SOLUTION COMBUSTION SYNTHESIS OF NB-AL AND W-AL OXIDE CATALYSTS FOR
DIRECT PRODUCTION OF 5-HMF FROM GLUCOSE

By

MR. Poramathe JARUNOTHAI

A Thesis Submitted in Partial Fulfillment of the Requirements

for Master of Engineering (CHEMICAL ENGINEERING)

Department of CHEMICAL ENGINEERING

Graduate School, Silpakorn University

Academic Year 2021

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Field of Study   (CHEMICAL ENGINEERING)

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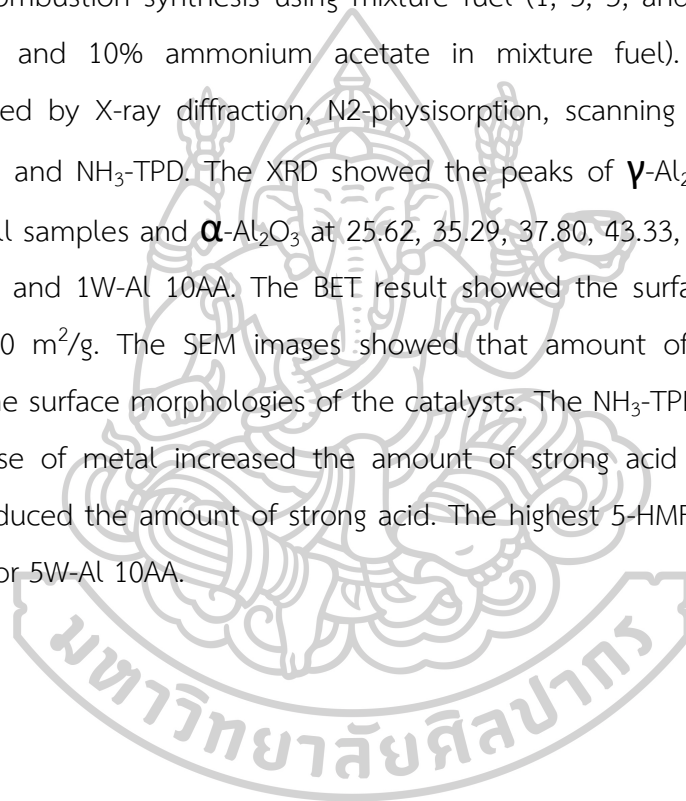(Professor Joongjai Panpranot, Ph.D.)
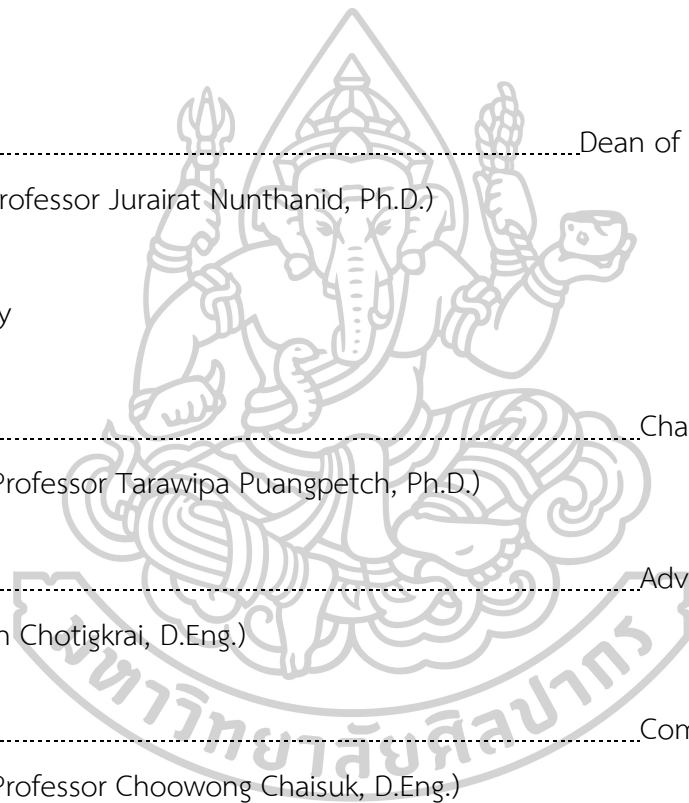
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MR. PORAMATHE JARUNOTHAI : SOLUTION COMBUSTION SYNTHESIS OF NB-AL AND W-AL OXIDE CATALYSTS FOR DIRECT PRODUCTION OF 5-HMF FROM GLUCOSE THESIS ADVISOR : NUTCHAPON CHOTIGKRAI, D.Eng.

In this work, niobium- and tungsten- promoted aluminas were syntheses by solution combustion synthesis using mixture fuel (1, 3, 5, and 10% metal loadings and 0, 5, and 10% ammonium acetate in mixture fuel). The catalysts were characterized by X-ray diffraction, N2-physisorption, scanning electron microscopy, pyridine-IR, and NH_3-TPD. The XRD showed the peaks of γ-Al_2O_3 at 36.9, 45.3, and 67.7° for all samples and α-Al_2O_3 at 25.62, 35.29, 37.80, 43.33, 52.52, and 57.46 $^\circ$ for 1W-Al 5AA and 1W-Al 10AA. The BET result showed the surface of all catalysts is around 290 m^2/g. The SEM images showed that amount of ammonium acetate affected the surface morphologies of the catalysts. The NH_3-TPD results showed that the increase of metal increased the amount of strong acid site and ammonium acetate reduced the amount of strong acid. The highest 5-HMF yield at 41.46% was obtained for 5W-Al 10AA.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1.1   Motivation

Thailand is an agricultural country. Thus, there are many biomass wastes each year such as straw and sugarcane leaves. It is used in many processes for reducing whether it be making fertilizer for agriculture or using as a fuel for steam power plants, but the biomass weights remain a lot. The biomass wastes consist of cellulose, hemicellulose, and lignin which can be used as a precursor for synthesis of high volume substant. 5-hydroxymethylfurfural is one of the substances which have a high price and many applications such as levulinic acid, 2,5-diformylfuran, 1,6-hexanediol, and 2,5-dimethylfuran[1-7]. To synthesize 5-hydroxymethylfurfural, cellulose is hydrolyzed to glucose monomers under acid conditions. After hydrolysis reaction, glucose is isomerized to Fructose under Lewis acid condition. Then fructose is dehydrated to 5-hydroxymethylfurfural under Brønsted acid condition. Thus, the ratio of Lewis and Brønsted acidity is so important for 5-hydroxymethylfurfural synthesis.

From early research, 5-hydroxymethylfurfural synthesis was studied using homogeneous acid catalysts which give high yield and selectivity, even so, they do damage to equipment and are hard to separate the catalyst from the product[8-11]. Then solid acid catalysts were used to synthesize 5-hydroxymethylfurfural in the water system because they are easy to separate and do not do damage to equipment. Many solid acid catalysts have been studied and adjusted to find the condition which give high yield of 5-hydroxymethylfurfural whether it be adjusting the ratio and acidity of catalysts and methodology of catalysts synthesis. Aluminium oxide is the one that has a high surface area and Lewis acid site to promote isomerization reaction. Niobium oxide is the one which has a Brønsted acid site to

promote dehydration reaction to produce 5-hydroxymethylfurfural. Both niobium and aluminium oxide have each acid site property, but niobium is a relatively strong Brønsted acid site on the surface. Thus, a high surface of a niobium active site can make a Brønsted acid site too. Thus, catalyst preparation is important for catalyst properties for 5-hydroxymethylfurfural production. Solution combustion synthesis is a catalyst preparation which has been known as the method using metal nitrate and fuel mixture is combusted to get nanoparticles side and high surface area of metal oxide. The catalysts can be adjusted by adding gas generating agents to gain more gases which make metal oxide more porous. However, the selectivity is low because 5-hydroxymethylfurfural can be dehydrated to levulinic acid and formic acid in water. To solve the dehydration problem, biphasic systems which have been known as a 2-phase liquid system consisting of aqueous and organic liquid have been used for synthesis 5-hydroxymethylfurfural to extract the product before they convert to another substance. Many kinds of salts were used in biphasic systems to improve 5-hydroxymethylfurfural extraction such as NaCl. However, byproducts still occur because the reaction appears in water phase. Ionic liquid has been replaced with water to decrease the side reactions because they have functional groups such as alcohol and carboxylic acid. The results show Ionic liquid gives a high 5-hydroxymethylfurfural yield. However Ionic liquid is expensive and toxic. Therefore, Deep eutectic solvents which have been known as a liquid mixture between hydrogen bond donors such as oxalic acid and hydrogen bond acceptors such as choline chloride have been attentive because they have properties similar to Ionic liquids whether it be high vapor pressure and have many kinds of the functional group but less expensive and toxic than Ionic liquids.

This research aims to niobium oxide and tungsten oxide support on aluminium oxide catalyst using solution combustion synthesis method with gas-generating agent to synthesize 5-hydroxymethylfurfural.

1.2 Objective of Research

1.2.1 To adjust the catalyst properties by varying Nb_2O_5 and WO_3 loadings and concentrations of ammonium acetate via solution combustion method.

1.3 Scope of Research

1.3.1 Effect of metals loadings and amount of gas-generating agent.

Part I: Niobium oxide and tungsten oxide loadings (1, 3, 5, and 10 wt%)

Part II: Ammonium acetate as gas-generating agent (0, 5, 10 wt% of combustion mixture)

Table 1 Catalysts loading and gas generating agent

Catalysts	wt% of catalyst	mole% of Ammonium acetate		
1Nb-Al	1	0	5	10
3Nb-Al	3	0	5	10
5Nb-Al	5	0	5	10
10Nb-Al	10	0	5	10
1W-Al	1	0	5	10
3W-Al	3	0	5	10
5W-Al	5	0	5	10
10W-Al	10	0	5	10

CHAPTER II

LITERATURE REVIEWS

2.1 5-HMF Production

5-hydroxymethylfurfural (5-HMF) is one of the platform molecules which has been used to synthesize various chemicals which use in polymer, pharmaceutical, fragrances and fuels such as levulinic acid, 2,5-diformylfuran, 1,6-hexanediol and 2,5-dimethylfuran[1-7]. To synthesizes 5-HMF, a component of biomass wastes could be used as feedstock. The first step is hydrolyzation of lignocellulose and separating cellulose to convert to glucose. Glucose will be converted to fructose which is called isomerization. The reaction can be catalyzed by Lewis acids[12]. The isomerization is important to yield of 5-HMF because the amount of fructose depends on glucose conversion. fructose can be converted to 5-HMF by dehydration which removes 3 molecules of water from fructose to 5-HMF by using Brønsted acids[12]. Thus, the ratio of Lewis and Brønsted acidity is so important for 5-hydroxymethylfurfural synthesis. By the way, 5-HMF can be reacted and converted to levulinic acid and formic acid when 5-HMF is solved in water.

2.2 Acid catalyst for 5-Hydroxymethylfurfural synthesis

Before the 1980s, most 5-HMF production was focused on heterogeneous acid catalysts in water. A mineral acid catalyst such as HCl was used to study the 5-HMF production which gave a moderate yield of 5-HMF (20-50%) and partway of the reaction. Subsequently, the 5-HMF production was developed. The first part is Glucose was isomerized into fructose by using an enzyme catalyst. Then HNO_3 was used to dehydrate fructose into 5-HMF with high yield. The autocatalysis was studied in 5-HMF production from fructose by using formic acid which forms from rehydration of 5-HMF to levulinic acid with gave high yield (47%)[13]. However, the increase of formic acid affected to increase in humins formation. The studying of fructose and glucose dehydration in water system with homogeneous acid catalyst can summarize

the conversion were high in the range of 2.1-1 pH[14], some of the heterogeneous acid catalysts which contain Cl^-, Br^-, I^- and NO_3^- decrease rate of the 5-HMF reaction which make low selectivity[15] and homogeneous acid catalyst do damage to equipment and are hard to separate the catalyst from product[8-11].

Heterogeneous acid catalysts which have Lewis and Brønsted acidity have been used for 5-HMF production to solve the problem which occurs in homogeneous acid catalysts. Phosphate-based catalysts with metal oxide which good to activate fructose and glucose dehydration giving HMF yields of 20–21% and 34–39%[8]. To develop the catalysts, the homogeneous acid catalyst was used with copper nanostructure which consists of Lewis and Brønsted acidity in fructose dehydration with the water system and gave 36% of 5-HMF yield[11]. Metal oxide and zeolite have been tested in the water systems which has strong Lewis acids. However, Lewis acidity has an effect on humins formation[13, 16, 17].

The catalysts which were studied in 5-hydroxymethylfurfural synthesis can classified many types such as metal oxide and hydrocarbon compounds with sulfate groups as shown in table 2.

Table 2 Conversion of fructose to 5-HMF in water using acid catalysts.

