio. On the other hand, a noticeable intense peak, chemical shift of approximately -100 ppm, is related to the terminal silanol group in the zeolite catalyst. The terminal silanol group may be active Lewis that accelerates hydrogenation to xylitol from xylose, resulting in xylitol as the main product for this catalyst.



Scheme 11 Probability of xylose conversion to furfural and furfuryl alcohol over HY-100 catalyst

Summary of part I

1. The amount of total acidity of the HY-zeolite catalyst has no effect on the catalytic activity.
2. Catalysts with only Brønsted acid sites, such as amberlyst-15, were found to cause the conversion of xylose to furfural.
3. Compared to the non-porous amberlyst-15 catalyst, the zeolite-based catalyst can result in the other products such as furfuryl alcohol and xylitol formed during the reaction.
4. Combination of Bronsted and Lewis acid sites result in selective hydrogenation to furfuryl alcohol from furfural.
5. In the zeolite Y series, HY-100 with very low Bronsted has produced xylitol.

**Part II.** The study of the effect of zeolite structure and its characteristics for a single-step reaction in the conversion of xylose to furfural and furfuryl alcohol.

## 4.5 Characterization of each structure of zeolite catalysts

### 4.5.1 X-ray diffraction (XRD)

The XRD patterns of zeolite catalysts are exhibited in **Figure 10**. The diffraction angles were measured from 20° to 80°. The diffraction peaks at $2\theta$ = 20.3, 20.8, 23.0 (main peak), 23.2, 23.7, 23.9, 24.4, and 29.9° correspond to H-ZSM-5. The intense diffraction patterns with $2\theta$ = 21.5, 22.4 (main peak), 25.3, and 26.9° peaks were detected for the hydrogen form of beta zeolite. The diffraction peaks at $2\theta$ = 20.6, 23.1, 24.0 (main peak), 26.1, 27.4, 30.1, 31.2, 31.8, 32.9, 34.6 and 35.2° correspond to the hydrogen form of Y zeolites, with Si/Al ratio of 500. In opposite, the hierarchical structure in the Y zeolite, the Si / Al = 500 ratios, the XRD results showed a broad peak indicating the collapse of structure due to dealumination of the HY zeolite structure. Watmanee, S., and co-workers stated that the zeolite HY exhibits high crystallinity in contrast to the hierarchical structure, denoted Hi-HY, exhibiting a broad peak as evidenced by the XRD pattern due to zeolite erosion from dealumination treatment [21].

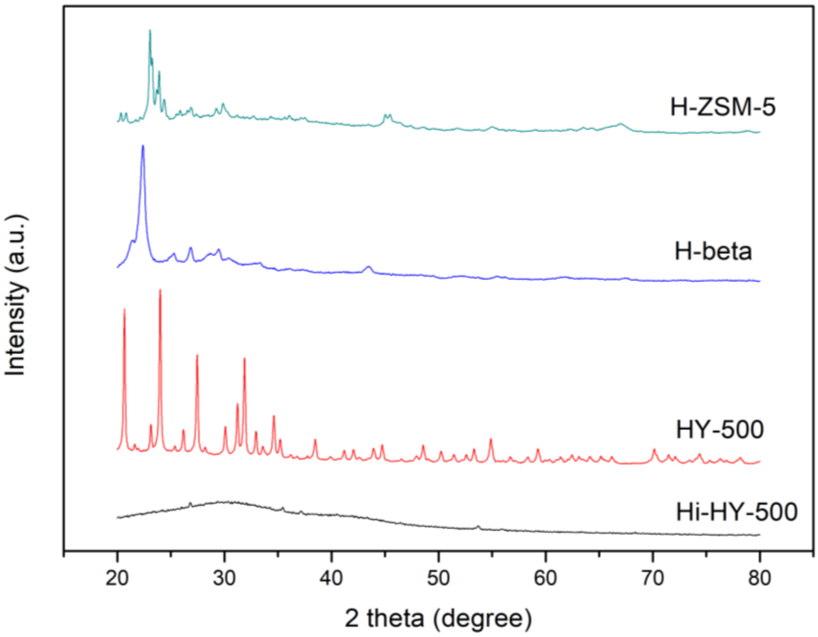


**Figure 12** XRD patterns of different zeolite catalysts

### 4.5.2 Scanning electron microscope (SEM)

The morphology of zeolite catalysts was investigated by SEM analysis and the results are shown in **Figure 11**. The shape of H-ZSM-5 zeolite grains is heterogeneous as show in **Figure 11 (a)**. The morphology of beta zeolite crystals presents that this zeolite has round crystals, as display in **Figure 11 (b)**. The morphology of parent HY zeolite and modified HY zeolite catalysts are shown with SEM images in **Figure 11 (c)** and **Figure 11 (d)**, respectively. The surface morphology has changed for the Hi-HY-500, which is noticeable compared to the HY-500 owing to the structure that has been destroyed after dealumination treatment.

