VALORIZATION OF FURFURAL TO FUEL ADDITIVES BY ALUMINOPHOSPHATE AND METAL-ORGANIC FRAMEWORK CATALYSTS

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A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in Petrochemistry and Polymer Science
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การเพิ่มมูลค่าของเฟอร์ฟิวรัลไปเป็นสารเติมแต่งเชื้อเพลิงด้วยตัวเร่งปฏิกิริยาอะลูมิโนฟอสเฟตและโครงข่ายโลหะอินทรีย์

น.ส.เจนจิรา รัตถิวัลย์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
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Thesis Title	VALORIZATION OF FURFURAL TO FUEL ADDITIVES BY ALUMINOPHOSPHATE AND METAL-ORGANIC FRAMEWORK CATALYSTS
By	Miss Janejira Ratthiwal
Field of Study	Petrochemistry and Polymer Science
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เจนจิรา รัตถิวัลย์ : การเพิ่มมูลค่าของเฟอร์ฟิวรัลไปเป็นสารเติมแต่งเชื้อเพลิงด้วยตัวเร่งปฏิกิริยาอะลูมิโนฟอสเฟตและโครงข่ายโลหะอินทรีย์. (VALORIZATION OF FURFURAL TO FUEL ADDITIVES BY ALUMINOPHOSPHATE AND METAL-ORGANIC FRAMEWORK CATALYSTS)
อ.ที่ปรึกษาหลัก : รศ. ดร.ประเสริฐ เรียบร้อยเจริญ

ในงานวิจัยนี้ ตัวเร่งปฏิกิริยาอะลูมิโนฟอสเฟต (APAl-A) และตัวเร่งปฏิกิริยาโลหะออกไซด์ที่ได้จากการเผาโครงข่ายโลหะอินทรีย์ (C-MOFs) ได้ถูกเตรียมขึ้น โดยตัวเร่งปฏิกิริยาอะลูมิโนฟอสเฟตได้รับอนุเคราะห์จากกลุ่มวิจัย FQM-383 ของ ศ.ดร. ราฟาเอล ลูเกะ ให้ชื่อตัวเร่งปฏิกิริยาอะลูมิโนฟอสเฟตว่า APAl-X/Y-A-Z โดย X/Y เป็นอัตราส่วนของฟอสฟอรัสต่ออะลูมิเนียม และ Z เป็นอุณหภูมิการเผาในการเตรียมตัวเร่งปฏิกิริยา โดยปัจจัยทั้งสองถูกปรับเปลี่ยนเพื่อศึกษาถึงผลที่มีต่อคุณสมบัติของตัวเร่งปฏิกิริยา เช่น พื้นที่ผิวและตำแหน่งกรดบนพื้นผิวของตัวเร่งปฏิกิริยา ในส่วนของวัสดุโครงข่ายโลหะอินทรีย์ (MIL-101(Fe) และ MIL-125(Ti)) ถูกเตรียมด้วยวิธีโซลโวเทอร์มอล และตัวเร่งปฏิกิริยาโลหะออกไซด์ถูกเตรียมได้จากการเผาโครงข่ายโลหะอินทรีย์ (C-MIL-101(Fe) and C-MIL-125(Ti)) โดยทั้งตัวเร่งปฏิกิริยาอะลูมิโนฟอสเฟตและตัวเร่งปฏิกิริยาโลหะออกไซด์ถูกใช้ในการเร่งปฏิกิริยาอะซีตัลไลเซชันและปฏิกิริยาไฮโดรจีโนไลซิสตามลำดับ เฟอร์ฟิวรัลถูกใช้เป็นสารตั้งต้นในปฏิกิริยาในการเพิ่มมูลค่าชีวมวลและผลิตเชื้อเพลิงชีวภาพและสารตั้งต้นที่สามารถเปลี่ยนเป็นสารเคมีอื่นๆได้หลากหลาย สารเฟอร์ฟิวรัลไดเอทิลอะซีตัลเป็นเชื้อเพลิงชีวภาพที่ผลิตได้จากปฏิกิริยาอะซีตัลไลเซชันของเฟอร์ฟิวรัลและเอทานอล โดยปฏิกิริยาอะซีตัลไลเซชันดังกล่าวถูกศึกษาในระบบแบบกะที่มีตัวเร่งปฏิกิริยาของแข็งแขวนลอยอยู่ในระบบ ศึกษาหาสภาวะที่เหมาะสมในการทำปฏิกิริยา ซึ่งที่อุณหภูมิ 25 องศาเซลเซียสเป็นอุณหภูมิที่เหมาะสม และตัวเร่งปฏิกิริยา APAl-85/15-A-773 เป็นตัวเร่งปฏิกิริยาที่ว่องไวที่สุดในการเร่งปฏิกิริยาอะซีตัลไลเซชันในระบบกะ โดยให้ค่าร้อยละการเปลี่ยนของเฟอร์ฟิวรัลสูงถึง ร้อยละ 89 และค่าร้อยละการเลือกเกิดของสารเฟอร์ฟิวรัลไดเอทิลอะซีตัล มากกว่า ร้อยละ 99 โดยตัวเร่งปฏิกิริยาสามารถนำมาใช้ซ้ำได้ นอกจากนี้ปฏิกิริยาอะซีตัลไลเซชันยังได้ถูกศึกษาในระบบแบบไหลที่ให้สารตั้งต้นไหลผ่านตัวเร่งปฏิกิริยา APAl-85/15-A-773 ที่บรรจุอยู่กับที่ภายในระบบ โดยให้ค่าร้อยละการเปลี่ยนของเฟอร์ฟิวรัลสูงถึง ร้อยละ 92 สำหรับปฏิกิริยาไฮโดรจีโนไลซิสของเฟอร์ฟิวรัลและ 2-โพรพานอล จะให้ผลิตภัณฑ์เป็นเฟอร์ฟิวริลแอลกอฮอล์ซึ่งเป็นสารตั้งต้นในสารผลิตสารเคมีอื่นๆ โดยปฏิกิริยาไฮโดรจีโนไลซิสถูกศึกษาในระบบแบบไหล โดยใช้ตัวเร่งปฏิกิริยาโลหะออกไซด์ที่เตรียมได้จากการเผาโครงข่ายโลหะอินทรีย์ โดยตัวเร่งปฏิกิริยา C-MIL-125(Ti) ให้ค่าร้อยละการเปลี่ยนของเฟอร์ฟิวรัลสูงถึง ร้อยละ 83 และค่าร้อยละการเลือกเกิดของสารเฟอร์ฟิวริลแอลกอฮอล์ เท่ากับ ร้อยละ 77

สาขาวิชา	ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์	ลายมือชื่อนิสิต ....
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Janejira Ratthiwal : VALORIZATION OF FURFURAL TO FUEL ADDITIVES BY ALUMINOPHOSPHATE AND METAL-ORGANIC FRAMEWORK CATALYSTS. Advisor: Assoc. Prof. PRASERT REUBROYCHAROEN, Ph.D.

In this research, aluminophosphate (APAl) catalysts and metal oxide catalysts from calcined metal-organic frameworks (C-MOFs) were successfully synthesized. APAl-A catalysts were obtained from the FQM-383 laboratory group of Prof. Dr. Rafael Luque. The catalysts were named APAl-X/Y-A-Z which X/Y was the ratio of P/Al ratio and Z was the calcination temperature. Both factors were varied to study their effects on the catalyst properties of surface area and active acid sites on catalyst surface. The MOFs (MIL-101(Fe) and MIL-125(Ti)) were prepared by the solvothermal method. The calcination of MOFs (C-MIL-101(Fe) and C-MIL-125(Ti)) provided metal oxide catalysts. The APAl catalysts and C-MOFs catalysts catalyzed acetalization and hydrogenolysis, respectively. The furfural was used as the reactant in the reactions to upgrade the biomass and produce biofuel and chemical building blocks. The furfural acetalization with ethanol produced furfural diethyl acetal (FDA) which is biofuel. The acetalization reaction was studied in the batch system with varying reaction temperature to find the optimum condition. The reaction temperature of 25°C was found to favor the reaction. The APAl-85/15-A-773 exhibited the best performance in the reaction through the batch system with 89% conversion providing >99% selectivity of FDA. The catalyst reuse was investigated. Moreover, the furfural acetalization was estimated with the flow system over the APAl-85/15-A-773 giving 92% conversion. For furfural hydrogenolysis with 2-propanol, the furfuryl alcohol (FOL) was obtained. The FOL is an important starting material to produce other chemicals. The furfural hydrogenolysis with 2-propanol was studied through the flow system varying the catalysts. The C-MIL-125(Ti) catalyst showed the best performance in the reaction offering 83% conversion with 77% FOL selectivity.

Field of Study:	Petrochemistry and Polymer Science	Student's Signature ....
Academic Year:	2022	Advisor's Signature ....

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Janejira Ratthiwal

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General background

1.1 Introduction

Renewable energy is currently getting attention, for example, wind energy, solar energy, hydropower, geothermal energy, and ocean energy because fossil fuels cause environmental problems through greenhouse gas emissions after fossil fuels combustion [1]. In addition, the rising world population dramatically demands energy consumption caused by transportation, power generation, residential sector, and industries. Wind energy is used to generate electricity from the kinetic energy of moving huge wind turbines for a long time. The limitation of wind energy is the wind speed and location of wind turbines. The energy of water moving from higher to lower places created hydropower that can produce green electric power. Hydropower generators need to be in the river or reservoirs. This restriction cannot be avoided. Geothermal energy and ocean energy are extremely high costs. Hence, they are not getting attention. Thus, biomass is one of the efficient alternative energies that will replace or reduce the use of fossil fuels. Moreover, biomass is not only produced power but also manufactured and upgraded to be value-added chemicals, fuel additives, and biofuels with a big market demand [2].

The biomass is getting more attention due to it is environmentally friendly and alternative energy as more people are concerned about global warming now. It can be generally transformed into energy by many methods, such as gasification (a chemical conversion method) [3, 4], solvolysis, pyrolysis, torrefaction, extraction of oil, and other chemical reactions. These are several ways for the biomass upgradation to value-added chemicals or biofuels. The selection of biomass transformation method depends on the desired products. For instance, gasification and pyrolysis can converted biomass to fuels but the obtained products have low quality. Thus, it needs further reactions (Fischer–Tropsch synthesis, hydrodeoxygenation, water–gas shift reaction) to improve its properties and improve energy content. Pyrolysis is a biomass thermal conversion without oxygen under 350-600°C to obtain the fuel with carbon monoxide and hydrogen. On the other hand, gasification is thermochemical process of biomass to provide syngas under 800-1200°C. Whereas solvolysis can transform biomass to chemicals.

The lignocellulosic biomass basically contains lignin, cellulose, and hemicellulose [5]. It has around 170 billion metric tons production per year. Each component of lignocellulosic biomass can be converted to useful chemicals or biofuels as mentioned above. Lignin is a complex polymer consists of methoxylated phenylpropanoid units of various types [6]. Lignin hydrolysis over based catalyst under mild conditions can produce aromatic compounds for chemical industry. Moreover, phenols can be generated by depolymerize of lignin over Lewis acid catalysts ($FeCl_3$, $AlCl_3$, $ZnCl_2$, and BF_3). Depolymerize reaction can convert lignin to benzene, toluene, and xylene (BTX compounds) as well [7]. Cellulose is a polymer consists of glucose molecules that connected by β-1,4-glycosidic bonds. It is main component in lignocellulosic biomass. Glucose can be prepared from cellulose hydrolysis reaction. In addition, conversion of cellulose produces 5-hydroxymethyl furfural (5-HMF), polyols, organic acids (such as lactic acid, pyruvic acid, acrylic acid), 2,3-pentanedione and acetaldehyde [8]. Hemicellulose is one of the important components in lignocellulosic biomass. Dehydration of xylose as a component is obtained from hemicellulose and it mainly creates furfural which is a starting chemical to further produce biofuels such as furfuryl alcohol (FOL) and furfural diethyl acetal (FDA).

Due to the huge production of biomass that is necessary to be upgraded and increased its value with the concerned issue of greenhouse gas emission, both reasons highly rise the interests of furfural transformation into biofuels. Furfural is a compound of the top third necessary chemical building block studied by the Department of Renewable Energy of the United States. It was first commercially produced in the 1930s at Quaker Oats Technology. Moreover, it is a versatile chemical for various applications. The furfural can be upgraded into many useful chemicals (2-methylfuran (2-MF) [9], tetrahydrofurfuryl alcohol (THFA) [10], 2-methyltetrahydrofuran (2-MTHF) [11], tetrahydrofuran (THF), 1-pentanol, furan [12], furanone, succinic acid, butanol, cyclopentanon and maleic acid) through organic reactions over catalysts. At the present, China is the biggest furfural manufacturer and more than 88% of furfural is converted to furfuryl alcohol [13].

Furfuryl diethyl acetal and furfural alcohol as fuel additive and biofuel are derived from furfural through acetalization and hydrogenolysis reactions, respectively. These valuable chemicals are from biomass valorization. The furfuryl diethyl acetal can be blended with gasoline very well because it has same range of boiling point with gasoline. Hence, this is an alternative way to reduce the use of fossil fuels which is non-renewable and non-sustainable energy. Furthermore, the additive (furfuryl diethyl acetal) with higher octane value improves the properties of the fuels. The use of biofuel leads to the decrease of greenhouse gas emissions into the atmosphere.