No.	Precursors	Catalyst	Temperature (ºC)	Time (min)	Yield (%)	Ref.
1	Fructose	H_3PO_4	200	5	28	[8]
2		$H_3PO_4:NaH_2PO_4$	150	30	63	[9]
3		H_2SO_4	166	200	56	[10]
4		Lactic acid	150	120	63	[18]
5		Levulinic acid	190	40	49	[13]
6		$InCl_3$	180	15	79	[19]
7		H-MOR	165	300	34	[20]
8		$(C_{16})H_4PW_{11}Ti$	130	90	76	[21]
9		AgSTA	120	120	86	[22]
10	Glucose	HCl	180	120	4	[18]
11		H_3PO_4	200	120	9	[8]
12		$AlCl_3$	120	300	11	[23]
13		$H_3PO_4:NaH_2PO_4$	150	90	10	[9]
14		$C_{16}H_4CrPW_{11}$	130	120	35	[24]
15		PCP(Cr)-SO$_3$H· Cr(III)	180	240	50	[25]

2.3 Niobium oxide and tungsten oxide on aluminium oxide

Niobium oxide is a superior feature acid heterogeneous catalyst due to niobium oxide has Lewis acid site and relatively strong Brønsted acid site on its surface, stability, and insolubility in aqueous media as shown in figure 2.1. Thus, Niobium oxide is attracted in industrial. However, niobium oxide can be deactivated due to the formation of polymer (Humin) which blocks the niobium oxide surface[26-28]. Tungsten oxide has been studied in much research for dehydration because tungsten oxide has Lewis acid on the structural unit and Brønsted acid site due to the coordinating between W and O atoms on the surface[29, 30]. Aluminium oxide is heterogeneous which has Lewis acid site, weak Brønsted acid site, and high surface area. The properties are dependent on the phase of aluminium oxide which is a result of the temperature of synthesis and calcination[31-33]. For niobium oxide on aluminium oxide, the acidity of the catalyst depends on bond between niobium oxide and aluminium oxide and niobium loading in catalysts. As shown in figure 3.8, there are 3 structures of niobium oxide on aluminium oxide as a result of niobium oxide loading and dispersing of niobium oxide. If the catalysts have highly dispersed niobium oxide, the catalysts will form to isolate niobia species which have strong Lewis site and relatively strong Brønsted acid site on its surface[34-36]. Tungsten oxide has been studied in much research for dehydration because tungsten oxide has Lewis acid on structure unit and Brønsted acid site due to the coordinating between W and O on the surface[29, 30].
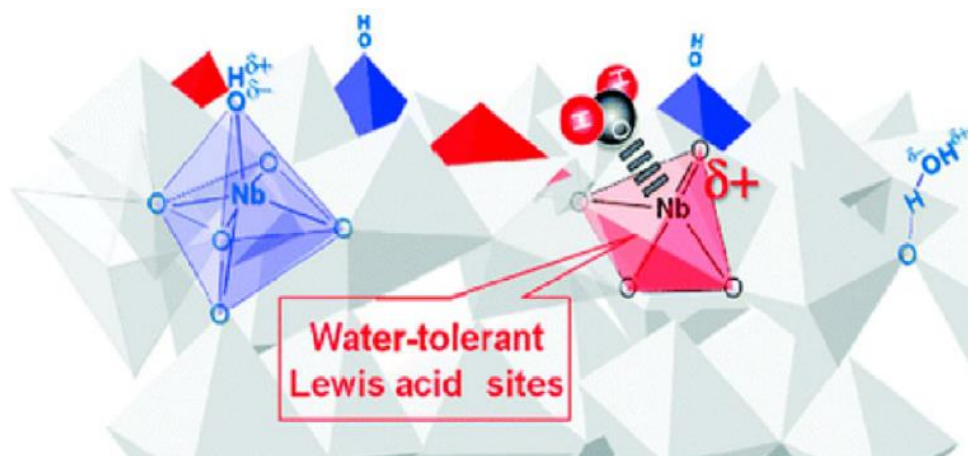
Figure 1 Schematic diagram of water-tolerant Niobium oxide[35].

Isolated niobia species   Two-dimensional polymerized niobia species

Three-dimensional polymerized niobia species-Nb$_2$O$_5$ crystallites
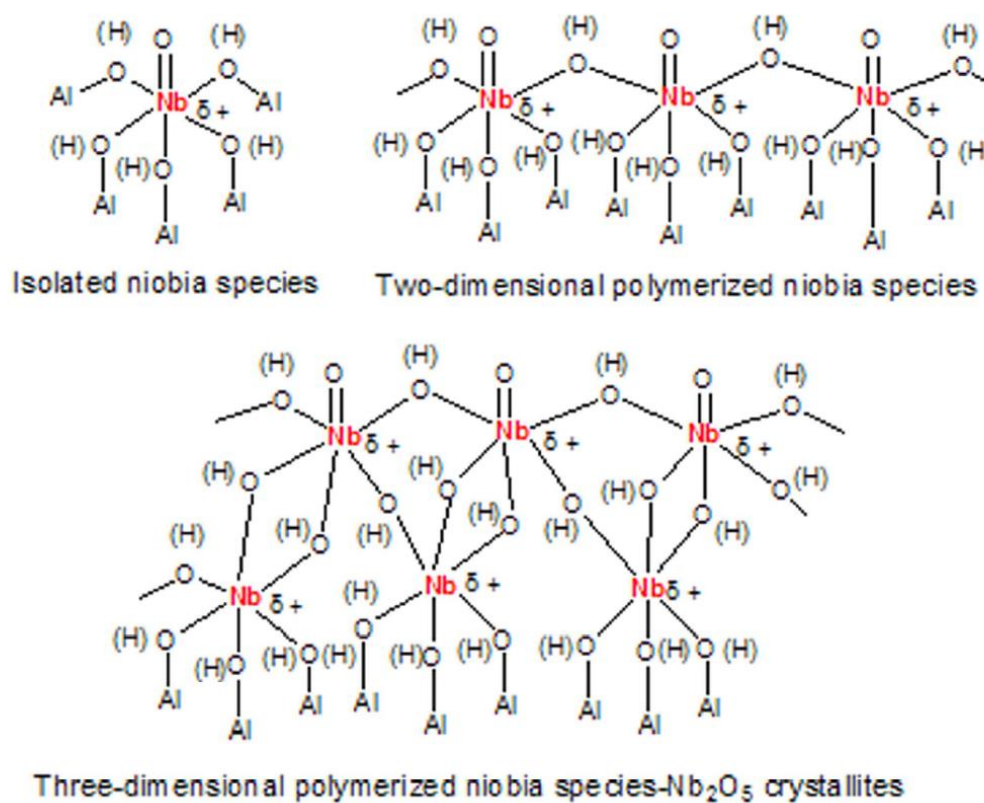
Figure 2 Schematic diagram of recycling the biphasic system for HMF

production[34].
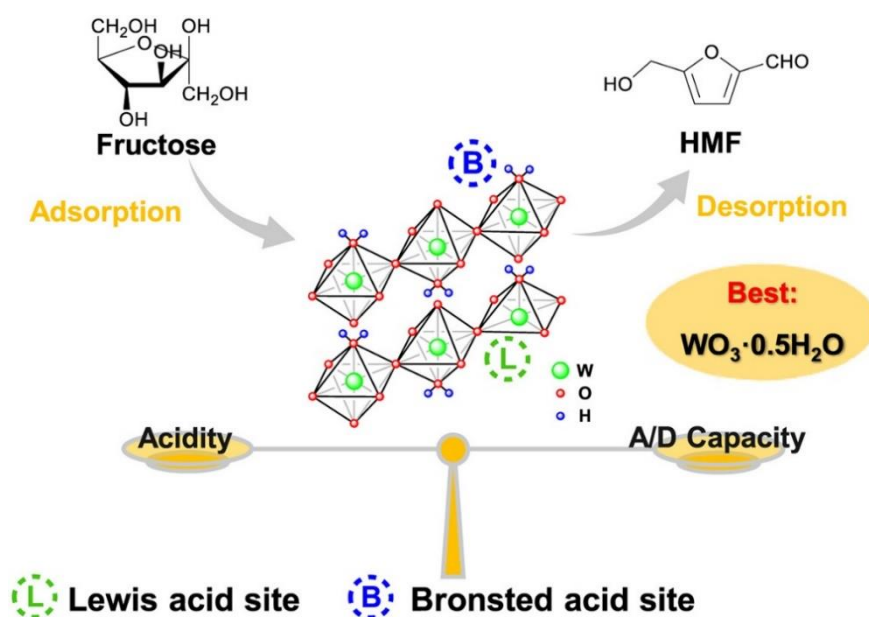
Figure 3 Schematic diagram of lattice water tungsten oxide[30].

2.4 Solution combustion synthesis

Solution combustion synthesis is a phenomenon which involves propagation of self-sustained exothermic reactions of metal nitrate and fuel cells as a solution. The process allows for the synthesis of a variety of nanoscale materials. Solution combustion synthesis has advantages of low cost and being easy to synthesize., First the solution is heated to get the gel. Then the gel is combusted with a fuel cell in which a large number of gases appear to make catalysts have more surface area as shown in table 3.

Table 3 Surface properties of catalysts using solution combustion synthesis method.

No.	Sample	Surface Area (m^2/g)	Total Pore Volume (ml/g)	Pore Size (nm)	ref.
1	$Fe_2B(PO_4)_3$	5.59	0.009	68	[37]
2	$Cr_2B(PO_4)_3$	15.56	0.023	59	[37]
3	NiO/Al_2O_3	208	0.205	3.9	[38]
4	NiO/MgO	34	0.083	4.3	[38]
5	$NiO/MgAl_2O_4$	65	0.069	3.9	[38]

2.5 Deep eutectic solvents

To solve the dehydration of 5-hydroxymethylfurfural, deep eutectic solvent is replaced with water to use as a solvent. Deep eutectic solvent is known as liquid mixture between hydrogen bond donors such as oxalic acid and hydrogen bond acceptors such as choline chloride have been attentive because they have properties similar to Ionic liquids whether it be high vapor pressure and have many kinds of functional group but less expensive and toxic than Ionic liquids. Deep eutectic solvents can be adjusted acidity by changing or adjusting the ratio of hydrogen bond acceptors and hydrogen bond donors to fine condition which can synthesize 5-hydroxymethylfurfural as shown in table 4.

Table 4 5-Hydroxymethylfurfural synthesis using deep eutectic solvents.

No.	DESs	Catalysts	Ratio	Temperature (c)	Time (min)	Yield (%)	ref.
1	ChCl: p-TSA	-	1:1	80	60	90.7	[39]
2	$C_6H_{16}ClNO$: p-TSA	-	1:0.5	80	60	84.8	[40]
3	ChCl: Fructose	$AlCl_3$	1:4	60	240	9.1	[41]
4	ChCl: Fructose	HCl	1:4	60	240	45.2	[41]
5	ChCl: Fructose	H_2SO_4	1:4	60	240	43.6	[41]
6	ChCl: Fructose	$ZnCl_2$	1:4	60	240	2.2	[41]
7	ChCl: Fructose	$CrCl_3$	1:4	60	240	75	[41]
8	ChCl: Fructose	$H_3PW_{12}O_{40}$	1:4	60	240	78.2	[41]
9	ChCl: Fructose	$H_3P_4MO_{12}O_{40}$	1:4	60	240	45.5	[41]
10	ChCl-phenol	SACS	1:4	110	240	67	[42]
11	ChCl-oxalic acid	SACS	1:1	110	240	43	[42]
12	ChCl-ethylene glycol	SACS	1:2	110	240	4	[42]
13	ChCl-urea	SACS	1:1	110	240	5	[42]

2.6 Biphasic system

Biphasic system which is a 2-phase liquid system consisting of aqueous and organic liquid is used to extract 5-hydroxymethylfurfural from water before 5-hydroxymethylfurfural is dehydrated to levulinic acid and formic acid. To enhance the extraction, adding salt can disturb the equilibrium in aqueous and make 5-Hydroxymethylfurfural extraction and yield are better as shown in table 5.

Table 5 5-Hydroxymethylfurfural synthesis using biphasic system.

No.	Substrate	Solvent	Catalyst	Temperature (c)	Time (min)	Yield (%)	Ref.
1		H_2O: DMSO	SiNP-SO3H-C16	120	180	87	[43]
2	Fructose	H_2O: MIBK	SAPO-44	175	60	78	[44]
3		H_2O: MIBK	HSO3-MCM41	170	80	75	[45]
4		H_2O: MIBK	Al-MCM41 20% NaCl	195	30	63	[46]
5		H_2O: n-butanol	15P-TiO2	175	180	60	[47]
6	Glucose	H_2O: n-butanol	P-TiO2	175	105	83	[48]
7		H_2O: n-butanol	TiO2-ZrO2: amberlyst	175	180	86	[49]