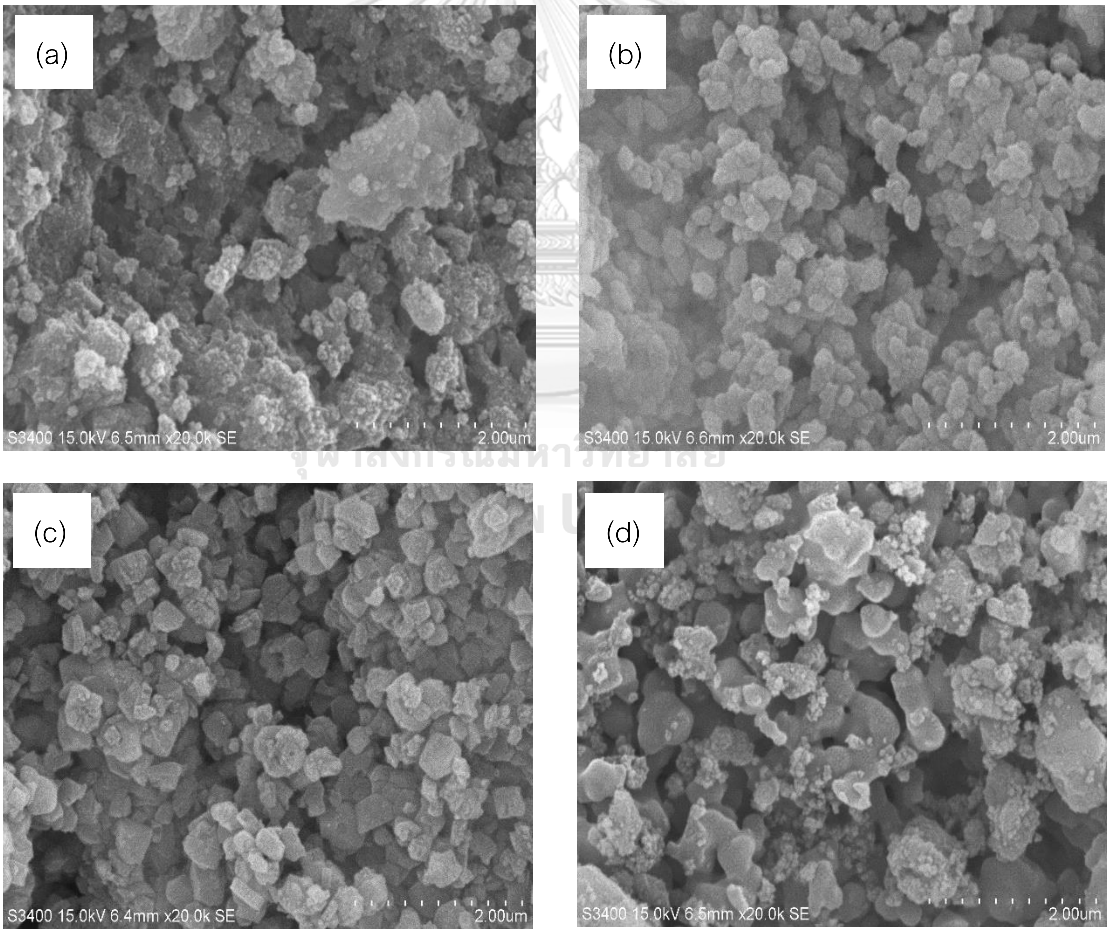


**Figure 13** SEM images of the zeolite and the modified HY zeolite catalysts: (a) H-ZSM-5, (b) H-beta, (c) HY-500 and (d) Hierarchical HY-500