There are plenty of catalysts to use in acetalization and hydrogenolysis reactions for example liquid acid catalysts, zeolites, metal-organic frameworks (MOFs), or natural clay, but heterogeneous catalysts are paid attention more than homogeneous catalysts due to it can be recovered and reused with less toxicity. Metal oxide catalysts are using widely in many chemical reactions but metal aggregation on the catalyst is occurred often, and it caused lower product yield or catalytic activity. Normally, metal was applied onto the support of the catalyst by impregnation or precipitation, but these methods may create the textural problem of metal leaching or metal dispersion that are generally found while the reaction is proceeded. Thus, metal oxide prepared by MOFs calcination can help to overcome these drawbacks due to the MOF have organized structure of metals and ligands. Meanwhile, aluminophosphate (APAl) is commonly used in organic fine chemical synthesis with or without applying metal on it [14]. Besides, it can be modified acid-base properties by varying some factor while preparation. It also can be reused with high stability of spent aluminophosphate catalysts in the reaction providing high catalytic activity.

This work is focusing on biomass upgradation and biofuel (Furfuryl diethyl acetal and furfural alcohol) production. Thus, it contains two topics of “Batch and continuous-flow room temperature furfural acetalization with ethanol over aluminophosphate (APAl) catalysts for biofuels production” and “Furfural conversion over calcined Ti and Fe metal-organic frameworks under continuous flow reactor” aiming to upgrade furfural through acid catalysts. This work is part of the dissemination of the graduation thesis.

1.2 Background and problems

Nowadays, global warming has become the main issue of environmental problems due to increased world population affects to the rising demand of chemicals and fossil fuel energy. Non-renewable energy (crude oil, coal, and natural gas) consumption in transportation, industries, or power generation is producing greenhouse gasses (carbon dioxide, methane, and nitrous oxide gasses) into the atmosphere causing global warming and environmental issues. Therefore, reducing the use of hydrocarbons and improving fuel properties are getting attention to solve the problems [15].

The biomass (for example, corn, husk, wood, sugarcane, oat hulls, and cottonseed hulls, etc.) with huge worldwide annual production is a renewable and sustainable organic carbon source from agriculture, woody, grassy materials, or waste streams. Woody biomass is more interesting due to it has less pesticide component in it, but higher energy compared to food crops. Moreover, woody materials have much more production than other biomass resources. Thus, woody material has high efficiency to use as an alternative energy resource and it is a good option to be upgraded to high value chemicals and biofuels. In addition, it is a choice to replace or reduce the use of fossil resources (natural gas and petroleum oil) and produce some chemicals efficiently.

Cellulose can be transformed into glucose and further continue converted to 5-HMF which is a bio-based platform chemical. The 5-HMF is used to produce many high-value products, such as 2,5-bis(hydroxymethyl)furan, 5-furandicarboxylic acid, 2,5-dimethyltetrahydrofuran, and 2,5-dimethylfuran. Xylose with plentiful pentose as a compound in hemicellulose that can be converted to furfural by hydrolysis reaction through the catalyst, followed by dehydration reaction.

Furfural (FF) is an aldehyde product with empirical formula C_5H_4O derived from the dehydration of xylose over acid catalysts from lignocellulosic biomass enriched with pentose derivatives. It is liquid with colorless and first isolated in 1821. It has various applications, for example, furfural can be used to separate unsaturated compounds from oil, or it can be used as fungicide. Moreover, it is an important initial substance to produce furfuryl alcohol (FOL), 2-methylfuran (2-MF), maleic acid, tetrahydrofuran (THF), levulinic acid (LA), furfural diethyl acetal (FDA), tetrahydrofurfuryl alcohol, 2-furonitrile, and other chemicals [16] as shown in figure 1.1 [17]. Since environmental issues caused by non-renewable fossil fuels were concerned, furfural production got attention again with 200,000 tons per year [18, 19]. These mentioned products are widely employed in bioplastics, solvents, resins, and biofuel additives. The use of biomass is a sustainable way to reduce fossil fuel consumption and greenhouse gas emission as it is urgent to seek for renewable energy replacement. In addition, furfural can be upgraded to valued products through many organic reactions, for example, aldol condensation, hydrogenation, and acetalization. The biofuels from biomass can be directly used or mixed with fossil fuels as bio-additives to improve density, flash point, and other relevant fuel properties [20, 21]. Interestingly, FDA and FOL are derivatives obtained from biomass and they are used as good performance biofuels. Thus, FDA and FOL production from biomass is biomass upgradation, and the use of biofuels can help reducing of the greenhouse gas releasing.

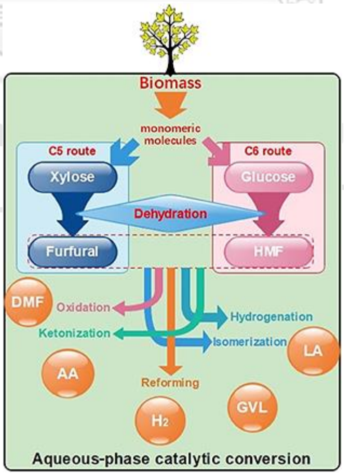


Figure 1.1 A general biomass conversion route.

Methyl tert-butyl ether (MTBE), ethanol, and tert-amyl methyl ether (TAME) are oxygenated biofuels [22]. Furfural diethyl acetal (FDA) as one of the oxygenated biofuels has been recently used as a fuel additive to blend with petrochemical fuels. Interestingly, FDA has a higher-octane value than gasoline. Moreover, the FDA boiling point is within the gasoline boiling point range. Therefore, it can be blended with gasoline effectively and reduce greenhouse gas emissions due to improved combustion. Furfural acetalization reaction with alcohols can generate acetal products including FDA over Brønsted acid sites of homogeneous (H_2SO_4, HCl, H_3PO_4, or HF) or heterogeneous catalysts (zeolites, metal oxide-based catalysts, or metal-organic frameworks). Both catalysts have advantages and disadvantages. The homogeneous catalyst has same phase as the reactant mixture which affects to high degree of interaction between catalyst and reaction medium due to it has good diffusion. Meanwhile, it is difficult to separate, and it also causes corrosive problem. Contrastingly, heterogeneous catalyst is easily to be recovered from the reaction solution as it is solid phase. Even though, it provides lower reaction rate compared to homogeneous catalyst. Thus, heterogeneous catalyst can be reused with long life which is good in term of economic and environmental issues.

There are plenty of literature reviews about reaction studies with the use of heterogeneous catalyst. For example,

Castellanos-Blanco *et al* studied the acetalization of furfural with ethanol over monometallic and bimetallic of Rh, Pt, and Ni on γ-Al_2O_3 catalysts. The γ-Al_2O_3 material was a good catalyst support because it has high thermal stability and mechanical strength with low price. There was no furfural conversion occurred in the reaction without catalyst. The bimetallic on the γ-Al_2O_3 performed in the reaction better than monometallic catalysts. Interestingly, all catalysts provided >99% FDA selectivity. The bimetallic of NiRh/ γ-Al_2O_3 gave the highest furfural conversion (85%) compared with other bimetallic catalysts (RhPt/γ-Al_2O_3, NiPt/γ-Al_2O_3) in the optimum conditions of 100^{o}C, 2h reaction time, and furfural: ethanol molar ratio of 1:100. The catalyst reusability was studied that after 4 times of catalyst recycling, there was a loss in catalytic activity of approximately 19%. The mechanism of the reaction over NiRh/γ-Al2O3 catalyst was proposed in the figure 1.2. The Ni atom reacted with carbonyl group of furfurals when the Rh atom coordinated with O atom of alcohol. The promoted hydride transferred to the O atom of the furfural carbonyl to form rhodium-ethoxide intermediate. The second molecule of ethanol was added into the rhodium. Finally, FDA was produced with water as a by-product [23].

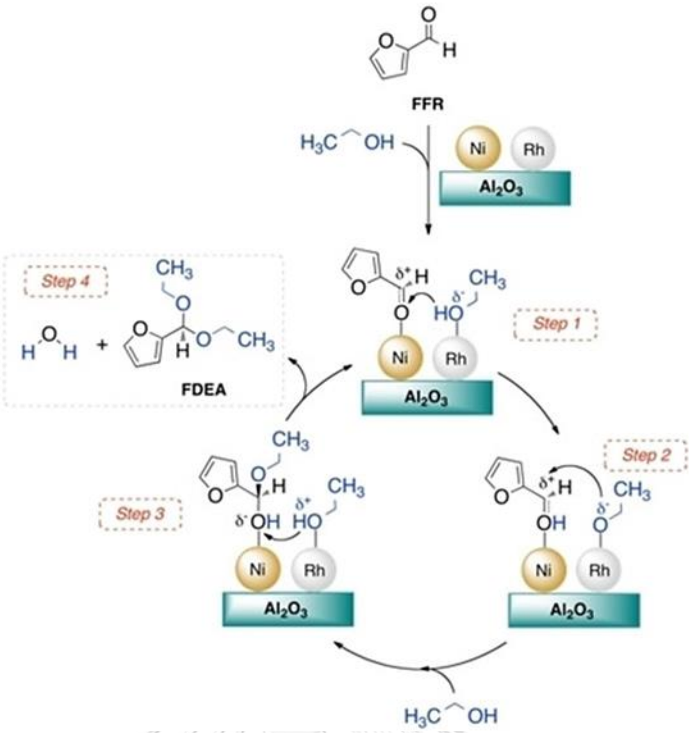


Figure 1.2 Proposed reaction mechanism for the acetalization of furfural over NiRh/γ-Al_2O_3 catalyst [23].

Rubio-Caballero *et al* was reported the study of furfural acetalization with ethanol over zeolite catalysts (Y, beta, ZSM-5, and H-USY). The reaction without catalyst or with Na-mordenite catalyst gave no catalyst activity implying that the reaction needed the acid catalyst. The FDA selectivity (>95%) was provided by the acetalization over all zeolite catalysts. The H-USY zeolite was the best catalyst giving the highest furfural conversion (79%) due to its high acid sites through furfural acetalization with ethanol in the room temperature. In addition, pore size of the catalyst played an important role to produce FDA product. The H-USY catalyst was reused for 5 cycles, and it maintained between 76-84% of FDA yield. Furthermore, the reaction mechanism of the reaction over brønsted acid sites of zeolite was proposed as shown in figure 1.3 [24].

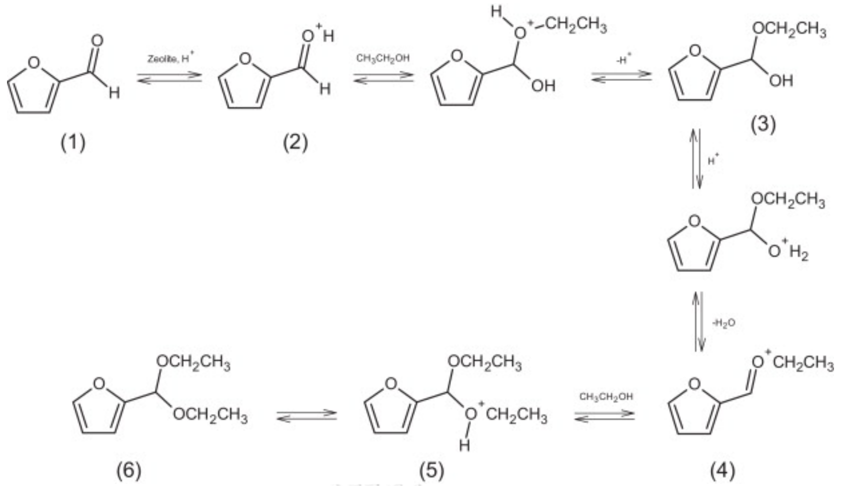


Figure 1.3 The mechanism of the acetalization of FUR to FDA over acid catalyst [24].

FOL is a chemical building block used in many industries to produce organic compounds, lubricants, additives for gasoline blends, plasticizers, adhesives, and resins. In the past, furfural hydrogenolysis could proceed with hydrogen under high pressure to produce FOL but it was concerned about safety issue. On the other hand, the reaction with alcohols as hydrogen donors (methanol, ethanol, n-propanol, i-propanol, n-butanol, or i-butanol) over the assistance of the catalyst with Lewis acid sites is much safer [25]. It has been reported that heterogeneous catalysts have been used widely for more reactions compared to homogeneous catalysts due to heterogeneous catalysts can be easier separated from the reactants and products and reused several times. Thus, this is a good reason for heterogeneous catalyst use in terms of economic, time-saving, and environmental issues [26].

Aldosari *et al* investigated the hydrogenation of furfural over Pd/TiO_2 and Pd-Ru/TiO_2 catalyst with different solvents in batch system at the room temperature to produce furfuryl alcohol (FOL) and 2-methylfuran (2-MF) as the main products. Toluene led to tetrahydrofurfuryl alcohol (THFA) and 2-MF selectivity, whereas methanol showed increase of THFA selectivity. Interestingly, 1,2-dichloroethane as the solvent gave 2-MF product from full conversion of FOL. Rising the Pd amount (1-5%) into

Pd/TiO_2 increased catalytic activity and 2-MF selectivity. The 5% Pd/TiO_2 provided 2-MF and FA in first 30 minutes of reaction time. Then, THFA from side reaction occurred when the reaction time was increased. Adding 1% of Ru into Pd/TiO_2 (1% Ru–4% Pd/TiO2 catalyst) could reduce side products and increase 2-MF and FA selectivity [27].