CHAPTER III

THEORY

3.1 Reaction of Glucose to 5-HMF

5-hydroxymethylfurfural synthesis from glucose which can be obtained from biomass waste is begun from glucose isomerization using Lewis acid as a catalyst to produce fructose as shown in figure 4 Then fructose is converted to 5-hydroxymethylfurfural by dehydration reaction in which fructose is removed 3 water molecules using Brønsted-Lowry acid as a catalyst as shown in figure 3.2. However, there are other partway reactions which can form to another substance such as humin, levulinic acid, formic acid, furfural, lactic acid and acetic acid.
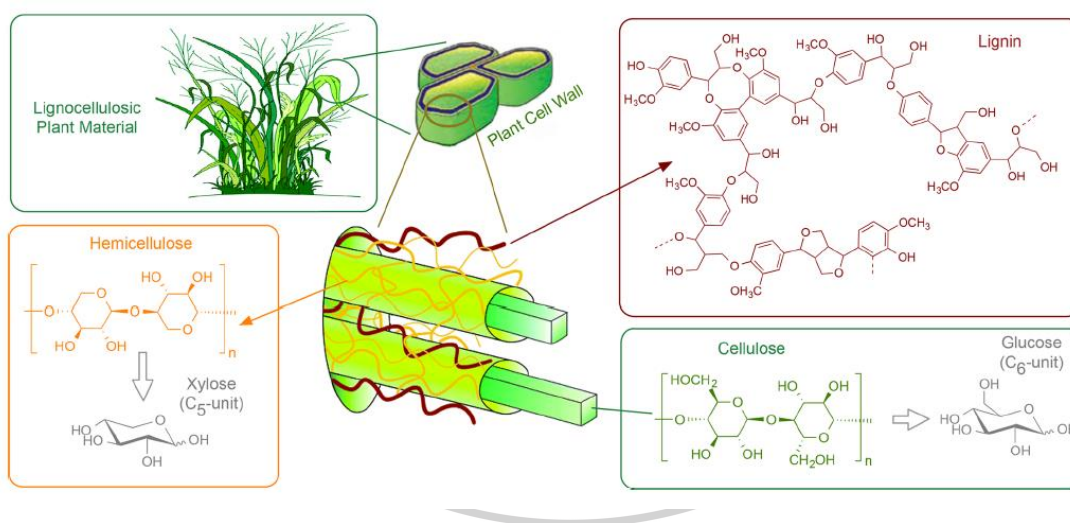
Figure 4 Component of lignocellulose and type of biomass wastes[12]
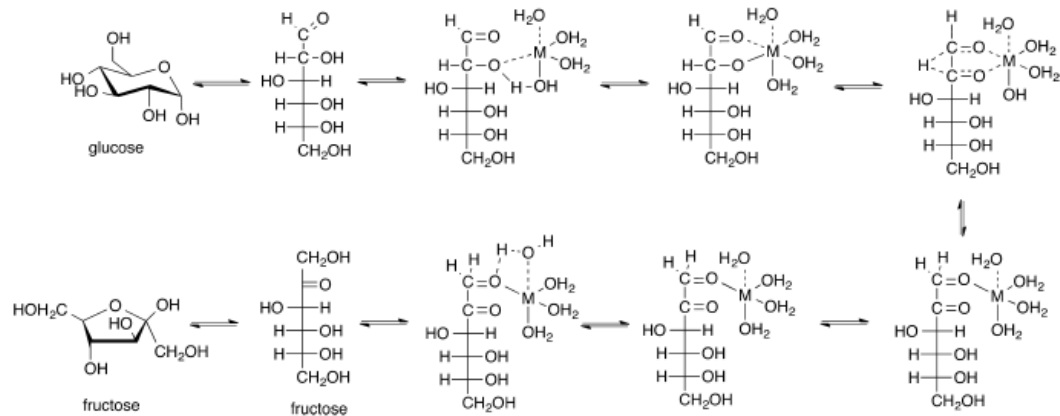
Figure 5 Isomerization of Glucose into Fructose in acids[12]
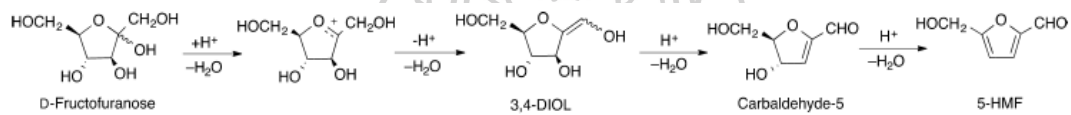
Figure 6 Dehydration of Fructose to 5-HMF in acid[12]
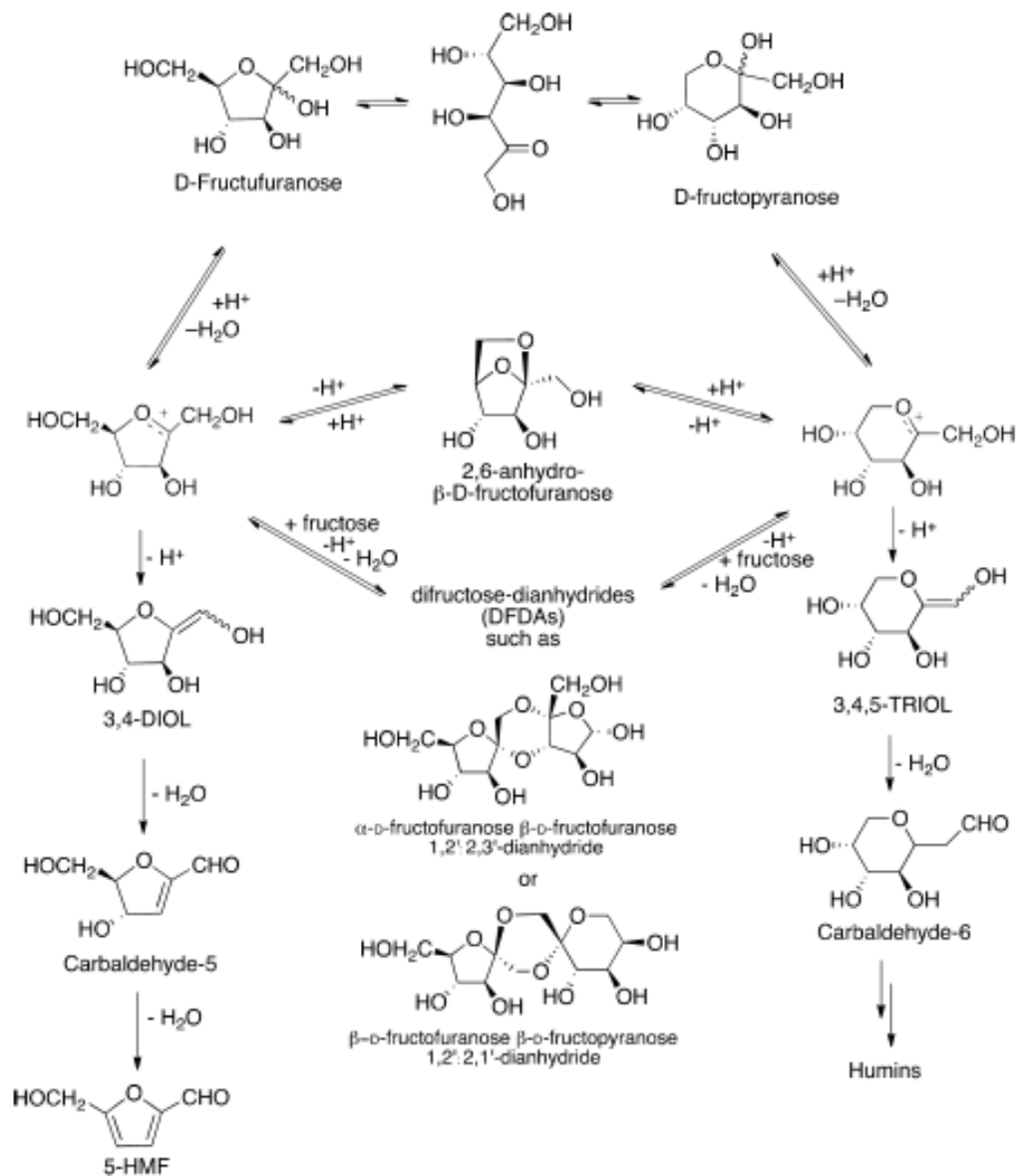
Figure 7 Dehydration of D-Fructose to 5-HMF and Humins[12]
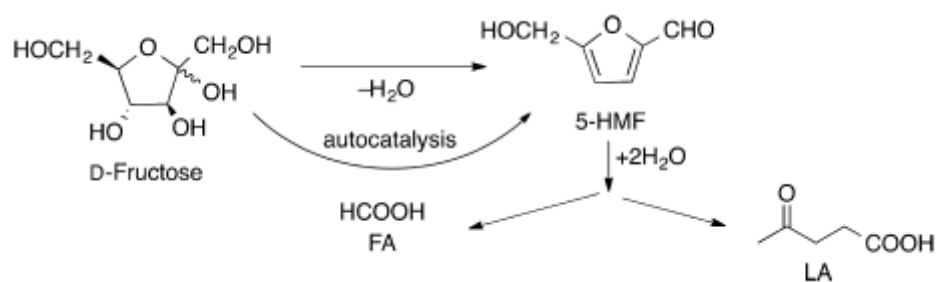
Figure 8 Formic Acid Assisted Conversion of Fructose[12]

3.2 Solution combustion synthesis

      Solution combustion synthesis is a method to synthesize nanoparticle size which uses fuel cells to combust the solution of metal nitrate and fuel cells to perform metal oxide. There are 2 parts of reaction that react in solution combustion synthesis. The first reaction is a combustion reaction which uses fuel cells to combust. The second reaction is a redox reaction which uses metal nitrate as an oxidizer to produce metal oxide. The fuel cell is heated until the fuel is burned as a glowing flame. The product is composed of metal oxide and a large amount of gas. all of the gas is produced to make metal oxide porous and finely dispersed which makes the solid product is nanoscale powders[50, 51].

(1) Combustion reaction (urea)

$$nNH_2CONH_2 + 2nO_2 \longrightarrow nN_2 + nCO_2 + 2nH_2O$$

(2) Redox reaction

$$Me^v(NO_3)_v \longrightarrow Me^vO_{2/v} + vN_2 + 3v/2O_2$$

(3) Solution combustion synthesis

$$Me^v(NO_3)_v + 3\phi/4vNH_2CONH_2 + 3v/2(\phi-1)O_2 \longrightarrow Me^vO_{2/v} + (v+3\phi/4v)N_2 + 3\phi/4vCO_2 + 3\phi/2vH_2O$$
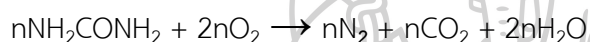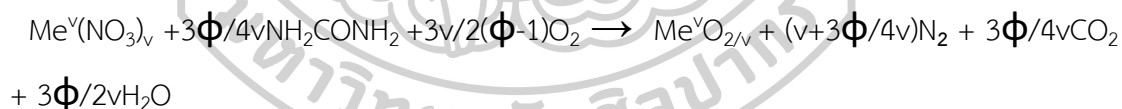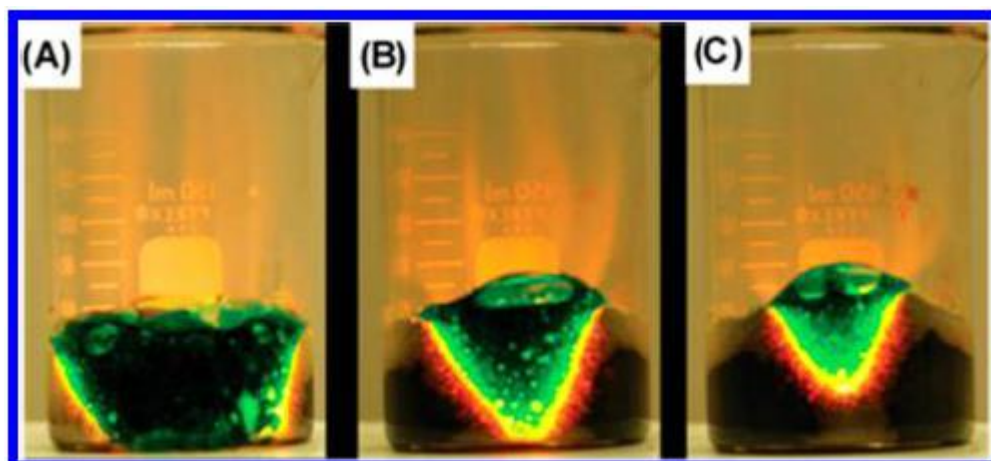
Figure 9 Solution combustion synthesis of nickel foam: The reaction ignites (A) and moves slowly through the reactive solution (B and C)[50]

3.3 Deep eutectic solvent

Deep eutectic solvents are liquid mixtures between hydrogen bond donors or metal salt and hydrogen bond acceptors or halide salts as shown in figure. That effect on liquid mixtures has lower freezing points than the ideal liquid mixture. The ratio between hydrogen bond donors and hydrogen bond acceptors which makes the lowest freezing point is called eutectic point. Deep eutectic solvents can write in formula in following.

$$Cat^+X^-zY$$

Where Cat^+ is principal in ammonium, phosphonium, or sulfonium cation. X^- is Lewis base anion. Thus Cat^+X^- is a symbol of Hydrogen bond acceptors or Halide salts. Y is a symbol of substance which is lewis or Brønsted acidity and z is mole of Y which is used per 1 mole of Hydrogen bond acceptors. Deep eutectic solvents can be classified following.

1.Hydrogen bond acceptors with metal chloride

$$Cat^+X^-zMCl_x$$

2.Hydrogen bond acceptors with metal chloride hydrate

$$Cat^+X^-zMClx \cdot yH_2O$$

3.Hydrogen bond acceptors with hydrocarbon which has lewis acidity

$$Cat^+X^-zRZ$$

4.hydrocarbon which has lewis acidity with metal chloride

$$MCl_x + RZ$$
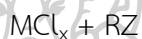
Where M is cation such as Al^{3+}, Fe^{3+}, Zn^{2+} and Z is a substance with a functional group such as amide, carboxylic acid and alcohol group. Due to deep eutectic solvents, it has many properties and can adjust properties by chance hydrogen bond donors or hydrogen bond acceptors or adjust the quality of hydrogen bond donors and hydrogen bond acceptors. Figure 3.6 shows the structures of some hydrogen bond donors and hydrogen bond acceptors[52, 53].
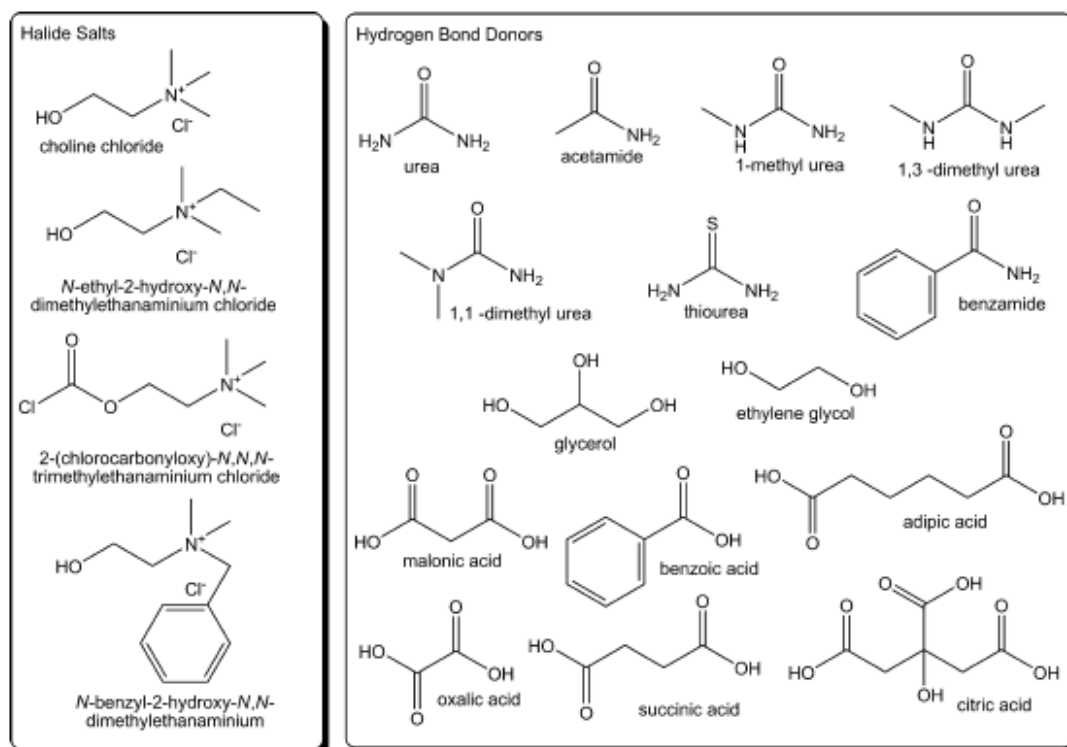
Figure 10 Structures of some hydrogen bond donors and hydrogen bond acceptors[52]