### 4.5.3 Nitrogen ($N_2$) physisorption

The $N_2$ adsorption-desorption isotherm of each zeolite catalyst are displayed in **Figure 12.** Type I isotherm classification was observed in three types of zeolite catalysts, H-ZSM-5, H-beta, and HY-500. The hierarchical structure of HY-500 indicates the classification of type IV isotherm, which indicates the existence of the mesoporous structure in the zeolite crystal domain. The textural properties of each zeolite structure are shown in **Table 13.** HY zeolite (Si / Al ratio of 500) has a high surface area, along with a large micropore volume. HY type of zeolites were modified from the HY-500 to have a hierarchical structure (Hi- HY-500). The external surface area was improved, but the micropore surface area was significantly reduced, resulting in decreasing of the total surface area. On the other hand, the average pore volume increased although the micropore volume was smaller. It is indicated that the hierarchical structure has a higher mesopore volume, resulting in a higher average pore volume compared to the parent HY-500. For zeolite, H-ZSM-5 demonstrated the existence of total surface area equal to the H-beta zeolite.

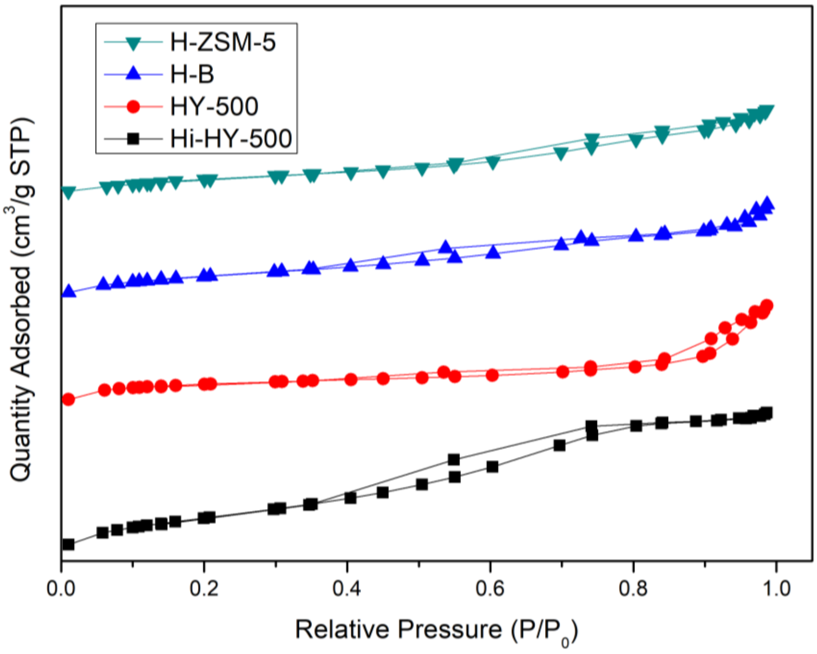


**Figure 14** $N_2$ adsorption-desorption isotherm corresponding to H-ZSM-5, H-$\beta$, HY-500 and Hi-HY-500 zeolite

**Table 13** The textural properties of zeolite catalysts

| Catalysts | Specific Surface area ($m^2/g$) | | Micropore volume ($cm^3/g$) [a] | Average pore volume ($cm^3/g$)[b] |
|---|---|---|---|---|
| | External surface area [a] | Total surface area | | |
| H-ZSM-5 | 179 | 292 | 0.052 | 0.262 |
| H-beta | 195 | 293 | 0.044 | 0.280 |
| HY-500 | 130 | 652 | 0.243 | 0.252 |
| Hi-HY-500 | 338 | 340 | 0.005 | 0.420 |

[a] Data were obtained using the t-plot method from $N_2$ physisorption data

[b] Determined from the Barret-Joyner-Halenda (BJH) desorption method.

### 4.5.4 Pyridine-IR

Bronsted acid sites and Lewis acid sites of zeolite catalysts can be estimated using the B / L ratio as shown in **Table 14**. The hierarchical HY-500 zeolite catalyst exhibited the highest B / L ratio, indicating that the Al content was reduced compared to the HY-500. It is confirmed that Al was eliminated due to the dealumination of the Hi-HY-500. H-ZSM-5 catalysts have a ratio of B / L = 0.66 which was higher than H-beta catalysts with B / L = 0.55.