Wang *et al* reported the pathway of furfural transformation to other chemicals as shown in figure 1.4. [28]. The hydrogenation of furfural with various solvents to produce FOL was studied over metal-organic framework (MOF) derived bimetallic Cu-Co catalyst (CuCo/Al). The Cu MOF was synthesized and followed by Co impregnation onto the MOF. The synthesized material was calcined under N_2 atmosphere obtaining CuCox/C-y catalysts where x denotes the molar ratio of Co to Cu (0.1, 0.2, 0.3, 0.4, and 0.5) and y denotes the calcination temperature (773 K, 873 K, 973 K, and 1073 K). The Co impregnation helped the Cu dispersion on the catalysts. The $CuCo_{0.4}$/C-873 provided the best catalytic activity with 98.7% furfural conversion and 97.7% FOL selectivity due to its high metal dispersion on the catalyst and its small metal particle size. The lower calcination temperature 773 K gave CuO which affected to low conversion. On the other hand, the higher calcination temperature 1073 K provided bigger metal particle size which dropped the furfural conversion dramatically. The optimum condition of the reaction were 413 K, 0.7 g of $CuCo_{0.4}$/C-873 catalyst, 15 wt% furfural in ethanol solution, 3 MPa, and ethanol as a solvent. After the catalyst was reused for 4 cycles, the furfural conversion and FOL selectivity were at 78% and 90%, respectively. The catalyst had good stability with small amount of coke occurred after reuse.

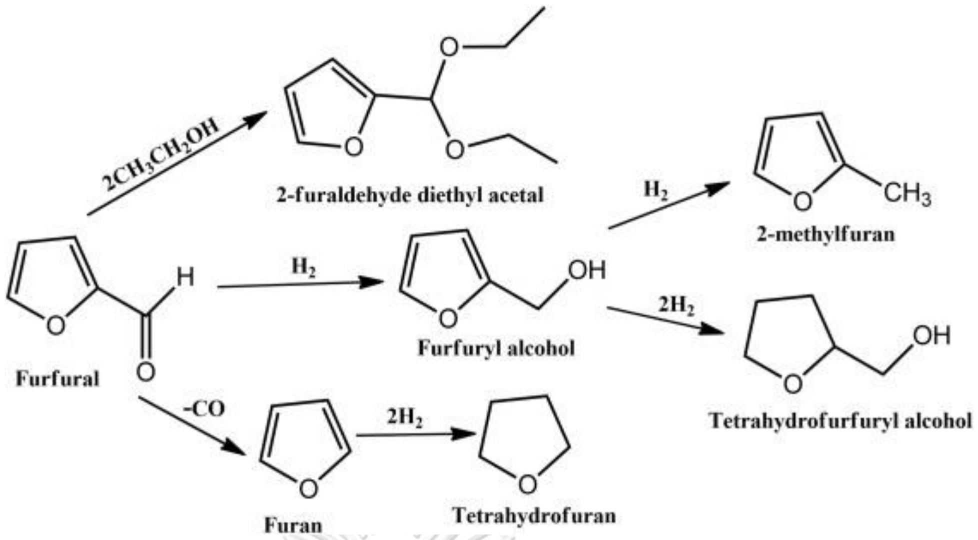


Figure 1.4 Possible products during hydrogenation of furfural [28].

Jiang et al studied the hydrogenation of furfural with alcohols as hydrogen donors over metal-organic framework derived magnetic Fe_3O_4/C catalyst. The Fe-MOF was prepared varying ligands and solvents to study whether their soluble affect MOF formation. Then, calcination temperature and calcination time were changed to study Fe_3O_4/C catalyst synthesis. The result showed that Fe_3O_4/C had higher BET surface area, pore volume, and pore diameter whereas both had mesopore structure. The isopropanol was the best hydrogen donor giving the highest catalytic activity through furfural hydrogenation over Fe_3O_4/C catalyst due to its low reduction potential. Moreover, the catalyst could be reused for 4 cycles and the furfural conversion maintained above 73%. In addition, the mechanism of furfural hydrogenation was proposed in this work as shown figure 1.5. Firstly, O and H atom of hydroxyl group of isopropanol were reacted with Fe^{2+}/Fe^{3+} and O^{2-} of Lewis acid sites of catalyst. Secondly, electron lone pair of C=O group of furfural were adsorbed onto electrophile of catalyst creating six-membered ring. Hydrogen transfer was occurred to form furfuryl alcohol product. Acetone was produced as by-product in the reaction from isopropanol. This mechanism was related to MVP reduction.

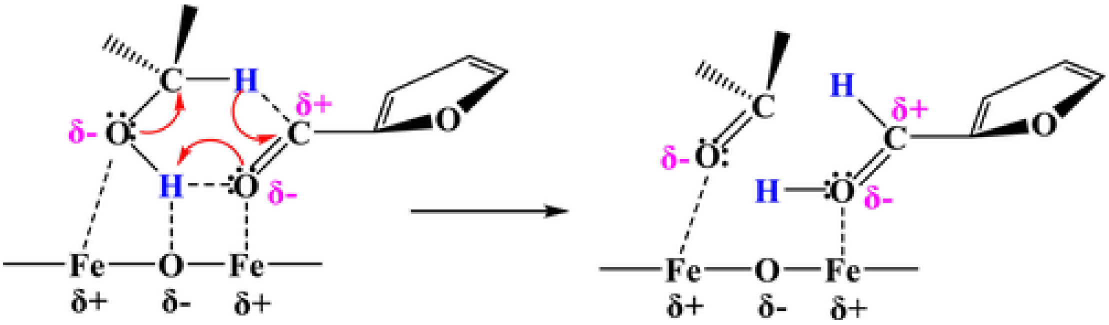
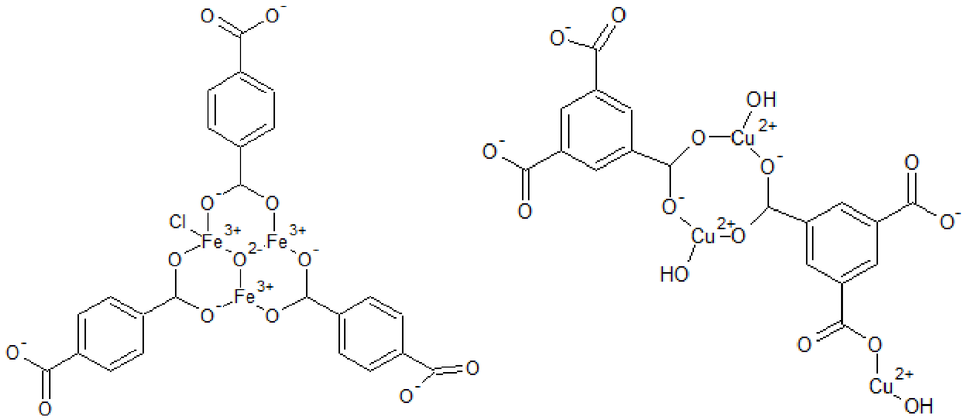


Figure 1.5 Mechanism for catalytic transfer hydrogenation of furfural over Fe_3O_4/C [29].

There are more than 20,000 different structures of MOFs, such as MIL-101(Fe), UiO-66(Zr), MIL-53(Al), MIL-125(Ti), HKUST-1, MIL-100(Fe), MOF-199 [30], and others MOFs as shown in figure 1.6. They are reported in many fields of research, for example, catalyst, pharmaceutical, gas or liquid storage, sensing, and other applications. MOFs have several advantages and useful functions, such as high thermal stability, high surface area, tunable pore size [31], and reusability. Moreover, it can be applied with other materials providing many outstanding properties. The MOFs are formed by metal atoms as nodes and ligands synthesized by many methods (solvothermal, mechanochemistry, or electrochemical methods) [32, 33]. In many reactions, metal oxide catalysts are chosen to catalyze the reaction due to acidity, basicity, or redox feature properties. However, metal leaching, metal aggregation, or metal dispersion are the problems using metal oxide as the catalysts. These problems directly affect decreased catalyst performance on the reactions. Thus, metal-containing MOF for metal oxide preparation can overcome these problems mentioned above due to metal oxides can be well dispersed on the catalyst as the metal atoms in the MOF are orderly located on its structure.



a. b.

Figure 1.6 Structure of MIL-101(Fe) (a) and HKUST-1 (b)

Deng *et al* synthesized Fe-MIL-101, Cr-MIL-101, Fe-MIL-100 and Cr-MIL-100 to evaluate with cyclization rearrangement of furfural and secondary amines (morpholine). The Fe-MIL-101 provided the best catalytic activity due to catalyst with Fe had more oxaphilic metal while MIL-101 had suitable pore size for main product production and smaller pore size suppressed macromolecule of byproduct. Moreover, MOF could promote the main reaction and stop the side reaction. In addition, the catalyst was stable and the catalytic activity slightly decreased after five runs [34].

Among all catalysts, aluminophophate is one of material that is getting interests for long time to use as a catalyst or a support of the catalyst providing high catalytic activity. Aluminophosphate (APAl) can be prepared by the sol-gel precipitation method or hydrothermal method. It has been used as a catalyst in many reactions, such as etherification, oxidehydration [35], esterification [36], hydrogenation, and other chemical reactions. The catalyst is employed in acid-catalyzed reactions because of their Brønsted/Lewis acid properties which is the active site to proceed the reactions. The structure of aluminophosphate has shown in figure 1.7. This outstanding aluminophosphate has been reported as effectively reusable, eco-friendly, and high stability material [37]. Moreover, the acid property of the material can be tuned by varying Al concentration or calcination temperature in the catalyst preparation procedure. These reasons drive the catalyst widely used for a long time.

Bautista *et al* estimated the N-alkylation of aniline with methanol over $AlPO_4$-Al_2O_3 catalysts (APAl-A). The Al_2O_3 content catalysts were varied from 5 to 25 wt%. The calcination temperature of the catalysts was studied its effect as well. The catalyst with 15 wt% of Al_2O_3 was modified with 2.5% fluoride and tested with the reaction. The aim of this study was to obtain N-methylaniline (NMA) and N,N-dimethylaniline (NNDMA) products. The APAl-15-773 was the best catalyst compared with pure $AlPO_4$, pure Al_2O_3, and other APAl-A catalysts and it provided the highest catalytic activity. Addition of Al_2O_3, to $AlPO_4$ improved the catalyst acidity which gained higher FF conversion. Applying fluoride ion increased acidity whereas decreased catalytic activity. These results showed that strong acid sites were not required for the reaction but weak to moderate acid sites were responsible for the reaction. Interestingly, there was no carbon deposition on the catalysts after 8 h time on stream at 250°C of the reaction [38].

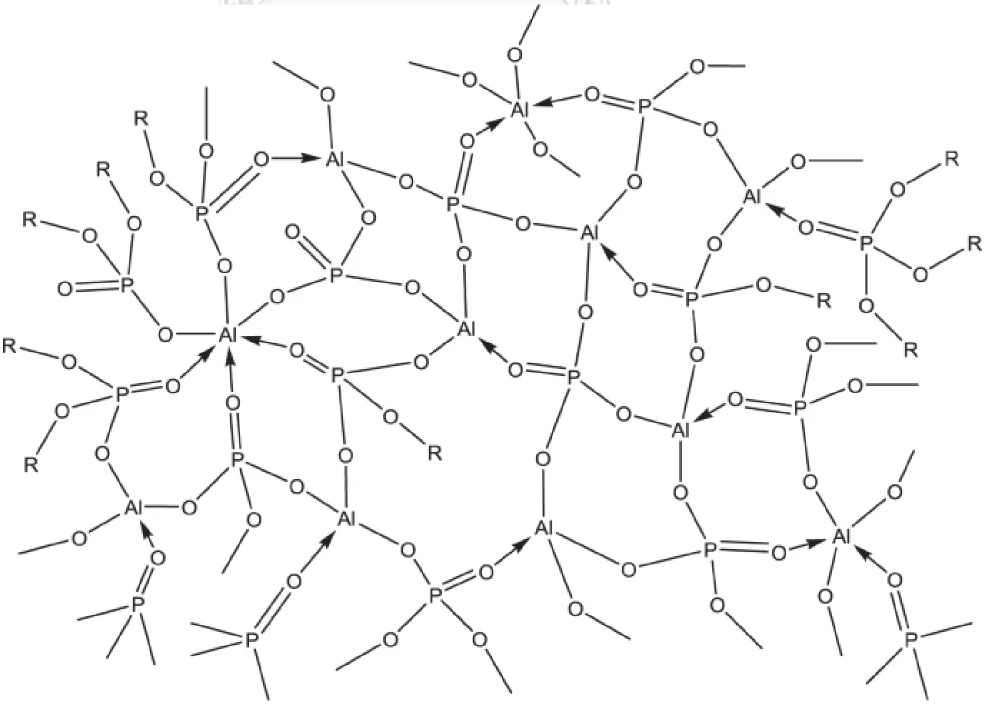


Figure 1.7 Aluminophosphate network structure.