3.4 Biphasic system

Biphasic system which is a 2-phase liquid system consisting of aqueous and organic liquid is used to extract substances such as biological products from the aqueous phase using the liquid-liquid extraction method. The system is characterized by low viscosity, easy recovery and reduced settling timThe biphasicasic system method has advantages over conventional extraction techniques like, environmentally friendly, low cost, ease of scaling-up and is efficient for many kinds of experiments specially for the concentration and purification of biological products[54-57].
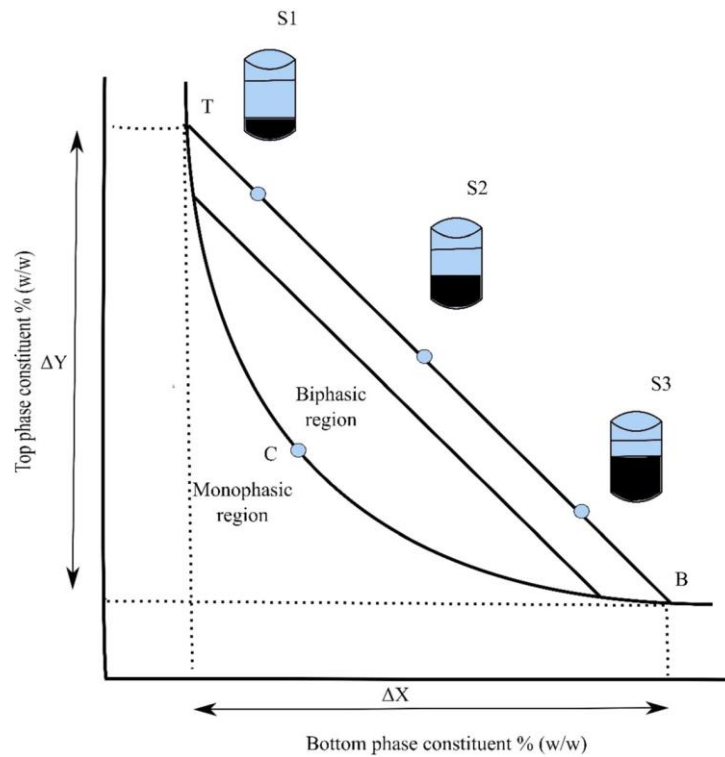
Figure 11Phase diagram and concentration of 2 phase liquid[57]
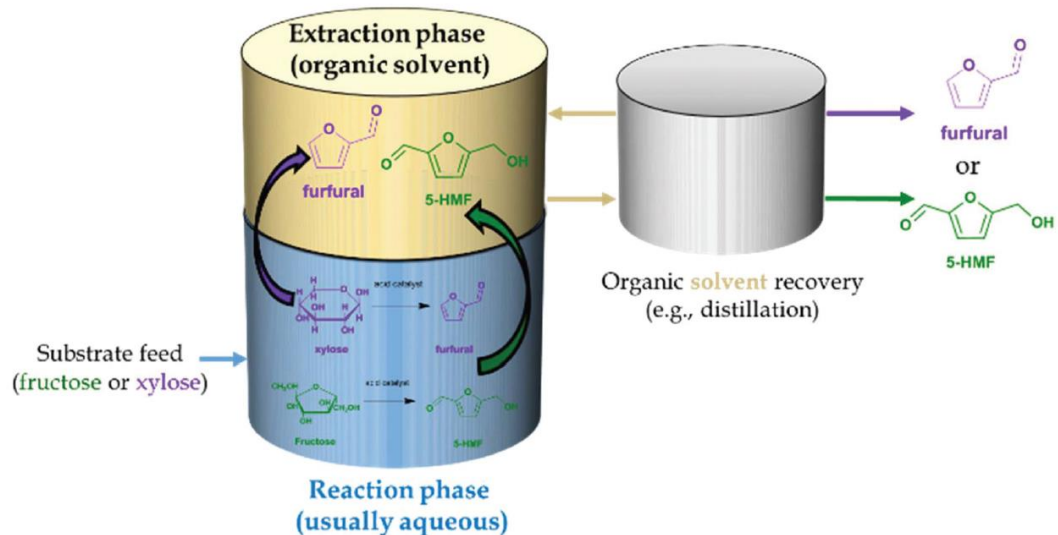
Figure 12 Schematic diagram of recycling the biphasic system for HMF

production[55].

CHAPTER IV

RESEARCH METHODOLOGY

4.1 Materials

4.1.1 Chemicals

Table 6 Chemicals

Symbol	Chemical	Formula	Grade
Niobium	Ammonium niobate (V) oxalate hydrate	$C_4H_4NNbO_9 \cdot H_2O$	99.99%
Tungsten	Ammonium metatungstate hydrate	$(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$	85%
Aluminium	Aluminium nitrate nonahydrate	$Al(NO_3)_3 \cdot 9H_2O$	98%
Ammonium	Ammonium acetate	CH_3COONH_4	97%
Urea	Urea	NH_2CONH_2	99%
Glucose	D-(+)-Glucose	$C_6H_{12}O_6$	99.99%
Fructose	D-(-)-Fructose	$C_6H_{12}O_6$	99%
Formic acid	Formic acid	$HCOOH$	85%
Levulinic acid	Levulinic acid	$C_5H_8O_3$	97%

4.1.2 Equipment

- High-Performance liquid chromatography (HPLC)

- Brunauer–Emmett–Teller (BET)

- Temperature programmed desorption (NH3-TPD)

- Batch-type stainless-steel autoclave

- Oven

- Cylinders

- Stirring rods

- Stirrer

- Beakers

- Thermocouple

- Scales

4.2 Methodology

4.2.1 Preparation of catalysts

The catalyst was synthesized by the solution combustion synthesis method. Metal nitrate was used as the oxidizer in solution combustion synthesis as the source of metal oxide. ammonium niobate (V) oxalate hydrate ($C_4H_4NNbO_9 \cdot xH_2O$, 99.99%), aluminium nitrate ($Al(NO_3)_3$, 98%), ammonium acetate ($CH_3CO_2NH_4$), and urea (NH_2CONH_2, 99.5%) was mixed with deionized water in a beaker to get the solution in condition which is calculated the percentage of the weight of metal oxide, the quantity of urea was used as fuel in solution combustion synthesis, and quantity of Ammonium acetate. By fixed x wt% Nb loading and 0.8 fuel/oxidizer ratio (xNb-Al). The solution was heated until the solution lights a fire. The solution would be burned and become powder. The synthesized catalysts were denoted as xNb-Al zAA where z was mole% ammonium acetate in fuel. The calculation for catalyst preparation is as follows.

(a) Redox reaction of Alumina

$$2Al(NO_3)_3 \cdot 9H_2O \longrightarrow Al_2O_3 + 9/2N_2 + 9H_2O + 15/2O_2$$
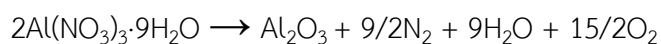
(b) Redox and Combustion reaction of Niobate

$$C_4H_4NNbO_9 + O_2 \longrightarrow Nb_2O_5 + H_2O + CO_2 + N_2$$

(c) Combustion of Urea reaction

$$nNH_2CONH_2 + 3/2nO_2 \longrightarrow nN_2 + nCO_2 + 2nH_2O$$
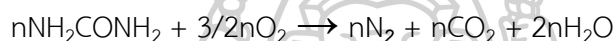
(d) Solution combustion synthesis reaction

$$C_4H_4NNbO_9 + Al(NO_3)_3 + NH_2CONH_2 + O_2 \longrightarrow Nb_2O_5Al_2O_3 + H_2O + CO_2 + N_2$$

4.2.2 Catalyst characterizations

- **Nitrogen physisorption**

Brunauer Emmett Teller (BET) was used to determine the surface area of the catalyst. The catalysts were pretreated in 50 ml/min of Helium gas for 3 hours at 455.15 K to remove moisture on the surface area of catalysts and cool down in ambient temperature. The catalysts were installed to the adsorption part to measure at different partial pressures of N_2 at -196 °C.

- **Automatic X-ray diffractometer**

Automatic X-ray diffractometer (XRD) was used to analyze the crystallinity of the catalyst. The pattern of XRD was recorded using Shimadzu 6100 in the range 2θ from 10° to 80° with a computer for full control of the XRD analyzer.

- **Scanning Electron Microscopy (SEM)**

Scanning Electron Microscopy (SEM) was used to focus beam of high-energy electrons to generate a variety of signals at the surface of catalysts specimens.

- **Ammonia-Temperature Programmed Desorption (NH$_3$-TPD)**

Ammonia-Temperature Programmed Desorption (NH$_3$-TPD) was used to detect the acidity of the catalyst. The catalysts were installed to the adsorption part for pretreatment in 25 ml/min of helium gas for hours at 485.15 K to remove moisture on the surface area of catalysts and cool down in ambient temperature. Then ammonia gas flowed in 25 ml/min for 1 hour to catalysts to adsorb gas. After the absorption, the ammonia gas was desorbed by heating at 823 K for 1 hour.

- **Acid and base titration**

The 0.1 g of catalysts were measured Brønsted acid and Brønsted base by stirring with 20 ml of 0.01 M of HCl or 0.01 M of NaOH at room temperature for 6 hours. The solution which separated the catalysts was titration with 0.01 M of HCl or 0.01 of M NaOH to find the acid or base which was absorbed on the catalysts

4.2.3 Reaction test

the catalyst was tested by preparing 5-HMF from glucose was carried out in a 25 mL batch-type stainless-steel autoclave with a magnetic stirrer, from with 0.25 g of glucose were dissolved in 5 ml of deionized water with 0.05 g of catalyst (20 wt.% of raw material) was contained. The reaction was carried out at a given reaction time for 4 hours and temperature at 423 K. After the reaction, the product was analyzed by Aminex 87H-NKS HPLC using UV detector with 254 nm to detect acid and furfural product and IR detector for detect sugar.

CHAPTER V

RESULT AND DISCUSSION

5.1 Physicochemical properties

XRD patterns of niobium series and tungsten series were displayed in Figure 13. The peaks at 36.88, 45.28, and 67.67 degrees can be observed for samples without ammonium acetate which are corresponding to the gamma phase of aluminum oxide[34, 58]. For 5% and 10% of ammonium acetate samples, there is a peak at 67.67 degrees same as the sample without ammonium acetate but the peak at 36.88 and 45.28 degrees are small. The peaks at 25.62, 35.29, 37.80, 43.33, 52.52 and 57.46 degrees in 1W-Al 5AA and 1W-Al 10AA samples which are corresponding to the Alpha phase of aluminium oxide. There is no peak of niobium oxide and tungsten oxide in XRD pattern suggesting that the sizes of niobium oxide and tungsten oxide are smaller than the XRD detection limit.
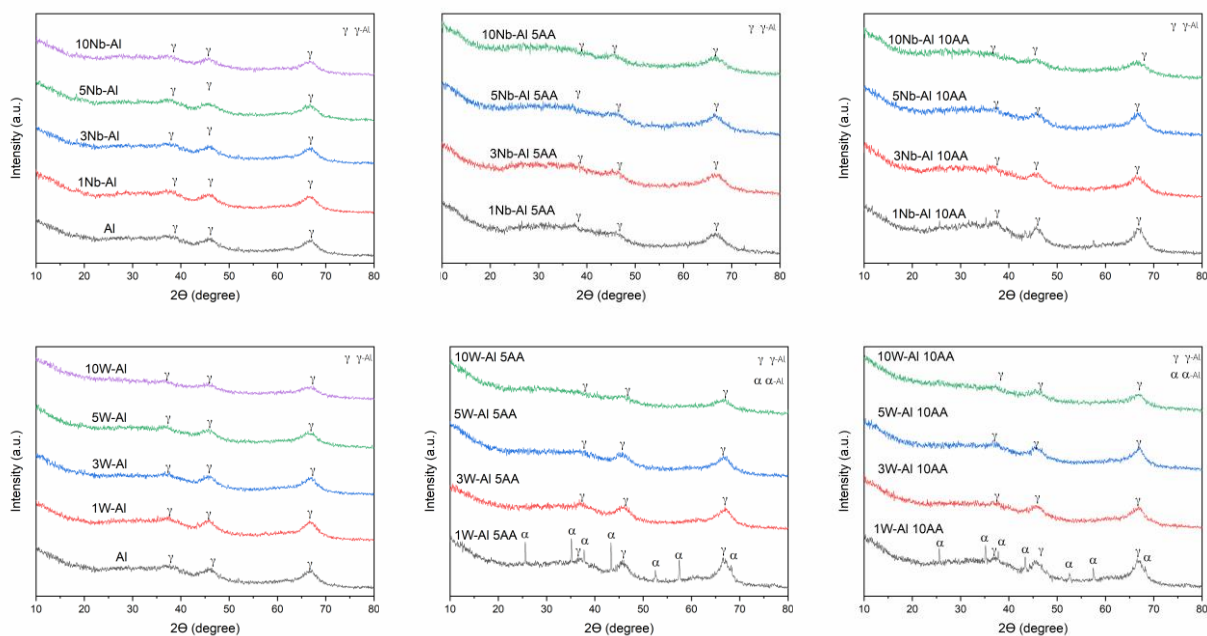
Figure 13 XRD patterns of catalysts.