**Table 14** The acid properties of zeolite catalysts

| Catalyst | B/L [a] |
|---|---|
| H-ZSM-5 | 0.66 |
| H-beta | 0.55 |
| HY-500 | 1.01 |
| Hi-HY-500 | 2.43 |

[a] Determined from pyridine-IR

### 4.6 The catalytic performances of each structural zeolite catalyst for liquid phase conversion of xylose

The catalytic activity of zeolite catalysts with different structures for liquid-phase reaction of xylose conversion is presented in **Table 15**. The highest activity of zeolites is found in the HY-500 structure. Because HY zeolite has a cage structure which is a large cavity, causing the reactant to easily diffuse inside the pores of the HY-500 catalyst. Both H-ZSM-5 and H-beta zeolites have a channel structure and smaller dimension than H-Y zeolite, which may resulting in diffusion limitations. Therefore, their catalytic activity is lower than HY zeolite catalyst. Literatures suggest the dimension of these zeolites as follows: H-ZSM-5 (5.1×5.5 Å↔5.3×5.6 Å, tridimensional structure), H-β (6.6×6.7 Å↔5.1×5.6 Å, tridimensional structure) and H-Y (7.4×7.4 Å, tridimensional structure) [2, 14].

Both H-ZSM-5 and H-beta zeolites exhibited xylulose as the main products (76.61% and 60% of xylulose selectivity, respectively). Some smaller amount of furfural was also formed in the products, with a tiny amount of the other products that were also detected, owing to the presence of the large amounts of Lewis acid sites (low B / L ratios 0.66 and 0.55, respectively). It is possible that xylose isomerization may occur on the Lewis acid site and some xylose encountered with the Brønsted acid site led to the formation of furfural in dehydration reaction. It is evidenced that H-ZSM-5 and H-beta had a small amount of furfural products due to the insufficient Brønsted acid sites. R. Weingarten et al. suggested that furfural selectivity is a function of the Bronsted to Lewis acid site ratio. Many solid acid catalysts have been studied, indicating that solid acid catalysts with a high B / L ratio are needed to obtain more furfural selectivity [25]. The other products have been found in relatively large quantities, possibly due to the large HY zeolite surface area and pore size, including the cavity structure. These characteristics contributed to the production of side products, making higher selectivity of the other products compared to the other zeolites (in this case compared to ZSM-5 and beta zeolite). R. Weingarten et al. [25] described that the production of the undesired solids humins, which are highly polymerized insoluble carbonaceous species, is formed by furfural and xylose react together, including furfural also reacting with itself. The humin formation rate is high due to the formation of the furfural polymerization in the large cavity of the HY catalyst, which reveals that the pore structure is important for the formation of solid humin [2, 25]. As for the hierarchical structure of the zeolite Y, it is shown that Hi-HY-500 promotes furfural formation (70.7% of furfural selectivity). **Table 14** indicates a higher amount of Bronsted acid sites promotes xylose dehydration as more furfural selectivity was obtained compared to the parent HY- 500 catalyst.

**Table 15** Catalytic conversion of xylose to furfural and furfuryl alcohol using zeolite-based catalysts

| Catalysts | Si/Al | Xylose Conversion | Selectivity (%) | | | | | Carbon balance |
|---|---|---|---|---|---|---|---|---|
| | | | xylulose | xylitol | FUR [a] | FFA [b] | Other | |
| H-ZSM-5 | 19 | 44.8 | 76.6 | 0 | 18.8 | 0 | 4.6 | 95.9 |
| H-beta | 27 | 21.0 | 60.0 | 0 | 39.9 | 0 | 0.1 | 99.9 |
| HY-500 | 500 | 61.7 | 0 | 0 | 58.5 | 8.8 | 32.6 | 67.4 |
| Hi-HY-500 | 500 | 34.0 | 0 | 0 | 70.7 | 3.1 | 26.2 | 73.8 |

Reaction conditions: Temperature = 130°C, Pressure = 30 bar $H_2$, 10 ml of water:iso-propanol (1:1) as a solvent and reaction time = 2 h

[a] Selectivity of furfural (FUR)

[b] Selectivity of furfuryl alcohol (FFA)

**Summary of part II**

1. The 3D channels structure of ZSM-5 and beta zeolite with small pore dimensions of 5.1 × 5.5 Å, 5.3 × 5.6 Å and 6.6 × 6.7 Å, 5.1 × 5.6 Å, respectively resulted in the xylose molecules being more difficult to diffuse, causing low xylose conversion.