1.3 Objectives

- I. To upgrade the furfural from biomass to valuable biofuel and chemical building block
- II. To catalyze the acetalization reaction of furfural with ethanol for furfural diethyl acetal production using APAl catalysts
- III. To prepare metal oxide catalysts by calcination of MOFs synthesized through the solvothermal method for furfuryl alcohol production from hydrogenolysis of furfural with 2-propanol

1.4 Scope of this work

This work contains two topics of acetalization and hydrogenolysis reactions over the catalysts. The first topic is batch and continuous-flow room temperature furfural acetalization with ethanol over aluminophosphate (APAl) catalysts for biofuel production. This topic aimed to produce FDA through acetalization of furfural and ethanol over APAl catalysts and to find the optimum conditions. The APAl catalysts were obtained from FQM-383 research group of Professor Rafael Luque which were successfully synthesized and varied ratio of P/Al and calcined temperature. The catalysts were characterized by N_2 adsorption-desorption isotherms and pyridine (PY), and 2,6-dimethyl pyridine (DMPY) pulse chromatography titration. The furfural acetalization reactions were investigated under batch conditions (parallel reaction system) varying the catalysts and reaction temperature to find the optimum condition and compared to the results obtained from continuous flow under room temperature without applying pressure. Moreover, catalytic reusability and stability were also studied in the optimum catalytic system as well.

The second topic is furfural hydrogenolysis with 2-propanol over calcined metal-organic frameworks using a continuous flow reactor. In this topic, metal oxides or calcined metal-organic frameworks (calcined-MIL-101(Fe), calcined-MIL-125(Ti), and calcined-Ti-Fe MOF) were synthesized by calcination of metal-organic frameworks which prepared by solvothermal method. The calcined metal-organic frameworks were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), N_2 adsorption-desorption isotherms, X-ray photoelectron spectroscopy (XPS), Transmission electron microscopy (TEM), and pyridine (PY), and 2,6-dimethyl pyridine (DMPY) pulse chromatography titration. The catalysts were tested with furfural hydrogenolysis reaction through a flow reactor system. The FOL was a desired product from the reaction.

1.5 Benefits from research

This study illustrated biomass valorization to fuel additives and chemical building blocks. The biomass can be from agriculture products or wastes, for example, sugarcane, corn, bark, or straw. This could increase demand of agriculture products and turn non-useful biomass waste to valued chemicals and further use in many industries. Especially, furfural is one of derivative from biomass with a huge production per year. The furfural can be converted into numerous useful chemicals and fuel additives. Moreover, the biofuels or additives obtained from biomass can reduce the use of fossil fuel and decrease greenhouse gas emission due to the improved properties of the fuel.

Chapter 2

Research articles

2.1 Batch and continuous-flow room temperature furfural acetalization with ethanol over aluminophosphate (APAl) catalysts for biofuels production

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Batch and continuous-flow room temperature furfural acetalization with ethanol over aluminophosphate (APAl) catalysts for biofuels production

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Abstract

The acetalization of furfural and ethanol was investigated over aluminophosphate (APAl) catalysts using both batch and flow reaction systems to produce furfural diethyl acetal (FDA). APAl catalysts were synthesized with varying P/Al ratios and calcination temperatures to study their effects on Brønsted acid active sites for the reaction. Catalysts were characterized by N2 adsorption and Pyridine (PY) and

2,6-dimethylpyridine (DMPY) pulse chromatography titration. A maximum of 89% furfural conversion and > 99% selectivity of FDA was obtained for the best catalyst (APAl-85/15-A-773) under batch conditions within 30 min at room temperature. On the other hand, the flow system provided a maximum of 92% furfural conversion. APAl-85/15-A-773 catalyst was also reusable, highly stable, and exhibited a high catalytic performance for furfural acetalization with ethanol at room temperature.

Keywords

Furfural acetalization; Aluminophosphate catalyst; Furfural diethyl acetal; Solid acid catalysts; Biofuels

Abbreviations

APAl, Aluminophosphate; FDA, Furfural diethyl acetal; PY, Pyridine; DMPY, 2,6-dimethylpyridine; MTBE, methyl tert-butyl ether; TAME, tert-amyl methyl ether; FF, furfural; BET, Brunauer-Emmett-Teller; BJH, Barrett-Joyner-Halenda; GC-MS, Gas Chromatography-Mass Spectrometry; GC-FID, Gas Chromatography-Flame ionization detector; SBET, Brunauer-Emmett-Teller surface area; RT, Room temperature; m2/g, Square meter per gram; nm, Nanometer; mL/g, Milliliter per gram; μmol/g, Microliter per gram

1. Introduction

Non-renewable energy (crude oil, coal, and natural gas) has been consumed in transportation, industry, and power generation for decades, and increasing demands in recent years due to the dramatical expansion of the world population [16, 39]. The rising demand of fossil fuel energy is producing greenhouse gasses (CO_2, CH_4, and nitrous oxides), causing global warming and environmental issues [40-42]. Nowadays, reducing the use of hydrocarbons and improving fuel properties are getting increasing attention to tackle such issues. It is interesting that biofuels are environmentally friendly and alternative energy as the new generation of people concern about global warming. Biofuels can be directly used or mixed with fossil fuel as bio-additives to enhance flash point, density, and other relevant fuel properties [20, 21].

Oxygenated biofuels are used in fuel components, for example, methyl *tert*-butyl ether (MTBE), ethanol, and *tert*-amyl methyl ether (TAME) [22]. Furfural diethyl acetal (FDA) as one of the oxygenated biofuels has been recently used as a fuel additive to blend with petrochemical fuels. Interestingly, FDA has a higher octane value than gasoline and the boiling point of the FDA is within the gasoline boiling point range [43]. FDA may also lead to lower greenhouse gas emissions due to improved combustion. Therefore, it can be mixed with gasoline effectively and reduce global warming effects instead of the use of fossil fuels without mixing bio-additives. Besides, this may decrease fuel energy costs as well.

Researchers have been recently focusing on biomass conversion for example corn, husk, oat hulls, wood, bagasse, cottonseed hulls, and sugarcane as renewable carbon sources. The use of biomass reduces fossil resource consumption to improve environmental and sustainability issues. Lignocellulose-biomass is used to produce furfural (FF) through an efficient and environmentally friendly process [44]. Furfural is one of the important building block chemicals and it has high production volume (200,000 tons a year) [15, 45, 46]. Moreover, derivatives of furfural include biofuel precursors and bio-based chemicals including acetals, furfuryl alcohol, 2-methylfuran, and 2,5-furandicarboxylic acid, and others are widely employed in bioplastics, solvents and biofuel blends [47]. Hence, the furfural is getting attention lately.

Acetalization is a relevant reaction to protect carbonyl groups for multistep organic synthesis. Furfural acetalization with alcohols can generate acetal products over Brønsted acid sites of homogeneous (HCl, H_2SO_4, H_3PO_4, or HF) or heterogeneous catalysts (metal oxide based catalysts, TiO_2/montmorillonite, zeolites, or metal-organic frameworks) [48-50]. Interestingly, heterogeneous catalysts are getting more attention with the possibility to be easily separated from products, reusability potential, uncomplicated management, and fewer corrosion issues while certain homogeneous catalysts cause corrosive problems and being also difficult to recycle [51]. Various types of alcohols can be used in furfural acetalization, for example, *n*-propanol, *n*-butanol, and ethanol. In addition, ethanol has been used widely for the manufacture of plastics, drugs, cosmetics, perfumes [23], and being largely employed as a bio-derived solvent [24].

Aluminophosphate (APAl) catalysts have been used as solid acid catalysts due to their relevant Brönsted/Lewis acid properties being prepared by sol-gel precipitation or hydrothermal method. These excellent materials have been reported as effectively reusable, eco-friendly, and highly stable in acetalization reactions [37]. It is worth noting that calcination temperature and Al concentration are significantly important factors that influence catalyst acidity and reaction performance [52-54].

Zhou et al. studied TiO_2 nanoparticles supported by exfoliated montmorillonite (MMT) in the acetalization of furfural with alcohols (methanol, ethanol, *n*-propanol, and *n*-butanol) [55]. The short chain length of alcohol gave high reaction activity due to low steric hindrance. Moreover, a high conversion was obtained at room temperature as compared to a higher reaction temperature because of the slower diffusion rate of reactants and products. Du et al. also investigated furfural acetalization with ethanol over Ni-Al layered double hydroxides (Ni-Al-NO_3-LDH), obtaining a maximum of 78.5% conversion and 99% selectivity to FDA [56].

This work reports the use of previously reported APAl catalysts [38, 57, 58] for the acetalization of furfural. The ratio of P/Al and calcined temperature were varied for catalyst preparation and studied in the selected catalytic reaction. FDA was produced through acetalization of furfural and ethanol over APAl catalysts to find the optimum conditions. Reactions were investigated under batch conditions (parallel reaction system) and compared to results obtained under continuous flow at room temperature (atmospheric pressure). Moreover, catalytic reusability and stability were also studied for the optimum catalytic system as well.

2. Materials and methods

2.1 Materials

Analytical grade of furfural ($C_5H_4O_2$) was purchased from Sigma-Aldrich. Ethanol (CH_3OH), ethanol (C_2H_5OH), and acetone (C_3H_6O) were also analytical grade purchasing from PanReac AppliChem. All chemicals were used without further purification. Deionized was using in all processes of the experiments.

2.2 Catalysts preparation

Catalysts were named APAl-X/Y-A-Z which X/Y was the ratio of P/Al ratio and Z was the calcination temperature of catalyst preparation. These systems were previously prepared by the research group, extensively characterized, and employed in a number of acid-catalyzed reactions as previously reported [38, 57, 58].

2.3 Catalysts characterization

Catalysts were characterized by N2 adsorption/desorption to measure the BET surface area by the multiple point BET method and determine the pore diameter and pore volume using the BJH method. Pyridine (PY) and 2,6-dimethylpyridine (DMPY) pulse chromatography titration were used to analyze surface acid properties of catalysts when PY measured total acidity and DMPY interacted only with Brønsted acid sites of catalysts.

2.4 Catalytic reactions

For the batch acetalization of FF and ethanol at various temperatures (25, 35, and 45°C), furfural (3.6 mmol) and ethanol (20 mL, Merck) were mixed with 0.1 g. of catalyst. The acetalization of furfural with ethanol was carried out in the parallel reaction system [59]. The reaction occurred at room temperature under stirring (800 rpm) [60]. The reaction time was 30 min. The solution of reaction was collected at 15 and 30 min by syringe extraction. After that, the reaction solutions were analyzed by GC-MS (5977B MSD) and GC-FID equipped with the HP-5 column. Catalysts were filtrated with methanol and acetone 3 times and dried at 80°C before they could be reused.

For the continuous-flow reaction system, an H-cube mini plus (ThalesNano) instrument was employed. For example, APAl-85/15-A-773 catalyst (0.13-0.14 g) was packed in a CatCart cartridge and placed in the reactor. The solution of furfural and ethanol was prepared. Ethanol was fed through the system while the temperature and feed flow rate were set at 25°C and 0.5 mL/min, respectively. After that, the solution was pumped into the system when the temperature and feed flow rate were stable. Collected samples were withdrawn every 15 minutes until 2 h of reaction time and analyzed by GC-MS and GC-FID [61]. The stability test was studied for 7 h under otherwise identical conditions. Furfural conversion was calculated as follows:

$$\text{FF conversion (\%)} = \frac{\text{Initial mole of FF} - \text{Final mole of FF}}{\text{Initial mole of FF}} \text{ x } 100$$

3. Results and discussion

3.1 Catalysts characterization

P/Al ratios of catalyst were varied at 85/15, 90/10, and 95/5, and calcination temperatures of catalyst preparation were 773, 923, and 1073K (500, 650, and 800°C, respectively). Table 2.1 shows the BET surface area, pore volume, and pore size of catalysts analyzed by N_2 physisorption and Brønsted acid and Lewis acid sites of catalysts. The catalysts with a P/Al ratio of 85/15 exhibited higher BET surface areas (233-279 m^2/g) and pore volumes (0.74-0.79 mL/g) as compared to other catalysts. On the other hand, the smaller pore size of the catalysts with P/Al ratio of 85/15 compared with other catalysts was probably related to the increased Al loading in the systems [62]. It was noticed that the BET surface area of catalysts decreased at increased calcination temperatures [63]. The calcination temperature definitely affected catalyst structure due to partial collapsing of APAl pores [64], having also an important influence on surface hydroxyl groups [65].

Surface acidity of catalysts were measured by Pyridine (PY) and 2,6-dimethylpyridine (DMPY) pulse chromatography titration when DMPY was selectively adsorbed by only Brønsted acid sites because of steric hindrance from methyl group of DMPY. On the other hand, PY was adsorbed on both of Brønsted and Lewis acid sites. Considering of DMPY and PY difference, Lewis acid sites could be estimated. Catalysts with P/Al ratio of 85/15 showed a larger concentration of acid sites as compared to catalysts with 90/10 and 95/5 P/Al ratios. This result indicated that increase of Al concentration enhanced catalyst acidity on APAl [66]. Additionally, calcination temperature influenced the presence of Brønsted acid sites in the catalysts. Materials with P/Al ratios of 85/15, 90/10, and 95/5 had higher Brønsted acid sites when calcined at 773K as shown in Fig. 2.1. This result showed that the rising of calcination temperature could decrease Brønsted acid sites because of reducing surface OH density on APAl catalysts and also contributing to the additional removal of P-OH species on the catalyst surface [67, 68].

Table 2.1 Textural properties of APAl catalysts.