The surface properties of catalysts were characterized by N_2 adsorption at -196 °C is shown in table 6 and Figure. 14 for catalysts in niobium series and table 7 and Figure 15 for catalysts in tungsten series. The isotherm is belonged to type IV Van Der Waal isotherm. All catalysts show the hysteresis loop shape types A. Type A hysteresis is attributed to cylindrical or tubular type pores of adsorbent with a narrow distribution of uniform pores. It is characterized by steep and narrow parallel adsorption and desorption curves following in Figure14. Surface area and pore volume decrease when the amount of niobium oxide loading increases for catalysts in niobium series. However, the surface and pore volume increase when the amount of tungsten oxide increases for catalysts in tungsten series. For effect of ammonium acetate, the surface area and pore volume increase when used 5% ammonium acetate in fuel mixture but decrease when used 10% ammonium acetate in fuel mixture for catalysts in niobium series. For catalysts in the tungsten series, the surface area and pore volume decrease when the amount of ammonium acetate increases in the fuel mixture.
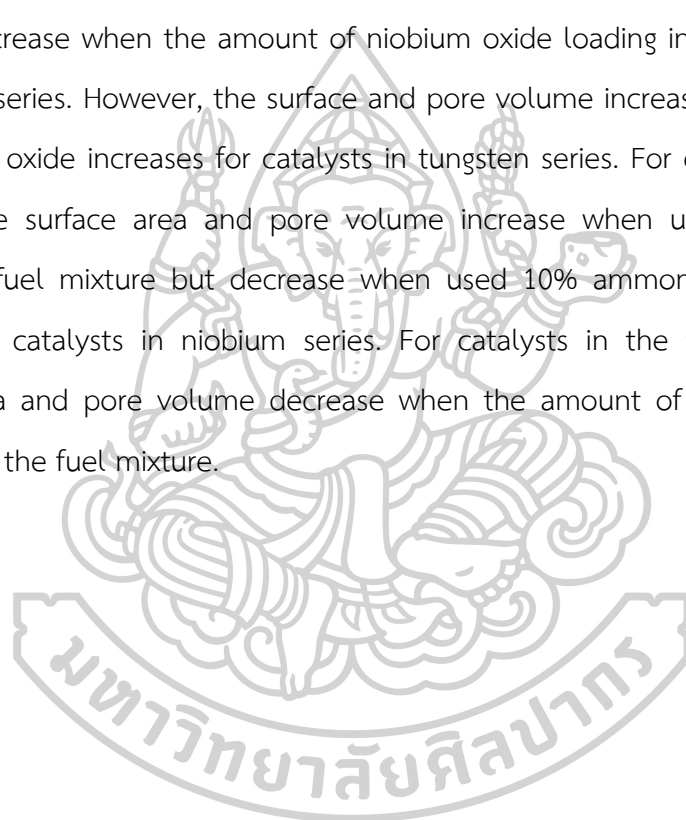
Table 7 Surface properties of catalysts in niobium series

No.	Catalysts	Surface area (cm^2g^{-1})	Pore volume (cm^3g^{-1})	Pore size (nm)
1	Al	203	0.24	4.65
1	1Nb-Al	286	0.29	4.06
2	1Nb-Al5AA	300	0.34	4.53
3	1Nb-Al 10AA	169	0.16	3.74
4	3Nb-Al	281	0.28	4.04
5	3Nb-Al 5AA	298	0.27	3.60
6	3Nb-Al 10AA	291	0.27	3.66
7	5Nb-Al	287	0.28	3.98
8	5Nb-Al 5AA	299	0.27	3.61
9	5Nb-Al 10AA	246	0.26	4.20
10	10Nb-Al	266	0.27	4.06
11	10Nb-Al 5AA	298	0.26	3.51
12	10Nb-Al 10AA	275	0.26	3.72
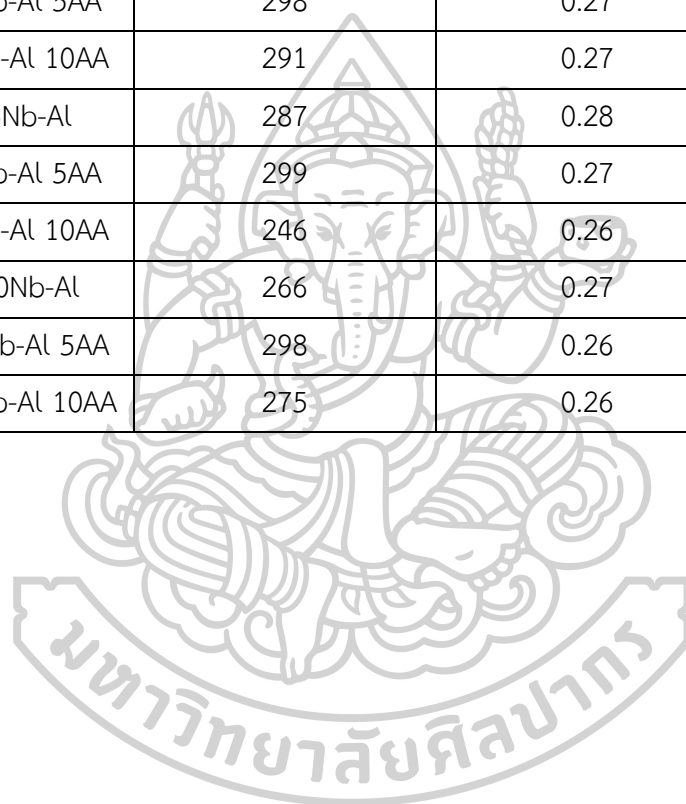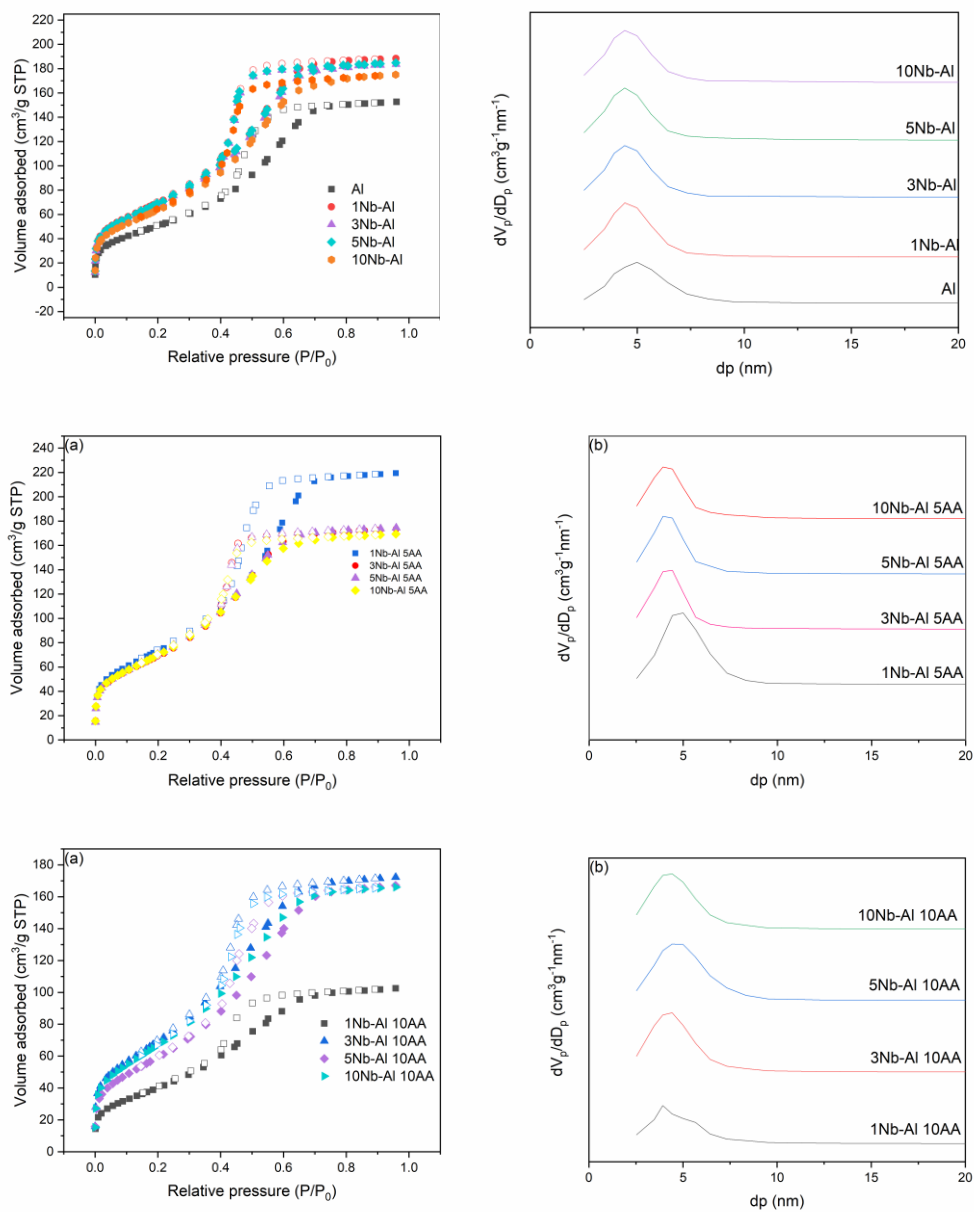
Figure 14 Isotherm and mesopore distribution of catalysts in niobium series

Table 8 Surface properties of catalysts in niobium series

No.	Catalysts	Surface area (cm^2g^{-1})	Pore volume (cm^3g^{-1})	Pore size (nm)
1	Al	203	0.24	4.65
1	1W-Al	253	0.28	4.48
2	1W-Al5AA	183	0.21	4.64
3	1W-Al 10AA	175	0.19	4.30
4	3W-Al	276	0.31	4.59
5	3W-Al 5AA	239	0.28	4.69
6	3W-Al 10AA	254	0.29	4.62
7	5W-Al	293	0.32	4.36
8	5W-Al 5AA	228	0.25	4.39
9	5W-Al 10AA	212	0.22	4.24
10	10W-Al	311	0.32	4.10
11	10W-Al 5AA	276	0.30	4.29
12	10W-Al 10AA	216	0.21	3.95
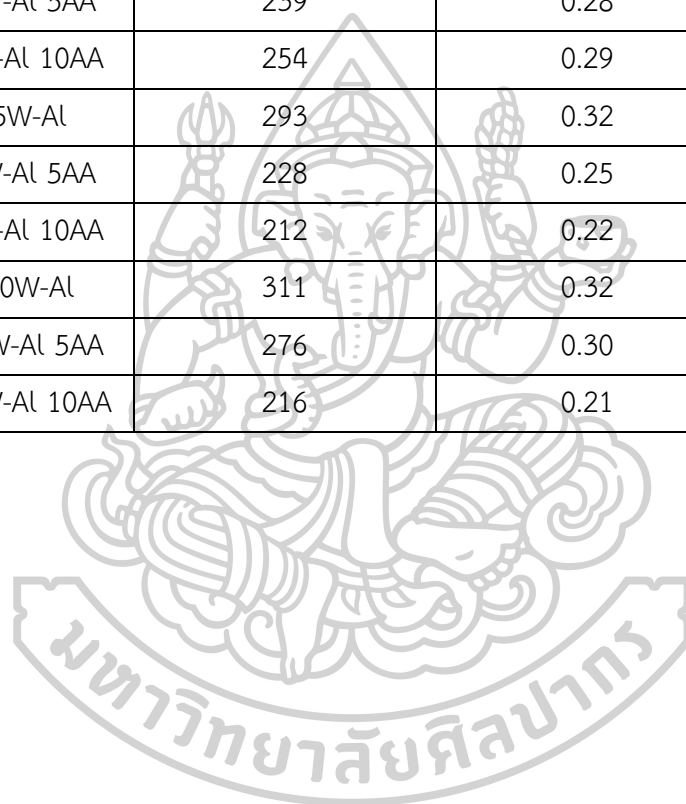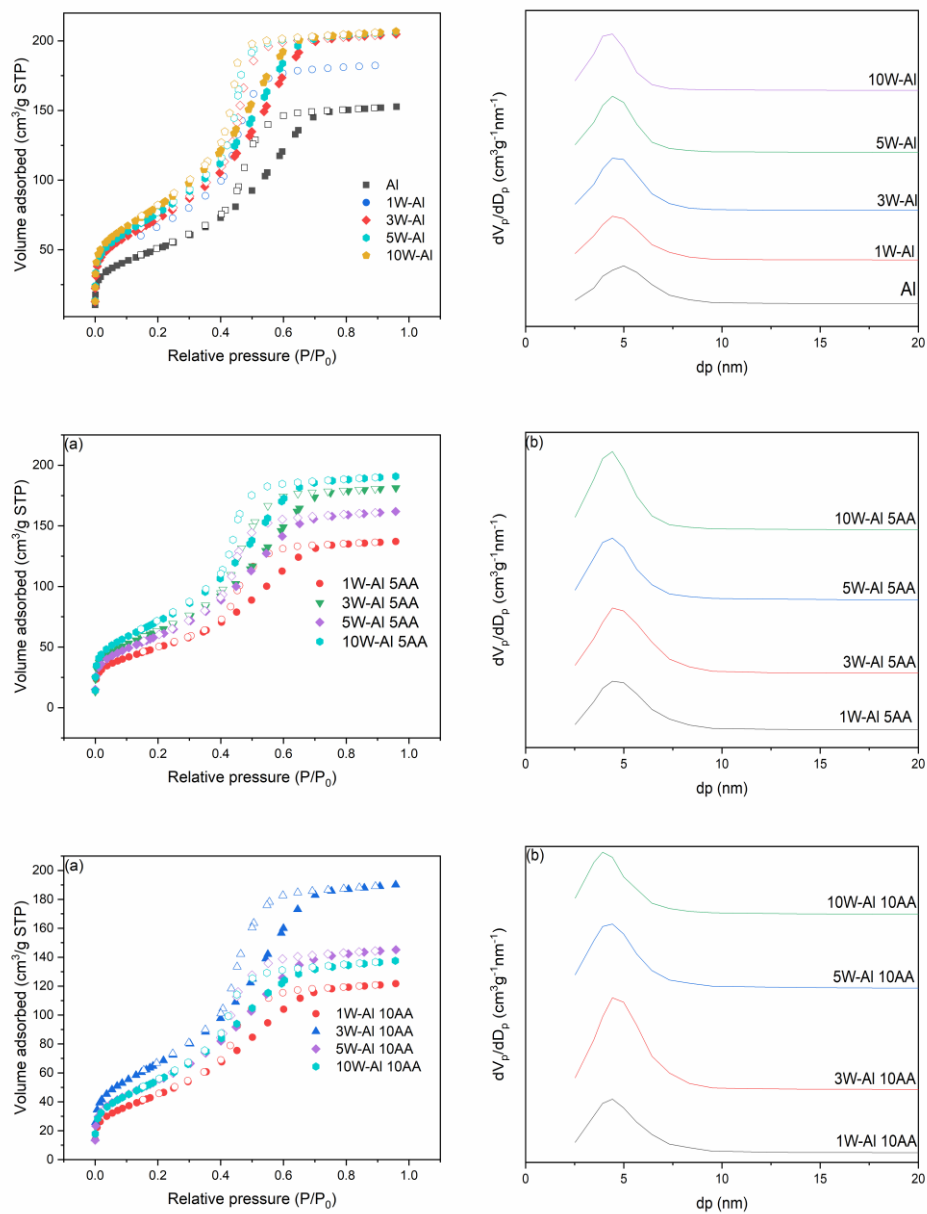
Figure 15 Isotherm and mesopore distribution of catalysts in niobium series

The surface properties were analyzed by Scanning Electron Microscopy with 1000x and 5000x time in Figure 14, 15, 16 and 17. The white spot occurred while increasing of niobium oxide loading for all catalysts. The distribution of niobium oxide on the catalysts (1Nb-Al and 10Nb-Al) is displayed in Figure 15 by EDX mapping which displays the niobium oxide regularly distribute on the catalysts. For the effect of ammonium acetate in the fuel mixture, the catalysts without ammonium acetate have chunk shape, almost smoot surface and have few pores on the surface. The catalysts which use 5% ammonium acetate in the fuel mixture have many pores that look like small bobble distributed on the surface suggesting because ammonium acetate converted to gas as small bobble while the solution of catalysts precursor got into gel before the combustion and have a plate shape for some particle and chunk shape like the catalysts without ammonium acetate. The catalysts which were prepared by using 10% ammonium acetate in fuel mixture have rod shape and large pore similar to large bobble distributed on the surface due the amount of ammonium acetate which were used to syntheses the catalysts create large bobble because of much gas occurred while the solution got to gel and combusted.