2. Isomerization of xylose to xylulose occurs on Lewis acid site while Bronsted acid site causes xylose dehydration to furfural.
3. Furfuryl alcohol was not detected for ZSM-5 and beta zeolite, possibly because the furfural produced was too little to further produce furfuryl alcohol.
4. The hierarchical structure of HY zeolite improves furfural selectivity and reduces other by-products.

**Past III** Study the effect of temperature and different environment on the reaction of xylose to furfural and furfuryl alcohol in one step.

## 4.7 The effect of temperature for catalytic performance of xylose conversion to furfural and furfuryl alcohol

The significance of temperature on the reaction of xylose conversion in the liquid phase when zeolites into catalysts are presented in **Table 16**. The increased temperature drastically increased xylose conversion. For the HY-500 zeolite, the conversion increased to 88.6% and for the amberlyst-15 catalyst the conversion increased from 24.2% to 52.6% of. Moreover, the distribution of the product is more diversified when the reaction took place t higher temperatures. Furfural, which is the main product, decreased as the temperature increased. It is possible that the distribution of the product is influenced by the reaction temperature, both the HY-500 catalyst that contains both Lewis and Brønsted acid sites and only Brønsted acid sites, such as amberlyst-15. Perez, R.F and partners also revealed that xylose conversion gradually increased with temperature. The product distribution was also shown to be influenced by the reaction temperature. At low temperatures, 110°C, xylulose and furfuryl alcohol are the main products. The formation of more balanced furfural and furfuryl alcohol at 130°C resulted in smooth distribution at 150°C. The furfural production of is further increased when the temperature increases to 170°C [20]. Deng, T. et al. studied the effect of temperature in the range of 110-160°C on one-pot xylose conversion. They reported that the xylose conversion was found to be significantly improved with increasing temperature. The product distribution has slight effect on temperature. Furfuryl alcohol is still the main product. The yield of xylitol and 2-methyl furan increased as the temperature and furfuryl alcohol hydrolysis further to produce levulinic acid at 160°C for the Cu/SBA-15-$SO_3H$ catalyst [7]. Delgado Arcaño, Y., et al., proposes that the hydrogenation reaction occurs in the presence of metal catalysts at high pressures and temperatures. D-xylose can be reduced by hydrogenation, with the xylose being adsorbed to the active site on the catalyst surface while the hydrogen molecules undergo dissociation. After that a nucleophile is formed whose electron pairs attack the carbon of the carbonyl group (C = O), forming D-xylitol as a reaction product. The optimum temperature range for xylitol production is 140-150°C, but during this process, an isomerization (irreversible) step may occur in an acidic medium [26]. Therefore, increasing the temperature from 130°C to 150°C degrees causes the production of xylitol and xylulose in the reaction.

**Table 16** The effect of temperature in xylose conversion

| Catalysts | T (°C) | P (bar) | Xylose Conversion | Selectivity (%) | | | | | C [e] |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Xylu [a] | Xyl [b] | FUR [c] | FFA [d] | Other | |
| HY-500 | 130 | 30 $H_2$ | 61.7 | 0 | 0 | 58.5 | 8.8 | 32.6 | 67.4 |
| | 150 | | 88.6 | 12.8 | 3.0 | 47.6 | 0.6 | 36.0 | 64.0 |
| Amberlyst-15 | 130 | 30 $H_2$ | 24.2 | 0 | 0 | 89.4 | 0 | 10.6 | 89.4 |
| | 150 | | 52.6 | 9.9 | 1.8 | 45.1 | 0.4 | 42.9 | 83.4 |

Reaction conditions: Temperature = 130°C, Pressure = 30 bar $H_2$, 10 ml of water:iso-propanol (1:1) as a solvent and reaction time = 2 h

[a] Selectivity of xylulose (Xylu)

[b] Selectivity of xylitol (Xyl)

[c] Selectivity of furfural (FUR)

[d] Selectivity of furfuryl alcohol (FFA)

[e] Carbon balance

## 4.8 The effect of different environment for catalytic performance of xylose conversion to furfural and furfuryl alcohol in liquid-phase reaction

The pressure was found to affect the selectivity to furfural and furfuryl alcohol from xylose with HY-500 zeolite, as seen in **Table 17**. Although the reaction is carried out under different atmospheres, nitrogen and hydrogen pressure, the selectivity to furfural is almost similar. More furfuryl alcohol was detected under the pressure of hydrogen. Furthermore, it also shows the higher conversion of xylose than nitrogen pressure. The distribution of products is distinctly different under 30 bar $N_2$ atmospheric. According to the work of Deng, T., et. al. using n-butanol in a biphasic solvent under 30 bar $N_2$, only furfural and xylulose were produced. It shows that the solvent used does not influence transfer hydrogenation for the occurrence of the hydrogenated product [7]. Conversely, the hydrogenation product, furfuryl alcohol, is detected in the nitrogen atmosphere, indicating that isopropanol can help to transfer hydrogen to the hydrogenation process as also found in this work.