Catalysts	S_{BET} (m^2/g)	Pore volume (mL/g)	Pore size (nm)	PY-300°C adsorption (μmol/g)	DMPY-300°C adsorption (μmol/g)
APAl-85/15-A-773	279	0.74	5.3	79	74
APAl-85/15-A-923	267	0.77	5.9	61	50
APAl-85/15-A-1073	233	0.79	7.1	52	18
APAl-90/10-A-773	194	0.59	6.1	57	45
APAl-90/10-A-923	182	0.49	5.3	50	45
APAl-90/10-A-1073	180	0.53	5.9	47	18
APAl-95/5-A-773	192	0.77	8.0	41	45
APAl-95/5-A-923	189	0.66	7.0	33	29
APAl-95/5-A-1073	165	0.55	6.7	29	12

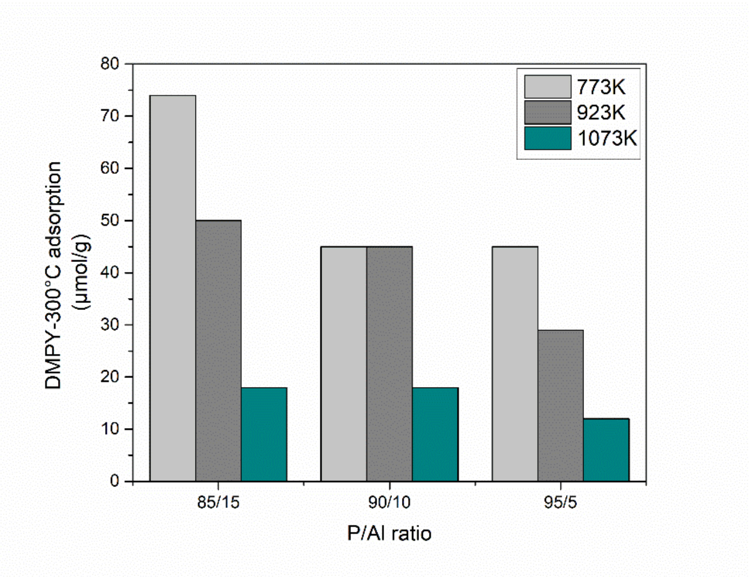

Figure 2.1 Brønsted acid sites of APAl catalysts with different calcination temperature and P/Al ratios.

3.2 Catalytic studies in furfural acetalization

Fig. 2.2 shows that the acetalization of furfural and ethanol in the absence of a catalyst (blank runs) gave virtually no furfural conversion (only traces of products detected after reaction), pointing to the need of a catalyst for the reaction [69, 70]. The reaction was investigated with different prepared catalysts varying P/Al ratio and calcination temperature. Surprisingly, reaction with all APAl catalysts provided > 99% FDA selectivity. Catalysts calcined at 773K furnished 84% furfural conversion within 30 minutes, improved as compared to catalysts calcined at 923K and 1073K. Calcination temperature was confirmed to have a strong effect on the catalytic activity as mentioned above. These findings were closely related to catalyst acidity (increasing calcination temperatures reduced Brønsted acidity as active sites of APAl in the reaction) [71]. Moreover, Al concentration was also a factor impacting catalytic activity. APAl-85/15-A-773 provided 89% conversion, superior to that of APAl-90/10-A-773 and APAl-95/5-A-773. APAl-85/15-A-773 was selected as the optimum catalyst under batch conditions, providing the highest furfural conversion due to optimum Al content and catalyst calcination temperature.

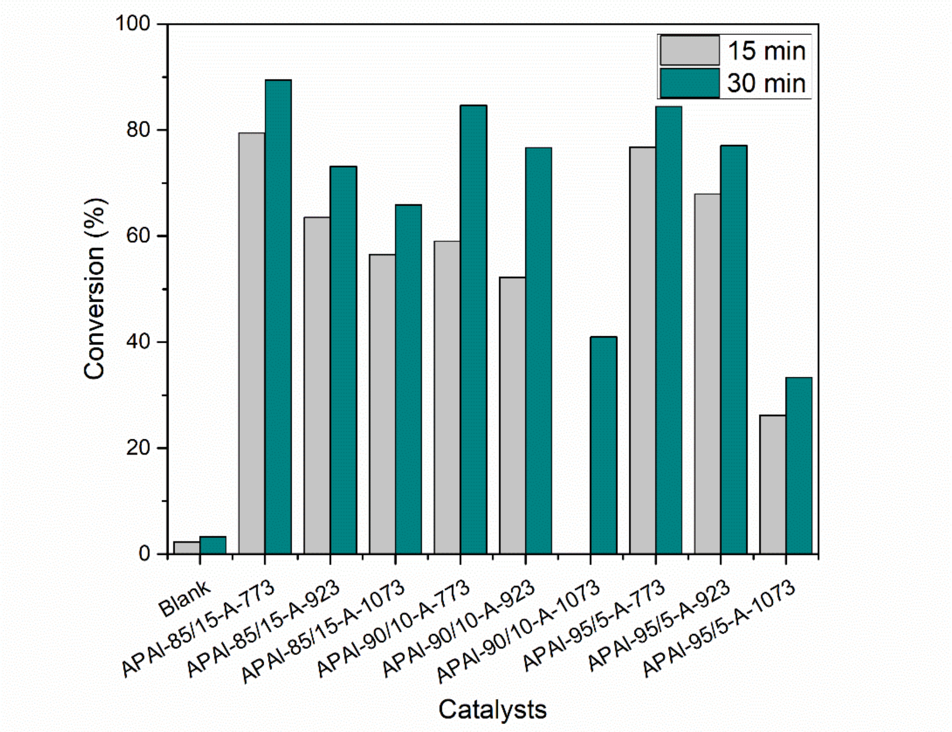

Figure 2.2 Comparison of catalytic performance of different catalysts. Reaction conditions: FF 3.6 mmol, Ethanol 20 mL, Catalysts 0.1 g, reaction temperature = 25°C, reaction time = 30 min.

The acetalization of furfural with ethanol was subsequently studied for optimum reaction temperature as shown in Fig. 2.3. Increasing reaction temperature from 25-45°C surprisingly decreased furfural conversion dramatically due to the reversible exothermic nature of the acetalization reaction. Thus, the optimum reaction temperature was 25°C [55]. Acetalization reactions have been previously reported to proceed well at room temperature [72].

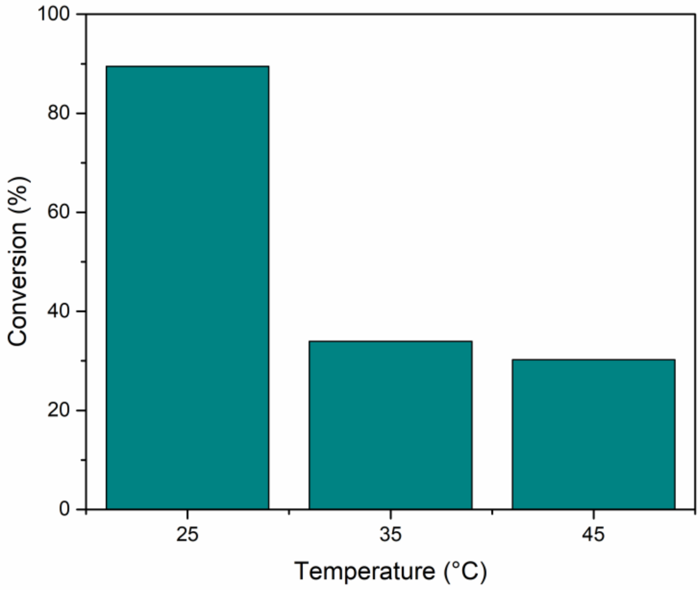

Figure 2.3 The effect of reaction temperature on catalytic performance. Reaction conditions: FF 3.6 mmol, Ethanol 20 mL, APAl-85/15-A-773 0.1 g, reaction time = 30 min.

Fig. 2.4 depicts the reusability studies performed for APAl-85/15-A-773 as an optimum catalytic system. Furfural conversion remained over 76% after 4 cycles and dropped down to 49% in the fifth cycle, showing good stability of APAl catalysts under the investigated reaction conditions. In addition to batch reusability studies, continuous flow experiments were conducted to further investigate the stability of APAl systems. Fig. 2.5 demonstrated the acetalization of furfural with ethanol over APAl-85/15-A-773 under continuous flow could reduce the catalyst and product separation process. The reaction was carried out for 2 h and samples were collected every 15 min. Furfural conversion was over 92% after 2 h of reaction (complete selectivity to FDA). Furthermore, the conversion remained stable for several hours, pointing to excellent catalytic performance and stability of APAl-85/15-A-773 under optimum conditions (RT, flow rate 0.5 mL/min). Comparing batch and flow reactions, higher catalytic activity was observed under continuous flow conditions due to a more effective mass and heat transfer, mixing, and homogeneity of reaction [73]. Moreover, the catalyst stayed in the packed column (separated from the products) which perfectly minimized energy and time saving of catalyst and products separation.

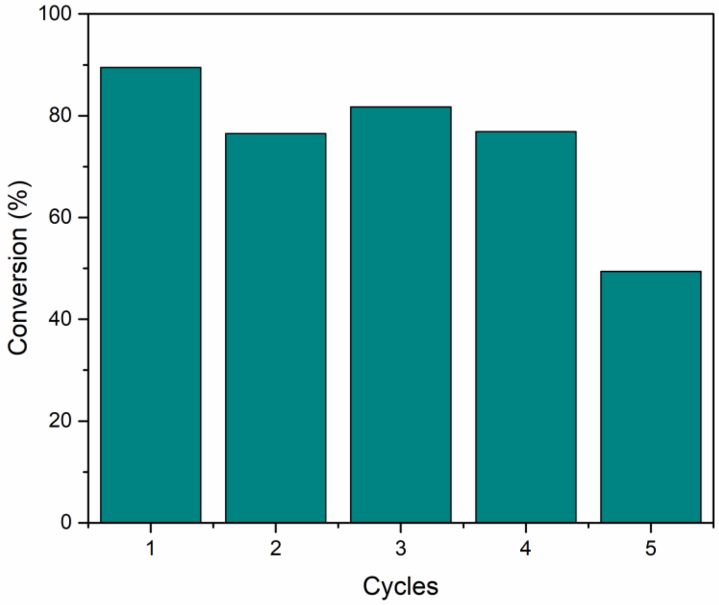

Figure 2.4 Reusability studies for APAl-85/15-A-773 in the acetalization of furfural with ethanol. Reaction conditions: FF 3.6 mmol, Ethanol 20 mL, APAl-85/15-A-773 0.1g, reaction temperature = 25°C, reaction time = 30 min.

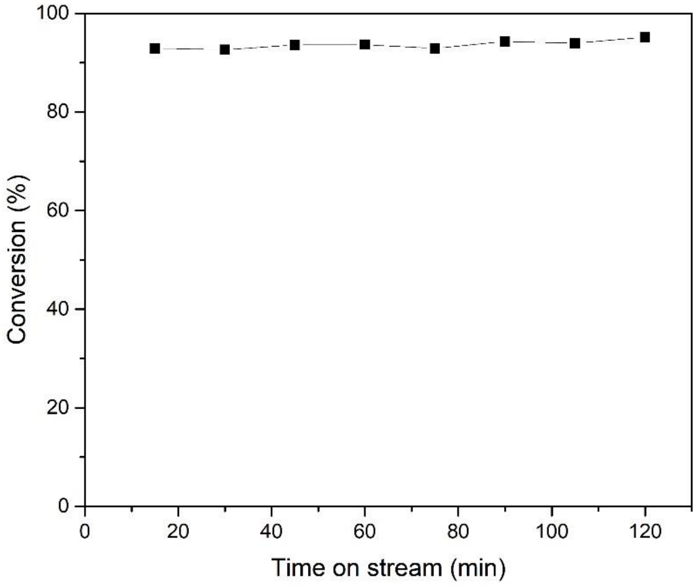

Figure 2.5 Continuous flow acetalization of furfural and ethanol over APAl-85/15-A-773 using H-cube mini-plus (ThalesNano). Reaction conditions: 0.18 M FF in ethanol, APAl-85/15-A-773 0.13-0.14 g, reaction temperature = 25°C, 2 h., feed flow rate = 0.5 mL/min.

In addition, Fig. 2.6 illustrates the high stability of APAl-85/15-A-773 in the acetalization of furfural and ethanol under optimum flow conditions, which could be maintained for 7 h on stream. Furfural conversion only decreased from 90% to 73% after 6 h of reaction time, further to 65% and 59% after 7 h on stream. Thus, the catalysts could be used for long time in flow system and reused several cycles in the batch system as well, demonstrating an excellent stability. Fig. 2.7.

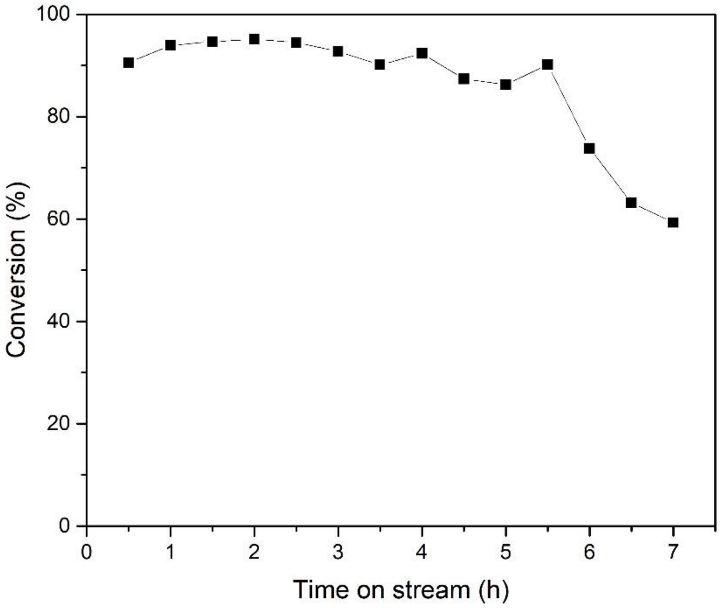

Figure 2.6 Continuous flow stability experiments of APAl-85/15-A-773 in the acetalization of furfural with ethanol (H-cube mini-plus, ThalesNano). Reaction conditions: 0.18 M FF in ethanol, APAl-85/15-A-773 0.13-0.14 g, reaction temperature = 25°C, feed flow rate = 0.5 mL/min.