Table 9 Catalysts loading from EDX

No.	Catalysts	Niobium/Tungsten loading (wt%)
1	1Nb-Al	1.37
2	3Nb-Al	3.00
3	5Nb-Al	4.06
4	10Nb-Al	10.24
5	1W-Al	0.97
6	3W-Al	3.62
7	5W-Al	3.81
8	10W-Al	7.57
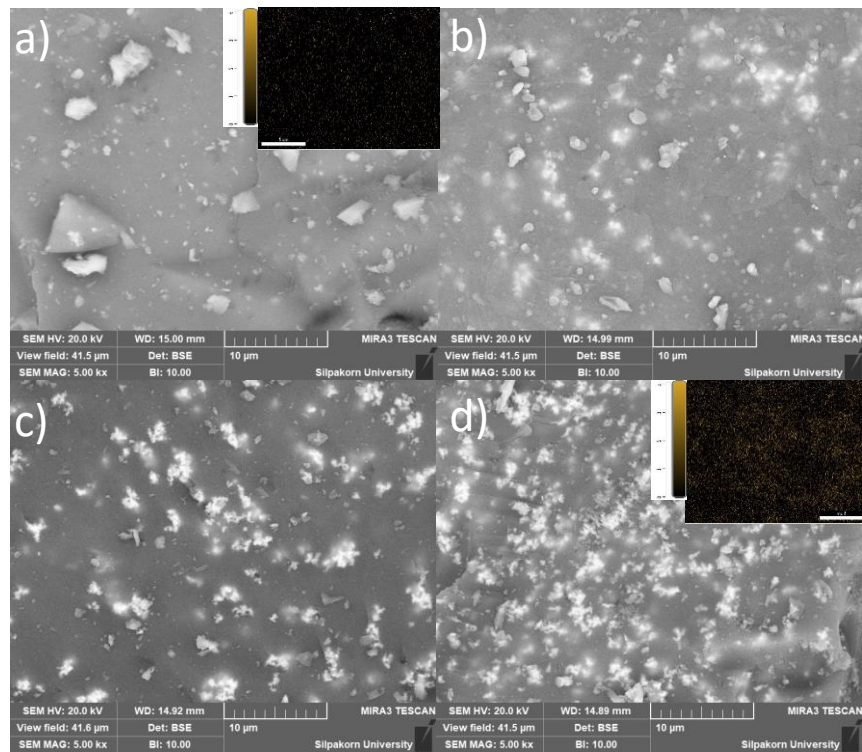
Figure 16 SEM picture and EDX mapping of (a) 1Nb-Al (b) 3Nb-Al (c) 5Nb-Al and (d) 10Nb-Al for 5000x zoom

Figure 17 SEM picture of (a) 1Nb-Al (b) 3Nb-Al (c) 5Nb-Al and (d) 10Nb-Al for 1000x zoom

Figure 18 SEM picture of (a) 1Nb-Al 5AA (b) 3Nb-Al 5AA (c) 5Nb-Al 5AA and (d) 10Nb-Al 5AA for 5000x zoom
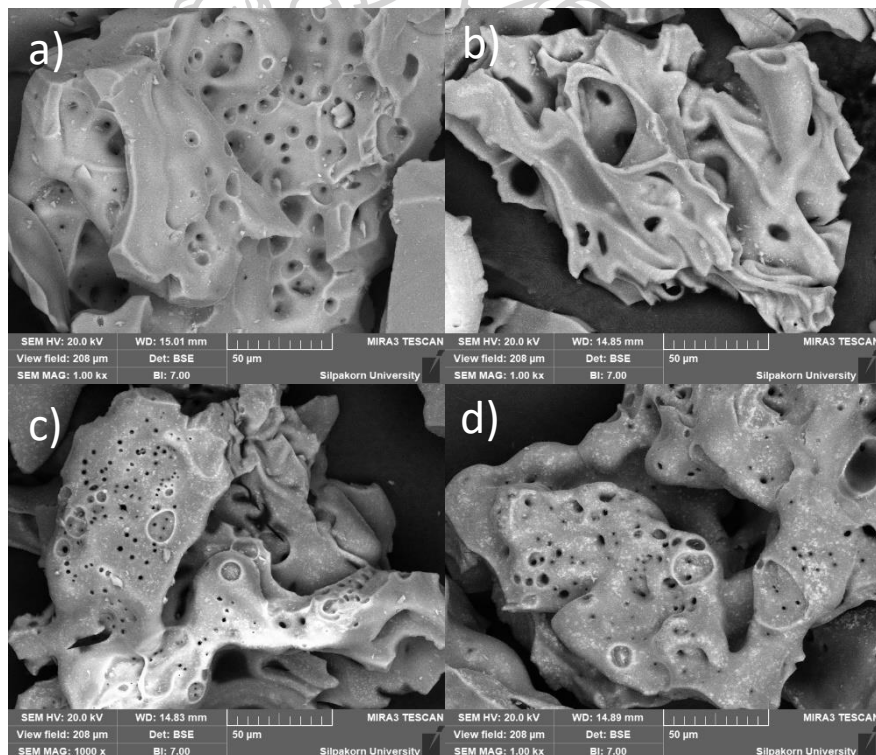
Figure 19 SEM picture of (a) 1Nb-Al 5AA (b) 3Nb-Al 5AA (c) 5Nb-Al 5AA and (d) 10Nb-Al 5AA for 1000x zoom
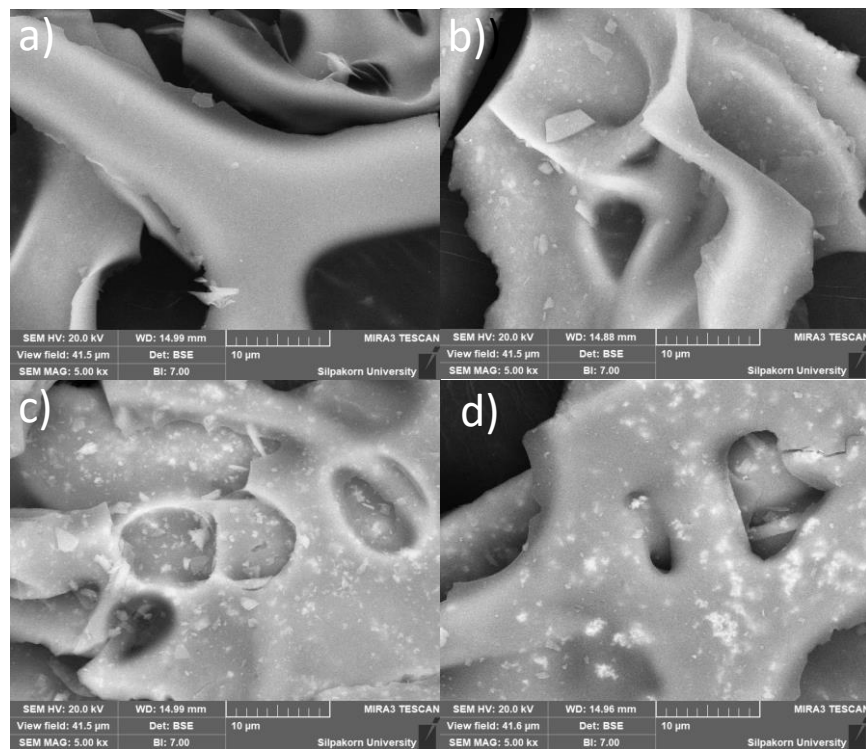
Figure 20 SEM picture of (a) 1Nb-Al 10AA (b) 3Nb-Al 10AA (c) 5Nb-Al 10AA and (d)
10Nb-Al 10AA for 5000x zoom
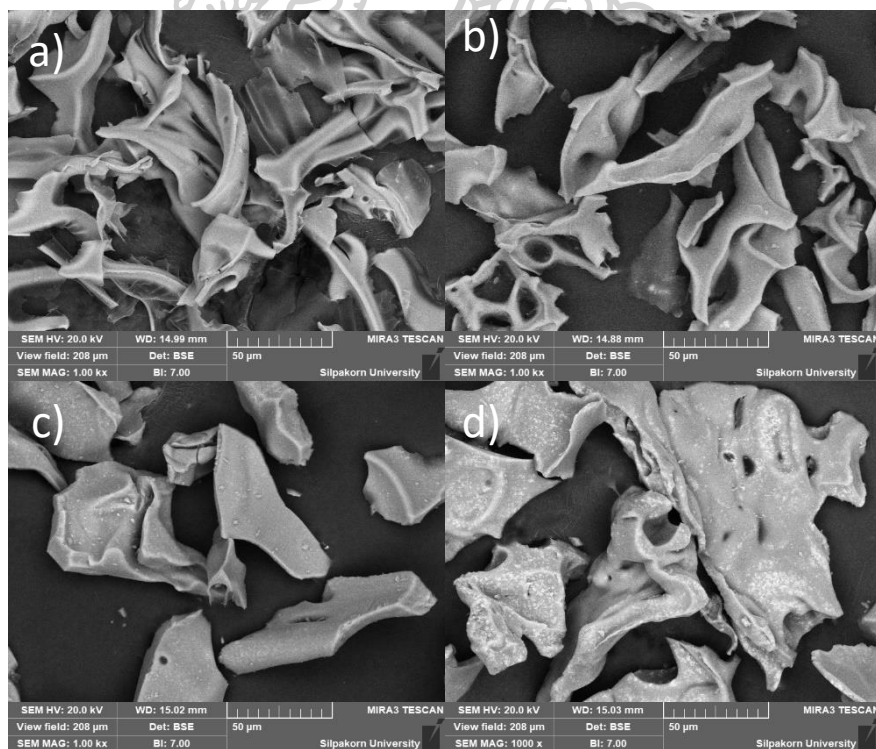
Figure 21 SEM picture of (a) 1Nb-Al 10AA (b) 3Nb-Al 10AA (c) 5Nb-Al 10AA and (d)
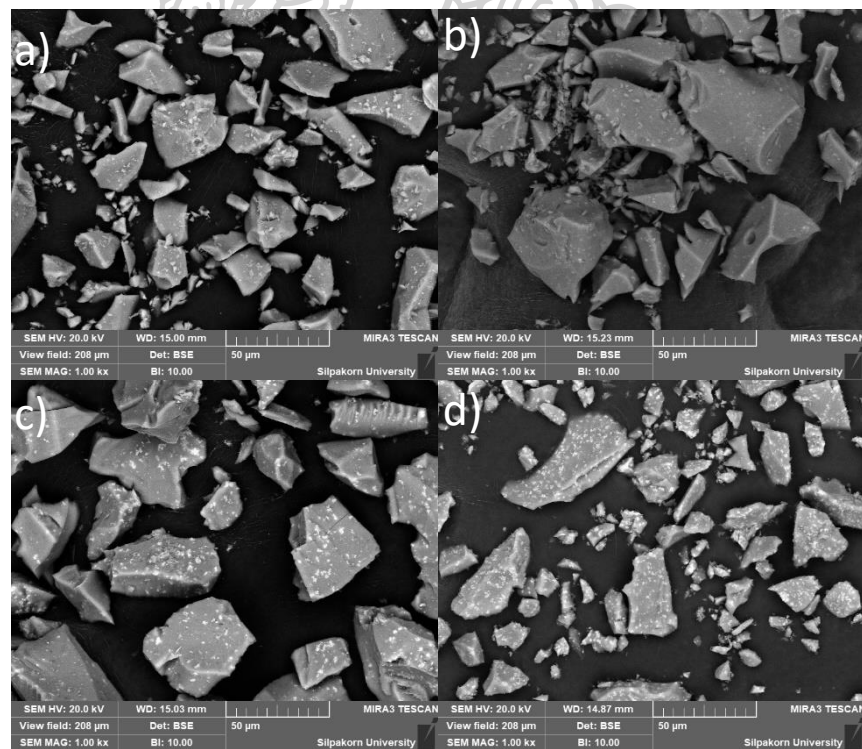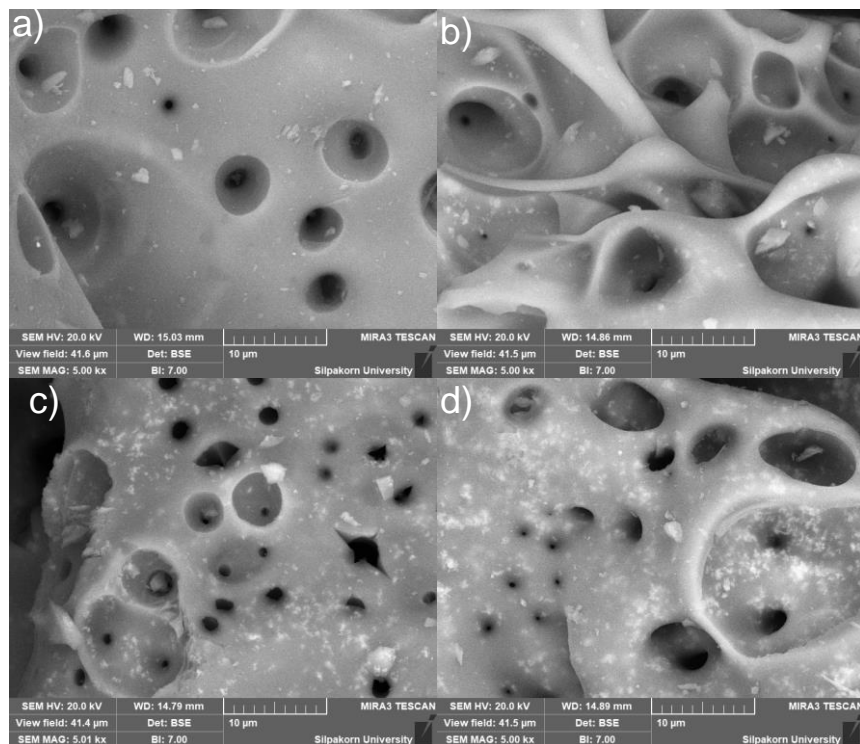*10Nb-Al 10AA for 1000x zoom*