**Table 17** The effect of different environment for xylose conversion

| Catalysts | T (°C) | P (bar) | Xylose Conversion | Selectivity (%) | | | | | C [e] |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Xylu [a] | Xyl [b] | FUR [c] | FFA [d] | Other | |
| HY-500 | 130 | 30 $N_2$ | 41.4 | 34.2 | 0 | 59.6 | 1.1 | 5.2 | 94.8 |
| | | 30 $H_2$ | 61.7 | 0 | 0 | 58.5 | 8.8 | 32.6 | 67.4 |

Reaction conditions: Temperature = 130°C, Pressure = 30 bar $H_2$, 10 ml of water:isopropanol (1:1) as a solvent and reaction time = 2 h

[a] Selectivity of xylulose (Xylu)

[b] Selectivity of xylitol (Xyl)

[c] Selectivity of furfural (FUR)

[d] Selectivity of furfuryl alcohol (FFA)

[e] Carbon balance

Summary of part III

1. As the temperature increased, the catalytic activity increased, as well as the changes on the distribution of the products.
2. In the absence of hydrogen pressure, isopropanol has been found to present a little contribution as a hydrogen donor for production of furfuryl alcohol.

# CHAPTER V

# CONCLUSIONS

## 5.1 Conclusions

In order to study the effect of zeolite acidity for the xylose conversion in the liquid phase reaction, HY-15, HY-100, and HY-500 were used as catalysts. The highest activity (66.9% conversion) was found on the HY-15 catalyst, followed by HY-500 (61.7%), in which furfural was the main product and furfuryl alcohol as the minor product.

The structure of the zeolite catalyst has a prominent influence on the catalytic activity. The zeolites structures affected the xylose conversion by limiting the accessibility of the reactant and products in the structure. In addition, acidic sites cause the changes in the distribution of products. The formation of xylulose is detected in the presence of large amounts of Lewis acid sites as were found on the H-ZSM-5 and H-beta catalysts. In contrast, more Brønsted acid sites led to more furfural selectivity, as confirmed by the results of the Y-type zeolite, especially for the hierarchical structure of the HY-500. In addition, FFA was also recorded as a product in the HY zeolite

The increase in temperature resulted in increased catalytic activity and changes in product distribution. In addition, when the reaction proceeds under the pressure of hydrogen, the conversion of xylose to furfuryl alcohol was greater than under nitrogen pressure.

## 5.2 Recommendations

1. Reaction with other reactant should be carried out
2. Deactivation should be study

# REFERENCES

# APPENDIX A

## CALCULATION FOR CATALYTIC PERFORMANCE

The catalysts performances for the xylose conversion are shown in this below

$$\%\text{Conversion}=\frac{\text{Mole (in) - Mole (out)}}{\text{Mole (in)}}\times 100$$

$$\%\text{Selectivity}=\frac{\text{Mole of product}}{\text{Mole of convert reactant}}\times 100$$

$$\text{Carbon balance }(\%)=\frac{\text{Mole of product + Mole of reactant remaining}}{\text{Mole of reactant fed}}\times 100$$

Example:

$$\%\text{Xylose conversion}=\frac{\text{Mole of xylose (in) - Mole of xylose (out)}}{\text{Mole of xylose (in)}}\times 100$$

$$\%\text{Furfural selectivity}=\frac{\text{Mole of furfural}}{\text{Mole of converted xylose}}\times 100$$

$$\%\text{Furfuryl alcohol selectivity}=\frac{\text{Mole of furfuryl alcohol}}{\text{Mole of converted xylose}}\times 100$$

$$\text{Carbon balance }(\%)=\frac{\text{Mole of product + Mole of xylose remaining}}{\text{Mole of xylose fed}}\times 100$$

[1-21, 23-35]

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