FDA product was produced in a multistep reaction. Firstly, the protonation of the furfural carbonyl group on Brønsted acid sites of APAl catalysts created an intermediate that reacted with ethanol to form the hemiacetal. After that, re-protonation and dehydration occurred with a further reaction with another ethanol molecule leading to FDA was formed [74-77].

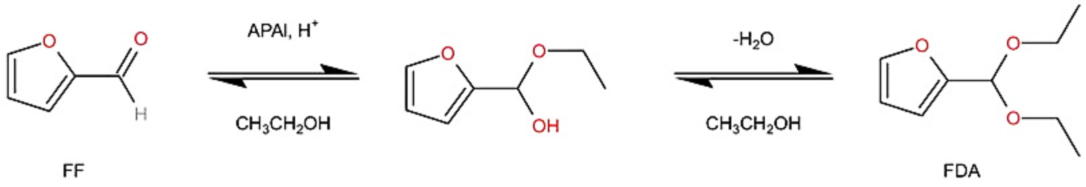

Figure 2.7 Acetalization reaction of FF with ethanol to FDA over APAl catalyst

4. Conclusions

APAl catalysts were successfully synthesized with an optimum combination of acid sites (Brönsted and Lewis) and high surface area. Al content and catalyst calcination temperature significantly influenced Brønsted acid site concentration, playing an important role in the catalytic activity. APAl-85/15-A-773 was found to be the optimum catalytic system for the selected acetalization of furfural with ethanol due to optimum catalyst calcination temperature and high Al concentration. A complete FDA selectivity was rapidly reached over 84% furfural conversion (within 30 min of reaction time) and remarkably obtained under batch reaction conditions at room temperature.

In addition, continuous flow experiments could push conversions in the systems to over 92% (complete FDA selectivity) with a particularly relevant high stability with time on stream. Moreover, the catalyst was stable and able to reuse for several cycle, with a significant stability with time-on stream (>7 h, >70% furfural conversion). These results demonstrate the potential of APAl catalysts in acetalization reactions that will be further explored for more challenging reactions including those with bulky alcohols (t-butyl alcohol) and relevant biomass-derived platform molecules (1,2-butanediol) that will be additionally reported in due course.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

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The FDA was successfully produced over APAl-85/15-A-773 as the best catalyst through acetalization of furfural and ethanol at room temperature without by-product occurred. The furfural conversion was more than 80% with >99% FDA selectivity from batch and flow system. As furfural is an important chemical building block which can be further synthesized other organic chemicals. Thus, it is interesting to study other reactions of furfural transformation. The furfural hydrogenolysis with 2-propanol was estimated. There is possibility to obtain furfuryl alcohol (FOL) by furfural hydrogenolysis over high performance metal oxides catalyst gained from MOFs calcination. This is another method to upgrade furfural as the aim of this work and generate FOL as biofuel. Hence, furfural conversion over calcined Ti and Fe metal-organic frameworks under continuous flow reactor will be reported next.

2.2 Furfural conversion over calcined Ti and Fe metal-organic frameworks under continuous flow reactor

This research manuscript is going to be submitted as a short communication in Journal of Industrial and Engineering Chemistry.

Furfural conversion over calcined Ti and Fe metal-organic frameworks under continuous flow reactor

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Abstract

The MIL-101(Fe) and MIL-125(Ti) were successfully synthesized by the solvothermal method. The metal oxide catalysts were obtained from the calcination of metal-organic frameworks. The hydrogenation of furfural with 2-propanol was catalyzed by calcined MIL-125(Ti) compared with calcined MIL-101(Fe) through the flow system reactor. The reaction without catalyst gave 14% conversion of furfural, and FOL was not produced obviously. Surprisingly, 83% furfural conversion of the reaction occurred over the calcined MIL-125(Ti) with 77% FOL selectivity. On the other hand, calcined MIL-101(Fe) provided lower furfural conversion and FOL selectivity compared with calcined MIL-125(Ti). Moreover, there was high selectivity of by product occurred through the reaction over calcined MIL-101(Fe). The catalysts were characterized by XRD, FT-IR, BET, XPS, and pyridine (PY) and 2,6-dimethyl pyridine (DMPY) pulse chromatography titration.

Keywords: MIL-101(Fe), MIL-125(Ti), Furfural hydrogenation, Solvothermal method, Furfuryl alcohol

1. Introduction

Biomass has been getting attention to use as a source of energy for a long time, especially in these decades due to the disadvantages of fossil fuels such as coal, natural gas, and petroleum oil. The utilization of non-renewable hydrocarbons causes air pollution and the greenhouse effect continuously. Thus, biomass from agriculture (sugarcane, cotton, wood, bagasse, corn) is an alternative option to replace or reduce using of fossil resources or produce some chemicals efficiently. Furfural (FF) is a product derived from the dehydration of xylose from lignocellulosic biomass enriched with pentose derivatives and it is an important initial substance to produce furfuryl alcohol (FOL), 2-methylfuran (2-MF), maleic acid, tetrahydrofuran (THF), levulinic acid (LA), and other useful chemicals [15], [78], [46]. Furfural production was established on an industrial scale in 1921 [45]. Since environmental problems caused by fossil fuels were concerned, furfural production got interested again with 200,000 tons a year [18], [19]. Moreover, about 62% of the furfural manufacture is converted to FOL.

Generally, FOL is starting material used in many industries to produce lubricants, plasticizers, vitamin C, adhesives, coatings, and resins [25], [79]. In addition, FOL is an intermediate to synthesize 2-MF which is used as a gasoline blend or as an intermediate in perfumery. FOL can be synthesized through the liquid or vapor phase. Typical hydrogenation of furfural with hydrogen under high pressure to produce FOL is concerned about safety issues. While catalytic transfer hydrogenation (CTH) of furfural with hydrogen donors (methanol, ethanol, *n*-propanol, *i*-propanol, *n*-butanol, or *i*-butanol) with the assistance of Lewis acid sites of the catalyst is much safer. It has been reported that homogeneous catalysts have been used for the reaction, but it caused many problems such as corrosiveness, and complicated separation between reactants and products. Thus, heterogeneous catalysts have been used widely for many reactions as it is easier for catalyst recovery after the reaction and more stable [26], [80]. Hydrogenation of furfural was catalyzed by many catalysts, for example, metal oxide (Fe_3O_4, TiO_2, and NiO) on support, alumina, or Metal-organic frameworks (MOFs). All the mentioned catalysts are heterogeneous catalysts which can be reused.

MOFs are known as multifunctional materials used in the pharmaceutical industry, catalysts, gas or liquid storage, sensing, separation, and other applications because of their high surface area, porosity, tunable pore size, and thermal stability [31], [81]. More than 20,000 different structures of MOFs are reported nowadays, such as UiO-66, UiO-67, MIL-100, ZIF-67, ZIF-8, HKUST-1, and other MOFs. They are formed by metal atoms as nodes and ligands synthesized by solvothermal, mechanochemistry, or electrochemical methods [32], [33]. MIL-101(Fe), and MIL-125(Ti) are well-known MOFs used in catalytic reactions and absorbents in wastewater. Moreover, they are the most surrogate materials of MIL-n series (MIL = *Matériaux de* l'Institut Lavoisier) [82]. Some previous works reported that metal oxides could catalyze furfural hydrogenation due to their Lewis acid sites that worked on the reaction. Moreover, metal oxides can proceed alkylation, reduction, condensation, cycloaddition, transesterification, dehydrogenation, and other chemical reactions efficiently with variety of reaction conditions. Calcination of the orderly regular structure of MOFs can convert metal ions to metal oxides that are well-dispersed on carbon material to prevent aggregation. This could help improvement of catalytic activity and reduce metal leaching after reaction. Mhadmhan *et al* studied evaluated the catalytic activity of synthesized Fe/Al-SBA-15, 53MOF/Al-SBA-15, 88MOF/Al-SBA-15 and 101MOF/Al-SBA-15 catalysts with different Fe sources for N-alkylation of aniline with benzyl alcohol. These catalysts were mesoporous materials with high surface area. The acidity of catalysts were higher than Al-SBA-15 material which increased aniline conversion. The use of MOF as seeds increased Fe oxide nanoparticles disperse on support surface. The 53MOF/Al-SBA-15 gave the best catalytic activity which indicated that the use of MOF as seeds was more effective than the use of $FeCl_3$. Moreover, the 53MOF/Al-SBA-15 could reuse due to its stability of mechanochemically synthesized catalyst [83].

Pirmoradi *et al* reported about furfural hydrogenation over Pd-TiO_2 supported on activated carbon catalyst [84]. Metal sites and TiO_2 acted as active sites for the reaction. The reaction occurred through a continuous reactor system with H_2 gas at 180°C and 2.1 MPa. The products were 2-MF, tetrahydrofurfuryl alcohol (THFA), 5-hydroxy-2-pentanone (5H2P), and FOL as an intermediate. The fractional conversion of furfural was about 0.50 mol/mol within 0.011 h with FOL as the main product. The 5H2P selectivity and furfural conversion were increasing over time. Moreover, mechanism and mass transfer analysis were studied in this work.

Li *et al* investigated furfural hydrogenation over Fe_3O_4@C magnetic catalyst [85]. The catalyst was synthesized by a solvothermal process forming Fe_3O_4 and graphitic carbon from glucose. Increasing glucose and Fe_3O_4 ratio caused thicker the coated carbon shell of the catalyst. The Fe_3O_4@C catalyzed furfural hydrogenation with isopropanol as a hydrogen donor and obtained FOL as the main product. Isopropanol was the best H_2 donor compared with other alcohol (methanol, ethanol, n-propanol, n-butanol, and *i*-butanol) as it is a secondary alcohol. The optimum condition was 473K with 4 h and 0.05 g of catalyst and this provided 93.6% of FF conversion and 98.9% of FOL selectivity. Moreover, the catalyst could be recycled efficiently.

In this work, calcined MIL-101(Fe) and calcined MIL-125(Ti) were synthesized by the solvothermal method and calcination, respectively. They were characterized by XRD, FT-IR, BET, XPS, TEM, and pyridine (PY), and 2,6-dimethyl pyridine (DMPY) pulse chromatography titration and tested with furfural hydrogenation reaction through a flow reactor system. The results were compared with the previous works of furfural hydrogenation over other catalysts. The calcined MIL-101(Fe) and calcined MIL-125(Ti) were interesting due to the well-dispersed iron and titanium oxides as the active sites on the catalysts. Moreover, these metals (Fe and Ti) are not as expensive as Pd or Au which were selected to catalyze in other work of furfural hydrogenation.

2. Experimental

2.1 Catalyst preparation

MIL-101(Fe) was synthesized using Iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) and terephthalic acid. These chemicals were dissolved in dimethylformamide (DMF) and stirred for 1 hour at room temperature. Then, the mixture was transferred into autoclave and placed in the oven at 120°C for 20 h. The solid was cool down, filtrated, and rinsed with DMF and ethanol, respectively, for few times. The obtained MIL-101(Fe) was dried in the vacuum oven for 70°C overnight.

MIL-125(Ti) was prepared using Titanium (IV) isopropoxide and terephthalic acid. The chemicals were dissolved in DMF and methanol solvents stirring for 20 minutes at room temperature. The mixture was added to the autoclave and heated to 150°C for 20 h. Then, the precipitate was cool down, filtrated and rinsed with DI water and ethanol for few times. After that, the white solid was dried at 80°C for 2 h. The DMF in the white solid was removed by calcination at 200°C for 10 h. Finally, MIL-125(Ti) was obtained.

Both MOFs were calcined to gain C-MIL-101(Fe) and C-MIL-125(Ti) (iron oxides and titanium oxides) using as the catalysts. All MOF and calcined MOFs were characterized by XRD, FT-IR, BET, XPS, and pyridine (PY), and 2,6-dimethyl pyridine (DMPY) pulse chromatography titration.