5.2 Acid properties

The catalysts were tested for the acid properties by Ammonia-Temperature Programmed Desorption. Raw data for alumina catalyst was fit in three Gaussians centered and for niobium and tungsten loading catalysts were fit in four Gaussians centered at approximately 10, 24, 50 and 75 minutes which can assign Weak, Medium, and Strong acid site on the surface of the catalysts in Figure 20, Table 9, and Table 10. For the niobium series, the Strong acid site of catalysts increases when the amount of niobium loading increase. The Medium acid site increased for 3% and 5% niobium loading and decreases for 1% and 10% niobium loading. The Total acid site of catalysts decreases when the niobium loading increasesd suggesting the amount of acid site of the catalysts depends on the niobium loading and surface area that niobium has relative strong Brønsted acid on the surface of the catalysts. For the effect of ammonium acetate which were used in catalysts preparation to acid properties, the acid site decreases when the ratio of ammonium acetate in fuel mixture increase.

The acid- base titration of the catalysts for measuring Brønsted acid and Brønsted base is displayed in table9 and table 10. The amount of Brønsted acid and Brønsted base increase for increasing of niobium but decrease at 10% of niobium loading which like the Medium acid from Ammonia-Temperature Programmed Desorption result.

The pyridine-IR spectra of 1Nb-Al and 10Nb-Al are shown in Figure 4. The band at 1450 cm^{-1} is referred to the pyridine adsorbs on the Lewis acid site and their areas are reported in Table 2. The amount of Lewis acid site increases with the increasing of niobia. The band at 1490 and 1590 cm^{-1} are referred to the pyridine adsorbs on Lewis and Brønsted acid sites and Nb-OH species, respectively[59]. The amount of adsorbed pyridine decreased to 31.3 and 19.1% when the temperature increased to 423.15 and 473.15 K, respectively. While the amount of adsorbed-pyridine decreased to 32.8 and 22.4% for 10Nb-Al, indicating that 10Nb-Al has stronger Lewis acid sits.
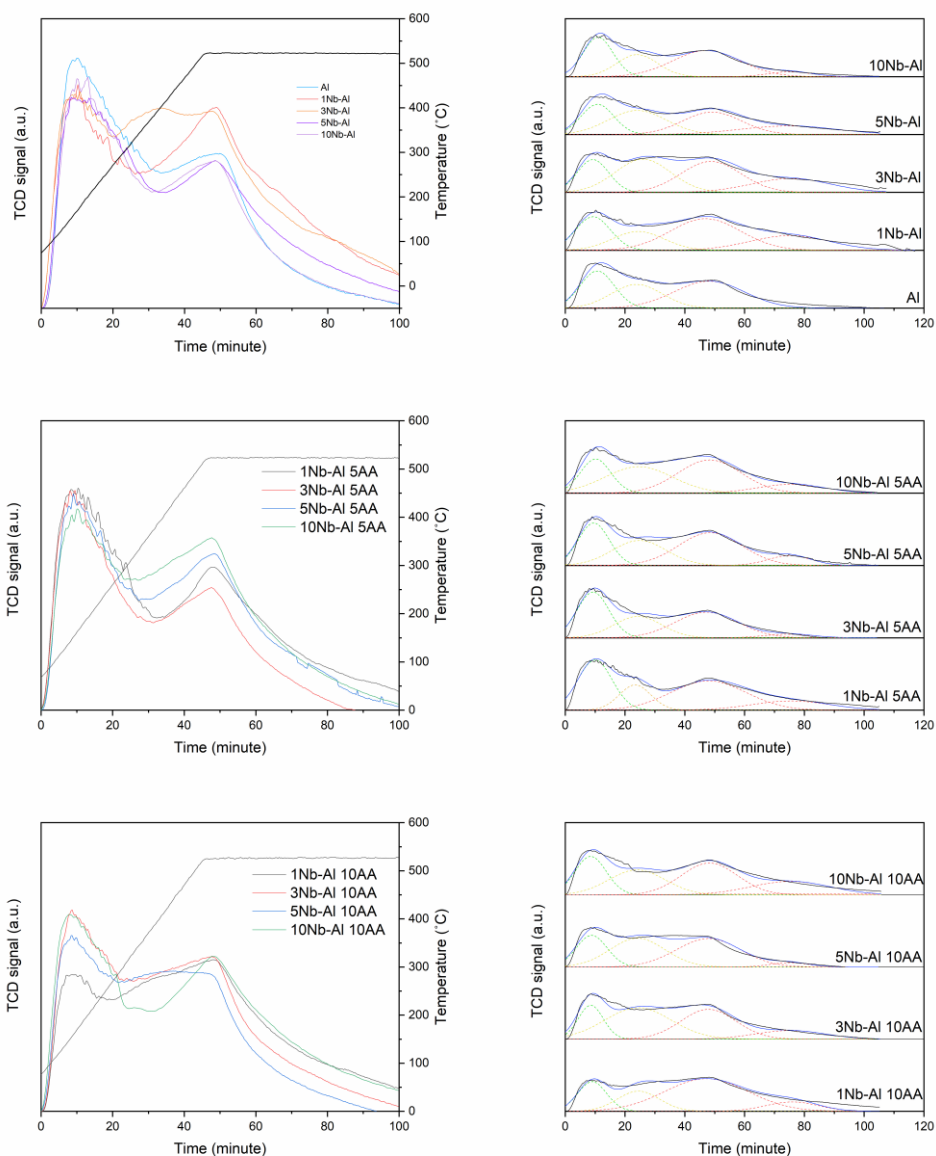
Figure 22 Ammonia-TPD of niobia series catalysts
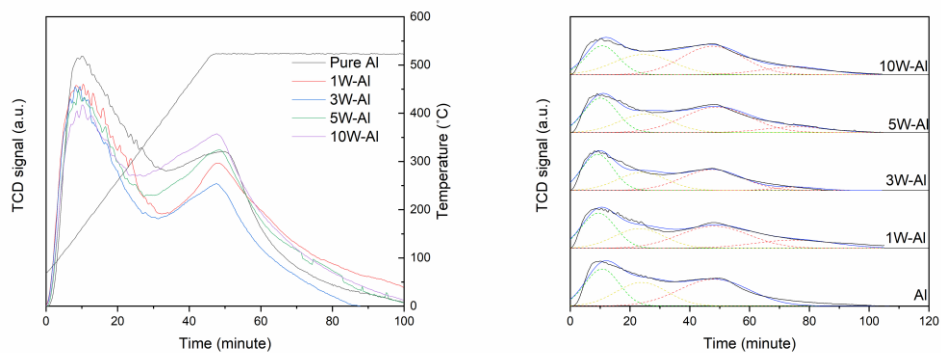
Figure 23 Ammonia-TPD of niobia series catalysts

Table 10 Acid and base properties of catalysts in niobium series

No.	Catalysts	Weak (mmol/g)	Medium (mmol/g)	Strong (mmol/g)	Total (mmol/g)	Brønsted acidity (mmol/g)	Brønsted basicity (mmol/g)
1	Al	0.216	0.213	0.332	0.761	0.249	0.199
2	1Nb-Al	0.194	0.170	0.595	0.959	0.382	0.537
3	3Nb-Al	0.175	0.322	0.515	1.012	0.543	0.552
4	5Nb-Al	0.170	0.242	0.373	0.785	0.411	0.558
5	10Nb-Al	0.204	0.158	0.346	0.707	0.376	0.516
6	1Nb-Al 5AA	0.233	0.112	0.406	0.751	0.323	0.523
7	3Nb-Al 5AA	0.196	0.143	0.252	0.591	0.335	0.52
8	5Nb-Al 5AA	0.179	0.189	0.351	0.719	0.397	0.565
9	10Nb-Al 5AA	0.143	0.247	0.377	0.768	0.331	0.483
10	1Nb-Al 10AA	0.117	0.119	0.452	0.688	0.504	0.428
11	3Nb-Al 10AA	0.117	0.291	0.315	0.722	0.553	0.552
12	5Nb-Al 10AA	0.131	0.221	0.281	0.633	0.564	0.626
13	10Nb-Al 10AA	0.163	0.201	0.172	0.536	0.424	0.458

Table 11 Acid and base properties of catalysts in tungsten series

No.	Catalysts	Weak (mmol/g)	Medium (mmol/g)	Strong (mmol/g)	Total (mmol/g)	Brønsted acidity (mmol/g)	Brønsted basicity (mmol/g)
1	Al	0.216	0.213	0.332	0.761	0.249	0.199
2	1W-Al	0.199	0.172	0.270	0.642	0.270	0.383
3	3W-Al	0.190	0.155	0.220	0.566	0.587	0.594
4	5W-Al	0.194	0.169	0.299	0.662	0.468	0.521
5	10W-Al	0.162	0.209	0.306	0.677	0.568	0.552
6	1W-Al 5AA					0.568	0.551
7	3W-Al 5AA					0.622	0.455
8	5W-Al 5AA					0.596	0.417
9	10W-Al 5AA					0.596	0.453
10	1W-Al 10AA					0.709	0.440
11	3W-Al 10AA					0.666	0.483
12	5W-Al 10AA					0.754	0.425
13	10W-Al 10AA					0.515	0.325

5.3 Conversion of glucose into 5-HMF

The conversion of glucose, 5-HMF yield, furfural yield and 5-HMF selectivity are reported in table 11. The conversions of glucose which contain of niobium and tungsten loading are high when compare with Al. the trend of 5-HMF yield depend on catalysts loading. 1% and 10% niobium catalysts have lower 5-HMF yield than 3% and 5% niobium catalysts which accord to Brønsted acidity by Titration in same amount of ammonium acetate which confirm niobium on alumina catalysts has relatively strong Brønsted acidity on the surface[34]. However, the active site of niobium oxide can be deactivated by blocking of Humin which can be occur from sugar dehydration and polymerization of 5-HMF by strong acid site[26, 27, 60]. For effect of ammonium acetate, 5% ammonium acetate has Higher yield of 5-HMF than 0% and 10% ammonium acetate catalysts in niobium series which contrast with acidity result suggesting because of surface area. The catalysts with 5% ammonium acetate have the high surface area but the amount of Brønsted acidity by Titration are lower than 0% ammonium acetate which make 5-HMF yield of 5% ammonium acetate are higher than 0% ammonium acetate. The catalysts in 10% ammonium acetate series have the highest Brønsted acidity on the surface but have lower surface than 5% ammonium acetate catalysts which make catalysts in 5% ammonium acetate have higher 5-HMF yield. For effect of difference metal oxide loading with 0% ammonium acetate, the 5-HMF yield of tungsten catalysts series are higher than niobium series suggesting the catalysts in tungsten series have higher ration of Brønsted acid and Lewis acid than catalysts in niobium series that decrease the by-product and tungsten catalysts series have lower strong acid site than niobium oxide catalysts series that make tungsten catalysts have low Humin when compare with niobium catalysts. Al and 3Nb-Al 5AA were tested for reusing. The catalysts were pretreated at 973 K for 5 hours before reused. Yield of 5-HMF and glucose conversion are equal.