2.2 Catalytic studies

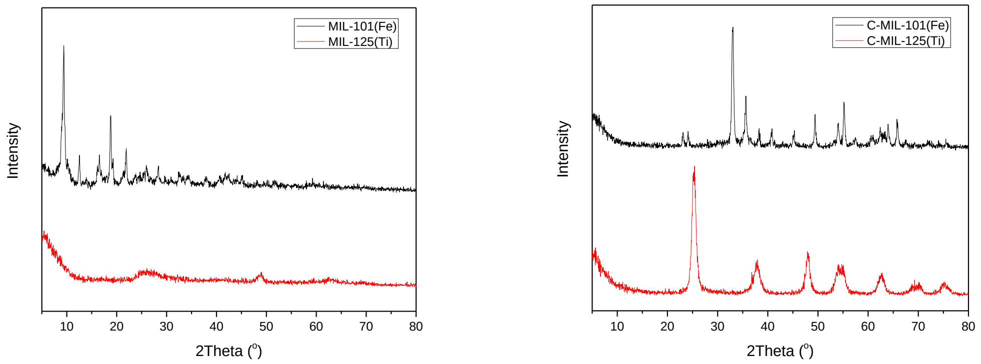
The catalysts were tested by hydrogenation of furfural (2 mmol) with 2-propanol (10 mL) under 200°C and 20 bar with reactants flow rate of 0.2 mL/min for 2 h by Phoenix flow reactor. The products were collected every 15 min. and analyzed by Gas Chromatography – Mass Spectrometry (GC-MS) and Gas Chromatography with Flame Ionization Detector (GC-FID).

3. Results and discussion

3.1 Catalyst characterizations

The MOFs and the calcined MOFs were characterized by X-ray diffraction (XRD). XRD patterns of MIL-101(Fe) and MIL-125(Ti) illustrate in Figure 2.8 a. The results show that MIL-101(Fe) had diffraction patterns at 9.42°, 9.66°, and 18.88° indicating the MIL-101(Fe) formation [86], [87].

Figure 2.8 b shows XRD patterns of calcined MOFs. C-MIL-125(Ti) illustrated diffraction peaks at 2Θ = 25.8°, 38.7°, 48.3°, 54.4°, 55.4°, 63°, 69.5°, and 75°, representing the typical anatase phase. Moreover, there were less intense diffraction patterns at 27.1° and 36.1° that ascribed to the rutile phase in the C-MIL-125(Ti). These indicated that MIL-125(Ti) had changed to anatase and rutile TiO_2 after calcination [88]. XRD diffraction of C-MIL-101(Fe) showed 2Θ at 24.12°, 33.12°, 35.61°, 40.88°, 49.51°, 54.22°, 57.63°, 62.45°, and 64.11° ascribed to hematite Fe_2O_3 phase [89]. In addition, there were weak diffraction patterns of Fe_3O_4 appeared at 2Θ values of 30.1°, 35.4°, 43.1°, 53.4°, 56.9°, and 62.3°. These specified that there were 2 species of iron oxides that occurred after MIL-101(Fe) calcination.



a. b.

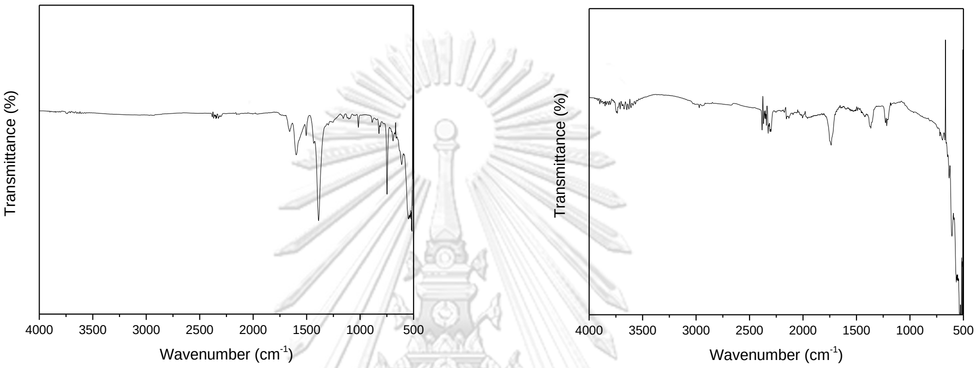
Figure 2.8 XRD patterns of MIL-101(Fe) and MIL-125(Ti) (a.) and XRD patterns of C-MIL-101(Fe) and C-MIL-125(Ti) (b.)

FT-IR patterns of MOFs are shown in Figure 2.9 There were apparent peaks in the region of 1600-1400 cm^{-1} representing asymmetric and symmetric O-C-O bonds of terephthalic acid ligands of MIL-101(Fe) in Figure 2a. Moreover, peaks at 590 and 790 cm^{-1} belonged to Fe-O vibration and C-H bending vibration of benzene of MIL-101(Fe), respectively [33], [82]. In Figure 2b, strong bands around 1650 and 1400 cm^{-1} ascribed to vibrational stretching of the carboxylate (-COO^{-}) group of the ligands of MIL-125(Ti). In addition, there were peaks between 500-800 cm^{-1} assigned to O-Ti-O vibrations [90].

Table 2.2 shows textural and porosity results of calcined MOFs (C-MIL-101(Fe) and C-MIL-125(Ti)) determined by N_2 adsorption/desorption isotherms. C-MIL-125(Ti) had the largest BET surface area, pore diameter, and mesopore volume compared to C-MIL-101(Fe). Moreover, all calcined MOFs showed a type IV isotherm with an H3 hysteresis loop that demonstrated mesopore materials with wedge-shaped pores as shown in Figure 2.10

Due to the hydrogenation reaction requires acid sites on the surface of the catalysts to drive the reaction. Thus, PY and DMPY pulse chromatography titration are needed to estimate the acid properties on the catalysts. This characterization presents Lewis and BrØnsted acid sites on the catalysts when DMPY is selectively adsorbed on only BrØnsted acid sites while PY is adsorbed on both of Lewis and BrØnsted acid sites.

Therefore, the difference between PY and DMPY adsorption could determine Lewis acid sites on the catalysts. Table 2.2 showed that the biggest difference between DMPY and PY belonged to C-MIL-125(Ti), demonstrating that C-MIL-125(Ti) had the largest amount of Lewis acid sites. On the contrary, the C-MIL-101(Fe) had a small amount of Lewis acid sites but it had higher amount of BrØnsted acid sites. It was noticed that titanium dioxides and iron oxides acted as the Lewis acid sites on C-MIL-125(Ti) and C-MIL-101(Fe), respectively.



a. b.

Figure 2.9 FT-IR patterns of MIL-101(Fe) (a.) and MIL-125(Ti) (b.)

Table 2.2 Textural properties obtained from N_2 sorption experiments and acid properties achieved from PY and DMPY pulse chromatography titration of calcined MOFs.

Catalysts	BET surface area (m^2/g)	Mesopore volume (cm^3/g)	Pore diameter (Å)	PY (μmol/g)	DMPY (μmol/g)
C-MIL-101 (Fe)	119.28	0.235357	38.4	69	62
C-MIL-125 (Ti)	122.41	0.282439	83.0	119	25

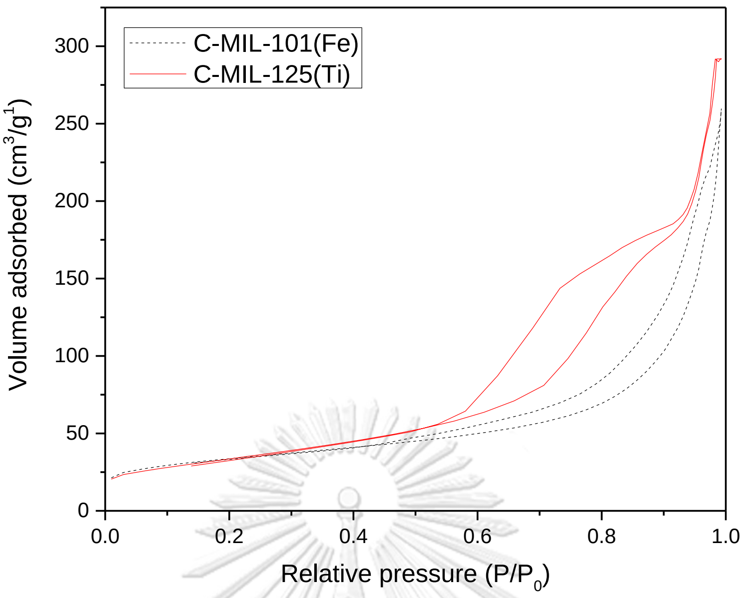


Figure 2.10 N_2 adsorption/desorption isotherms of calcined MOFs (C-MIL-101(Fe) and C-MIL-125(Ti))

Figure 2.11 shows the XPS spectrum of C-MIL-101(Fe) and C-MIL-125(Ti). The different peaks were observed at C 1s, O 1s, and Fe 2p representing C-MIL-101(Fe) material whereas there were C 1s, Ti 2p, and O 1s XPS spectrums which coexisted in C-MIL-125(Ti) catalyst. Moreover, different peaks of Ti 2p existed at 465 and 459 eV demonstrating to Ti $2p_{1/2}$ and Ti $2p_{3/2}$ of anatase and rutile of TiO_2. In addition, there were 2 peaks of Fe 2p at 710 and 724 eV which corresponded to Fe $2p_{3/2}$ and Fe $2p_{1/2}$ spin orbitals, respectively.

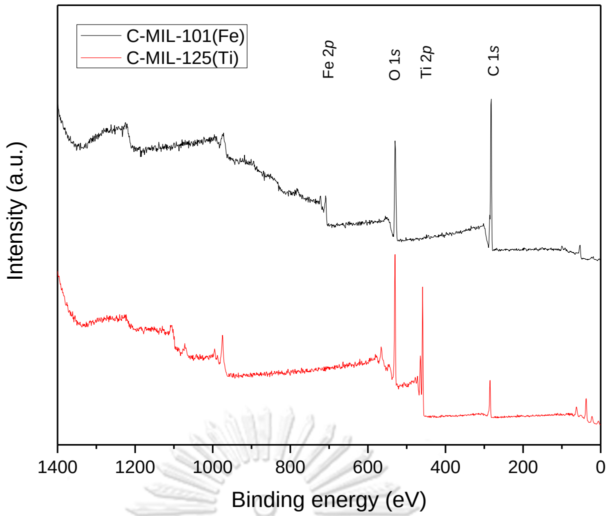


Figure 2.11 XPS survey scans of calcined MOFs (C-MIL-101(Fe) and C-MIL-125(Ti))

3.2 Catalyst tests

Furfural as an important chemical building block can be converted to useful chemicals for many industries as shown in figure 2.12. Furan and furoic acid were obtained through decarboxylation and oxidation, respectively [91]. There were many works studying about furfural conversion to 5-hydroxymethylfuran (5-HMF) with hydrolysis reaction [92]. It can be transformed to levulinic acid which can be used as biofuel or fuel additives [93]. Moreover, furfural of reductive amination and decarbonylation can produce furfurylamine and 2-methyl furan, respectively. In this work, furfural alcohol was focused as it was used in plenty fields.

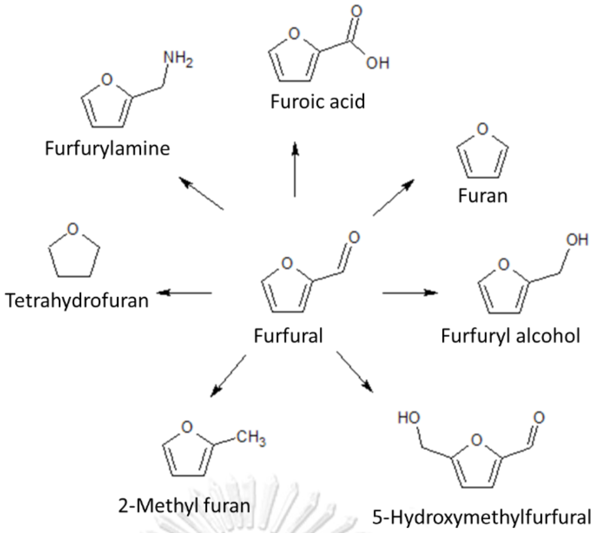


Figure 2.12 Furfural conversion into important chemical compounds.

Several works were studying about hydrogenation reactions with various catalysts. Feng Li, et al studied the optimum condition of furfural hydrogenation [85]. It was discovered that the type of alcohol (H_2 donors) plays an important role in the reaction. Interestingly, the 2-propanol had low reduction ability. Moreover, the H atom at the α-C position of 2-propanol was easy to activate and lead to the reaction. On the other hand, methanol was not good at offering proton as it had a strong reduction performance. Thus, 2-isopropanol is the best H_2 donor from the literature. The high FF conversion was achieved when the temperature was increased from 160 to 200°C.

The calcined MOFs were tested in furfural hydrogenation using 2-propanol as an H_2 donor to obtain furfuryl alcohol (FOL) as the main product and the catalyst performance was showed in Figure 2.13. The reaction without catalyst (blank) gained very low FF conversion and without generating FOL as the desired product. On the other hand, the reaction with catalysts could produce FOL with higher FF conversion. These results demonstrated that the furfural hydrogenation definitely needed the catalysts.

C-MIL-125(Ti) had the highest FF conversion which reached 83%. Moreover, the catalyst gave 77% FOL selectivity which is the main product due to C-MIL-125(Ti) contained the largest amount of Lewis acid sites of TiO_2 with the wildest BET surface area, compared with C-MIL-101 (Fe) catalyst. However, there were other products with about 20% selectivity occurred during furfural hydrogenation over C-MIL-125(Ti). This result revealed that Lewis acid is an active site to catalyze the reaction. Unexpectedly, the reaction with C-MIL-101(Fe) achieved FF conversion at 34%. This result showed that the textural properties of catalysts directly influence the FF conversion and FOL selectivity due to catalyst active sites were located on the catalyst surface and optimum pore diameter would affect FOL production from reactants and mass transfer in the reaction system.

Table 2.3 The catalytic activity of previous works of furfural hydrogenation over various catalysts compared to this work.

Catalysts	Conditions	FF conversion (%)	FOL selectivity (%)	References
Fe_3O_4/C	Furfural, 2-propanol, batch reactor, 200°C, 20 bar, and 4 h	76.4	98.5	[29]
5% Pd/TiO_2 5% Ru/TiO_2 1%Ru-4%Pd/TiO_2	Furfural, H_2, batch reactor, 200°C, 20 bar, and 4 h	65.4 8.2 39.3	28.6 100 45.3	[27]
C-MIL-125(Ti)	Furfural, 2-propanol, flow reactor, 200°C, 20 bar, 0.2 mL/min flow rate, and 2 h	83	77	This work

Table 2.3 shown catalytic activity of furfural hydrogenation with 2-propanol over Fe_3O_4/C catalyst in the autoclave obtained 76.4% FF conversion. The Fe_3O_4/C

catalyst was prepared by Fe MOF calcination. The well dispersed metal oxides on the catalyst could help to provide high FOL selectivity. On the other hand, the furfural hydrogenation without alcohol as the H_2 donor over 5% Pd/TiO_2 catalyst gave 65.4% FF conversion with low FOL selectivity. While 5% Ru/TiO_2 allowed 100% FOL selectivity with only 8% conversion. The bimetallic of 1%Ru-4%Pd/TiO_2 was prepared to increase both of desired product selectivity and conversion but the use of H_2 gas might cause safety issue during the reaction. In this work, the C-MIL-125(Ti) offered incredibly high conversion of FF to 83% with high FOL selectivity without adding another metal into the catalyst. In addition, flow reactor provided higher catalytic activity due to good mass and heat transfer. Moreover, the use of alcohol as H_2 donor is much safer while the reaction was proceeded.

The catalytic transfer hydrogenation (CTH) is used to explain the mechanism of the furfural hydrogenation with alcohol as an H_2 source through iron oxides or titanium dioxides as Lewis acid sites as shown in Figure 2.14 [94, 95]. The first pathway was that the electrophile of the catalyst and C=O of FF were having an interaction through lone pair electrons of oxygen while the oxide site of the catalyst will form with a hydrogen bond of 2-propanol creating a six-member transition state. After that, FOL was produced as a product from the reaction. The second pathway was that dehydrogenation of 2-propanol had occurred on the metal sites. The H atom activated the carbonyl group of FF, creating the alkoxide. Then, another H atom interacted with the O atom of the alkoxide intermediate and produced the FOL product.

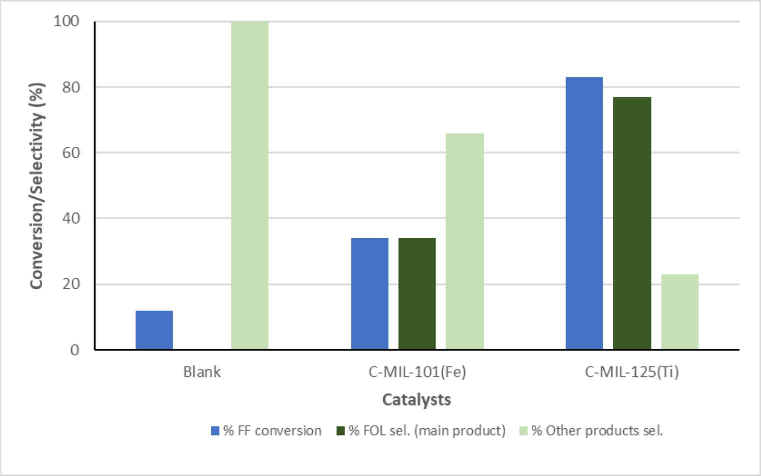


Figure 2.13 The catalytic activity of furfural hydrogenation with 2-propanol over calcined MOFs with Phoenix flow reactor. (Reaction conditions: 200°C, 20 bar, reactants flow rate of 0.2 mL/min, and reaction time = 2 h)

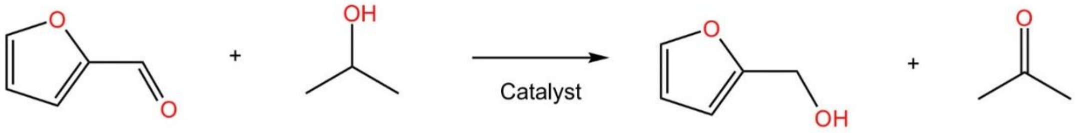


Figure 2.14 Catalytic transfer hydrogenation (CTH) of furfural to furfuryl alcohol over catalyst (calcined MOFs).

4. Conclusion

The MIL-125(Ti) and MIL-101(Fe) were successfully synthesized with hydrothermal method. The metal oxides were obtained directly from calcination of MOFs. The C-MIL-125(Ti) performed better than C-MIL-101(Fe) in furfural hydrogenation with 2-propanol. The C-MIL-125(Ti) provided 83% furfural conversion with 77% FOL selectivity which was higher than C-MIL-101(Fe) performance due to C-MIL-125(Ti) had higher amount of Lewis acid sites and larger BET surface area. Moreover, the flow system usually helps the reaction reach high conversion and product yield due to its good mass and heat transfer. In addition, metal oxides derived from MOFs had well metal dispersion on the catalyst with less metal leaching during the reaction. This may be a reason that the reaction hit high performance.

Chapter 3

Conclusions and recommendations

3.1 Conclusion

In this work, aluminophosphate and metal oxides derived from metal-organic frameworks were successfully prepared and used as the catalysts for acetalization and hydrogenolysis reactions to produce furfural diethyl acetal and furfuryl alcohol, respectively. As this thesis consists of two topics, there are three parts of conclusion (acetalization, hydrogenolysis, and overall conclusion).

In the first research topic “Batch and continuous-flow room temperature furfural acetalization with ethanol over aluminophosphate (APAl) catalysts for biofuels production”, the aluminophosphate catalysts were varied P/Al ratio (85/15, 90/10, and 95/5) and calcination temperature (773, 923, 1073 K) to find the best catalyst for furfural acetalization with ethanol. In the batch system with conditions of furfural = 3.6 mmol, ethanol = 20 mL, reaction temperature = 25°C, and reaction time = 30 min., the APAl-85/15-A-773 (0.1 g.) was the best catalyst. The catalyst provided 89% furfural conversion and >99% FDA selectivity due to P/Al ratio of 85/15 gave a larger concentration of acid sites which were active sites to proceed the reaction. Moreover, the calcination temperature at 773 K was not extremely high. Thus, the Brønsted acid sites were not destroyed by the calcination temperature. In addition, the optimum reaction temperature was 25°C. The acetalization was the naturally reversible exothermic reaction. Hence, decreased furfural conversion was caused by the increasing reaction temperature. Furthermore, continuous flow experiments could boost conversion to over 92% because the flow system provided better mass and heat transfer. Surprisingly, the catalyst was able to reuse for several cycles, with high stability over 6 h of the time-on stream (>70% furfural conversion).

In the second research topic “Furfural conversion over calcined Ti and Fe metal-organic frameworks under continuous flow reactor”, the MIL-101(Fe) and MIL-125(Ti) were successfully synthesized by hydrothermal method. Then, the metal oxide catalysts were prepared from the calcination of the MOFs. Both catalysts were measured through furfural hydrogenolysis with 2-propanol under the conditions of 200°C, 20 bar, reactants flow rate of 0.2 mL/min, and 2 h reaction time with the flow system. The C-MIL-125(Ti) catalyst with TiO_2 was the best catalyst (providing 83% furfural conversion and 77% furfuryl alcohol selectivity) due to its larger specific surface area and higher amount of Lewis acid active sites compared to C-MIL-101(Fe). Moreover, the flow system helped the catalyst reach high catalytic activity. The metal oxide prepared by calcination of MOF was another reason for offering high catalyst performance because of well metal dispersion on the catalyst with less metal leaching during the reaction.

For the overall conclusion of the thesis, furfural as a starting chemical obtained from biomass was upgraded to the valuable fuel additive and biofuel (furfural diethyl acetal and furfuryl alcohol) through chemical reactions. Meanwhile, the use of biofuel or fuel additives blending with gasoline could decrease greenhouse gas emission which affected to slow down of global warming issue. The APAl-85/15-A-773 (aluminophosphate) and C-MIL-125(Ti) (metal oxide) catalyst performed great efficiency and provided furfural diethyl acetal and furfuryl alcohol as desired products with high catalytic activity through furfural acetalization and hydrogenolysis reactions, respectively. Besides, the catalyst had high stability to catalyze the reactions.

3.2 research limitations

After each run of reaction with furfural had done, cleaning the flow reactors and the system line took long time due to the flow reactors (Phoenix flow reactor and H-cube mini plus (ThalesNano) instrument) had small diameter of the reactors and the system line. The furfural could be stuck easily due to its high viscosity.

3.3 Recommendations

In the topic “Batch and continuous-flow room temperature furfural acetalization with ethanol over aluminophosphate (APAl) catalysts for biofuels production”, the spent APAl-85/15-A-773 should be characterized by XRD and FT-IR to prove the textural structure after reaction or catalyst reuse (The XRD pattern of spent APAl-85/15-A-773 was further shown in appendix). Moreover, the APAl catalysts should be further explored in acetalization with bulky alcohols (t-butyl alcohol) and relevant biomass-derived platform molecules (1,2-butanediol) for more challenge. Besides, the reaction should be tested in different flow rate in the flow system.

In the topic of “Furfural conversion over calcined Ti and Fe metal-organic frameworks under continuous flow reactor”. The catalyst reuse should be characterized and tested in the reaction to study catalyst reusability as the catalyst had good stability. (The XRD pattern of spent C-MIL-125(Ti) was further shown in appendix)

Chapter 4

Appendix

4.1 Batch and continuous-flow room temperature furfural acetalization with ethanol over aluminophosphate (APAl) catalysts for biofuels production

In order to study the textural structure of the spent APAl-85/18-A-773, the catalyst was characterized by XRD as shown in figure 4.1. The spent APAl-85/18-A-773 had amorphous structure due to broad area was found in the range of 15°-26°.

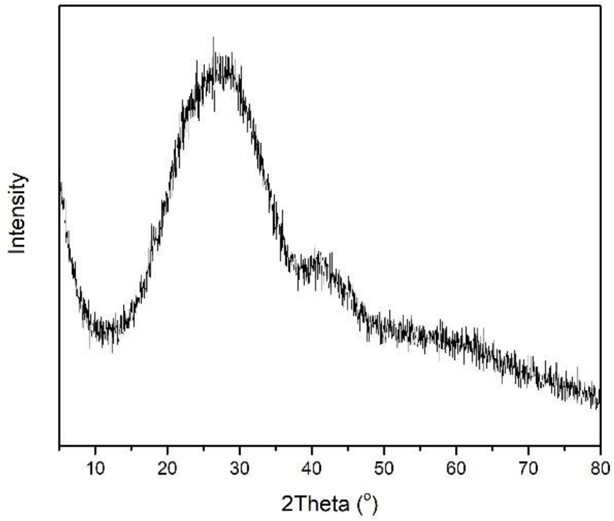


Figure 4.1 XRD pattern of spent APAl-85/18-A-773 in furfural acetalization with ethanol at 25°C

4.2 Furfural conversion over calcined Ti and Fe metal-organic frameworks under continuous flow reactor

In order to study the textural property of the spent C-MIL-125(Ti), the catalyst was characterized by XRD as shown in figure 4.2. The spent C-MIL-125(Ti) had diffraction peaks at 2ϴ = 25.8°, 38.7°, 48.3°, 54.4°, 55.4°, 63°, 69.5°, and 75° of the typical anatase phase. In addition, the spent C-MIL-125(Ti) had low intense diffraction patterns at 27.1°

and 36.1° that ascribed to the rutile phase. These results demonstrated that spent C-MIL-125(Ti) maintained anatase and rutile TiO_2 after furfural hydrogenolysis with 2-propanol at 200°C and 20 bar after 2 h of reaction time. This result showed that the spent C-MIL-125(Ti) catalyst was able to reuse in the reaction due to it kept the active sites after the reaction.

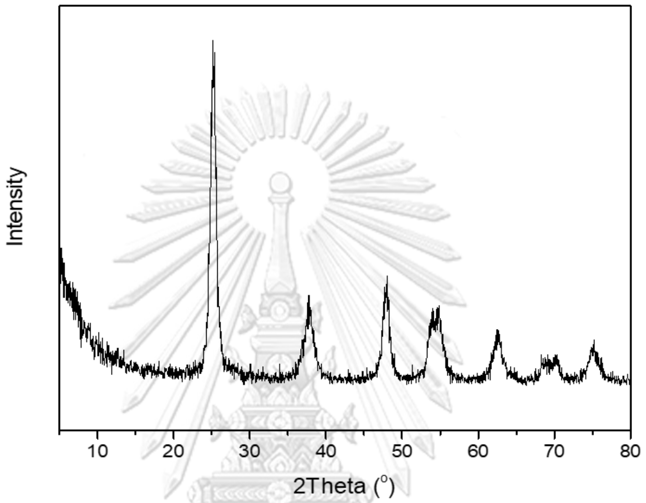


Figure 4.2 XRD pattern of spent C-MIL-125(Ti) after furfural hydrogenolysis reaction with 2-propanol in the Phoenix flow reactor. (Reaction conditions: 200°C, 20 bar, reactants flow rate of 0.2 mL/min, and reaction time = 2 h)

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