Table 12 Conversion of glucose to 5-HMF in catalysts test

No.	Catalysts	Yield and Conversion (%)		5-HMF selectivity (%)
		Glucose	5-HMF	
1	-	94.58	23.47	22.19
2	Al	59.11	36.92	62.46
3	1Nb-Al	82.42	20.68	25.09
4	3Nb-Al	83.51	25.92	31.04
5	5Nb-Al	86.26	21.00	24.35
6	10Nb-Al	87.60	20.91	23.87
7	1Nb-Al 5AA	88.42	35.66	40.33
8	3Nb-Al 5AA	93.37	37.91	40.60
9	5Nb-Al 5AA	90.33	37.84	41.89
10	10Nb-Al 5AA	92.73	31.12	33.56
11	1Nb-Al 10AA	93.49	28.97	30.99
12	3Nb-Al 10AA	90.37	34.16	37.80
13	5Nb-Al 10AA	87.47	37.07	42.38
14	10Nb-Al 10AA	82.48	30.59	37.09
15	1W-Al	96.54	39.02	40.42
16	3W-Al	90.41	37.96	41.99
17	5W-Al	91.31	39.33	43.07
18	10W-Al	89.24	36.40	40.79
19	1W-Al 5AA	87.54	32.39	37.00
20	3W-Al 5AA	92.60	37.58	40.58
21	5W-Al 5AA	85.94	35.75	41.60
22	10W-Al 5AA	100.00	38.55	38.55
23	1W-Al 10AA	100.00	36.02	36.02
24	3W-Al 10AA	100.00	39.76	39.76
25	5W-Al 10AA	100.00	41.46	41.46

| 26 | 10W-Al 10AA | 82.48 | 33.75 | 40.92 |

Table 12 Conversion of glucose to 5-HMF in recycle test

No.	Catalysts	Yield and Conversion (%)		5-HMF selectivity (%)
		Glucose	5-HMF	
1	Al 1	84.15	32.51	27.35
2	Al 2	84.76	32.48	27.53
3	3Nb-Al 5AA 1	88.04	35.26	31.04

Figure 24 catalysts after the reaction test (a) and catalysts after pretreatment (b)

Table 13 Weight of catalysts before and after pretreated

No	catalysts	Weight before pretreated (g)	Weight after pretreated (g)	Solid product (g)
1	Al	0.0657	0.0411	0.0246
2	3Nb-Al 5AA	0.0713	0.0442	0.0271

CHAPTER VI

Conclusion

The results showed that the solution combustion synthesis using mixture fuel can synthesize high surface and adjustable physicochemical properties of niobium- and tungsten-promoted aluminas. The highest BET surface area of Nb- and W-promoted aluminas were obtained using 5% and without ammonium, respectively. The amount of gas generating agent which used in catalysts preparation can make difference kind of shape and pore of the catalysts. The solution combustion synthesis can disperse the promoted metals on the support well. The amount of Brønsted acid and Brønsted base increased with increasing of niobium but decreased at 10% of niobium loading. The highest yield of 5-HMF at 41.46% was obtained for 5W-Al   10AA
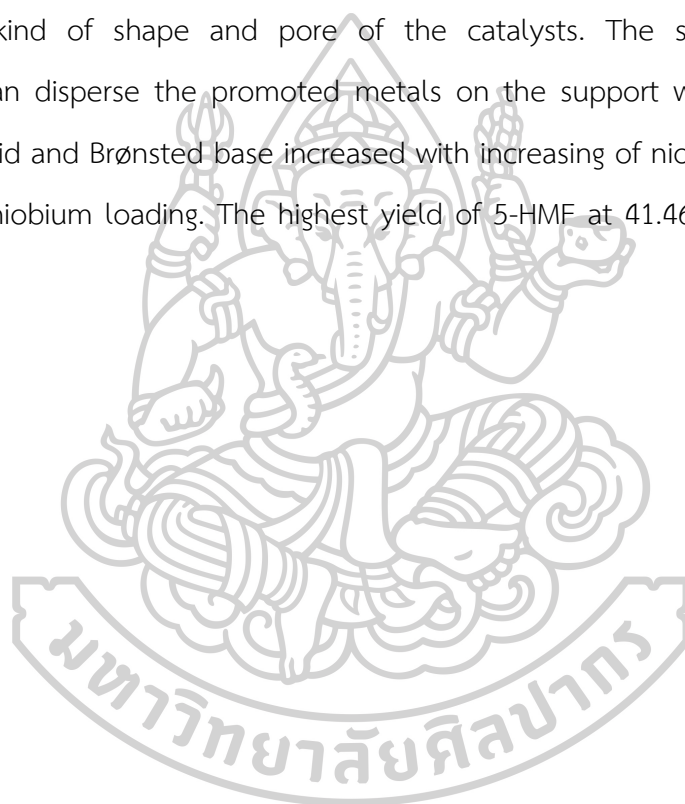
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APPENDIX A

CALCULATION FOR CATALYST PREPARATION

Table 14 Chemical Properties

Metal oxide	Mw of metal	Metal Precursor
Al	375.13	$Al(NO_3)_3 \cdot 9H_2O$
Nb	302.98	$C_4H_4NNbO_9 \cdot xH_2O$
W	2956.30	$(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$

A.1 Calculation of catalyst prepared by solution combustion synthesis

Example: Calculation for the preparation of the 10Nb/Al1 catalyst. Aluminium nitrate and Ammonium niobate (V) oxalate hydrate were used as precursor.

Based on 2 g catalyst 10 wt % Nb/Al the composition of the catalyst will be follow:

For 2 g catalyst

Al_2O_3 = 2 g catalyst × 0.9 g Al 1 g catalyst=1.8 g Al_2O_3

Nb_2O_5 = 2 g catalyst × 0.1 g Nb 1 g catalyst=0.2 g Nb_2O_5

Alumina was synthesized by solution combustion synthesis using urea as a fuel cell and then niobium precursor was dropped on alumina support.

Gram of precursor

Aluminium nitrate

$$= 1.8 \text{ g } Al_2O_3 \times \frac{1 \text{ mole } Al_2O_3}{101.96 \text{ g } Al_2O_3} \times \frac{2 \text{ mole } Al(NO_3)_3}{1 \text{ mole } Al_2O_3} \times \frac{375.13 \text{ g } Al(NO_3)_3}{1 \text{ mole } Al(NO_3)_3} \times \frac{1}{0.98}$$
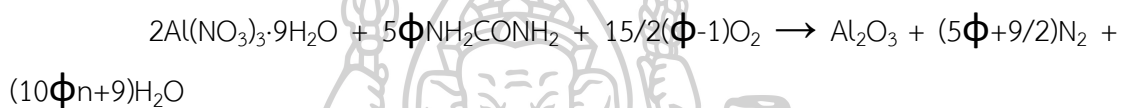
= 13.52 g Aluminium nitrate

Ammonium niobate (V) oxalate hydrate

= 0.2 g Nb_2O_5 × $\dfrac{1\ mole\ Nb_2O_5}{101.96\ g\ Nb_2O_5}$ × $\dfrac{2\ mole\ C_4H_4NNbO_9}{1\ mole\ Nb_2O_5}$ × $\dfrac{302.98\ g\ C_4H_4NNbO_9}{1\ mole\ C_4H_4NNbO_9}$ × $\dfrac{1}{0.9999}$

= 0.23 g Ammonium niobate (V) oxalate hydrate

Solution combustion reaction of Alumina

$$2Al(NO_3)_3 \cdot 9H_2O\ +\ 5\phi NH_2CONH_2\ +\ 15/2(\phi-1)O_2\ \longrightarrow\ Al_2O_3\ +\ (5\phi+9/2)N_2\ +\ (10\phi n+9)H_2O$$

Urea used in solution combustion synthesis for alumina support

= 1.8 g Al_2O_3 × $\dfrac{1\ mole\ Al_2O_3}{101.96\ g\ Al_2O_3}$ × $\dfrac{5\ mole\ urea}{1\ mole\ Al_2O_3}$ × $\dfrac{60.06\ g\ urea}{1\ mole\ Al(NO_3)_3}$ × $\dfrac{1}{0.99}$

= 5.35 g urea
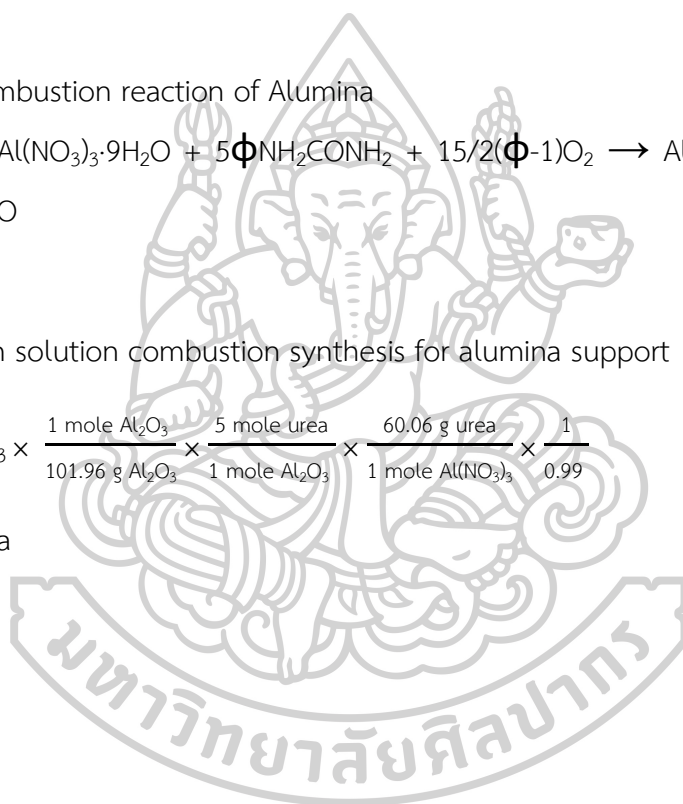
APPENDIX B

Calibration for HPLC

For HPLC calibration, 5-hydroxymethylfurfural was prepared in solution form with concentration 5, 10, 20, 25 and 30 ppm. The sample were injected in HPLC to get area of peak that appeared as follow:

Table 15 Data for 5-HMF calibration with HPLC

Area	Concentration (ppm)
49987107	2000
42974534	1750
37155104	1500
25741628	1000
12957775	500
2615546	100
2255806	50

Form the data form HPLC, the data were plot calibration curve for calculate amount of 5-HMF can be detected as follow:
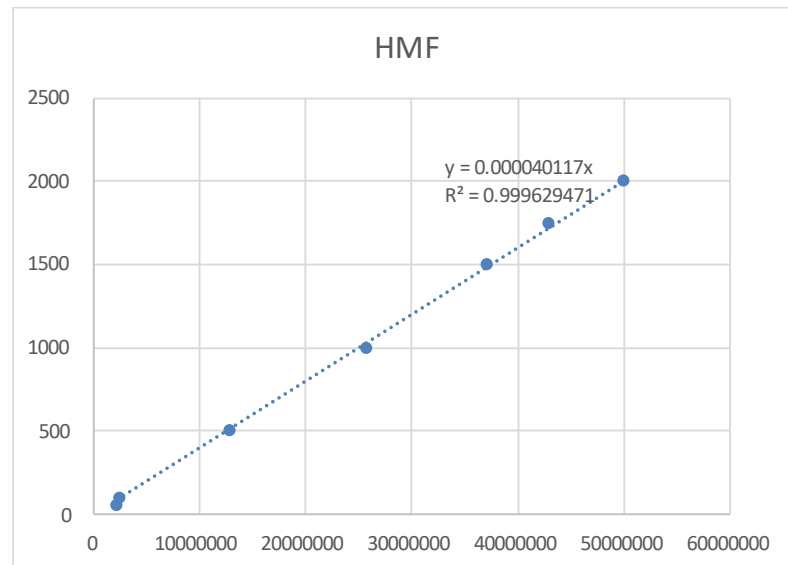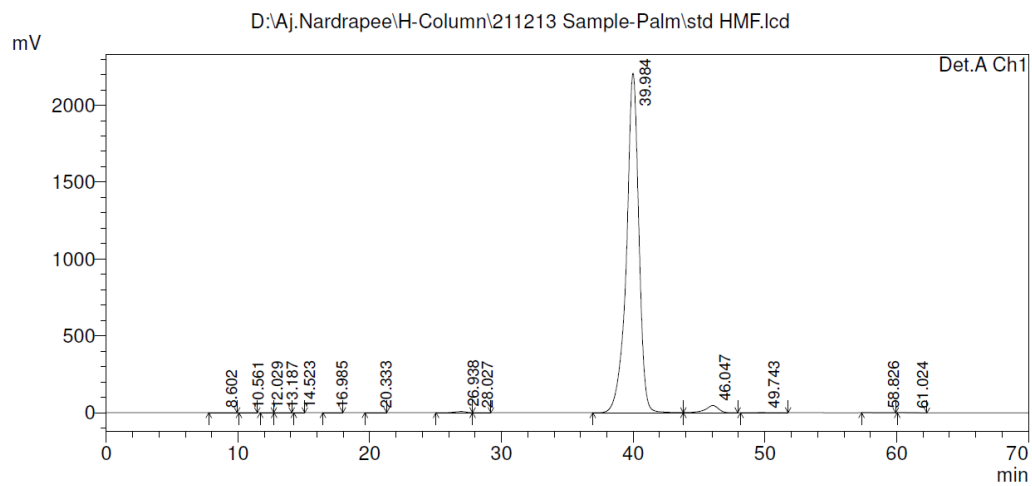

Figure 25 Calibration Curve for 5-HMF

Figure 26 Data for 5-HMF form HPLC

For HPLC calibration, Glucose was prepared in solution form with concentration 1000, 1500, 2000, 2500, 3000, 3500 and 4000 ppm. The sample were injected in HPLC to get area of peak that appeared as follow:

Table 16 Data for 5-HMF calibration with HPLC

Area	Concentration (ppm)
490530	3000
409531	2500
328291	2000
171722	1000
81635	500
17714	100
8733	50

Form the data form HPLC, the data were plot calibration curve for calculate amount of Glucose can be detected as follow:
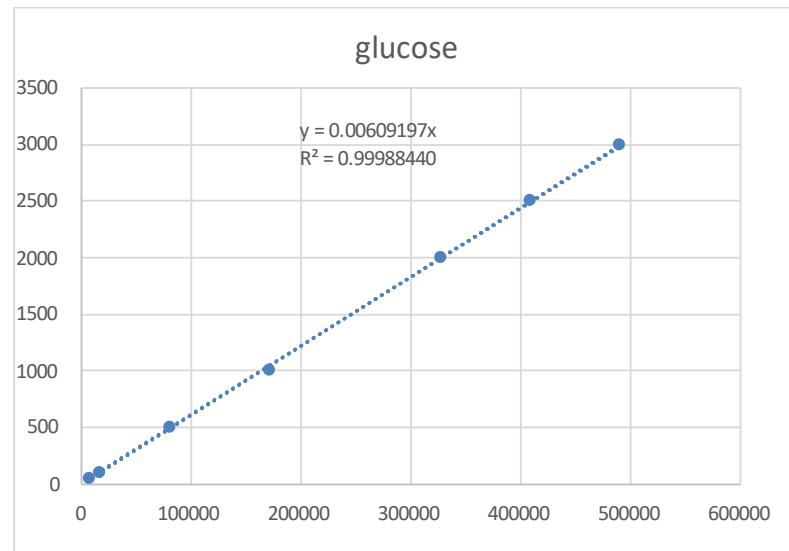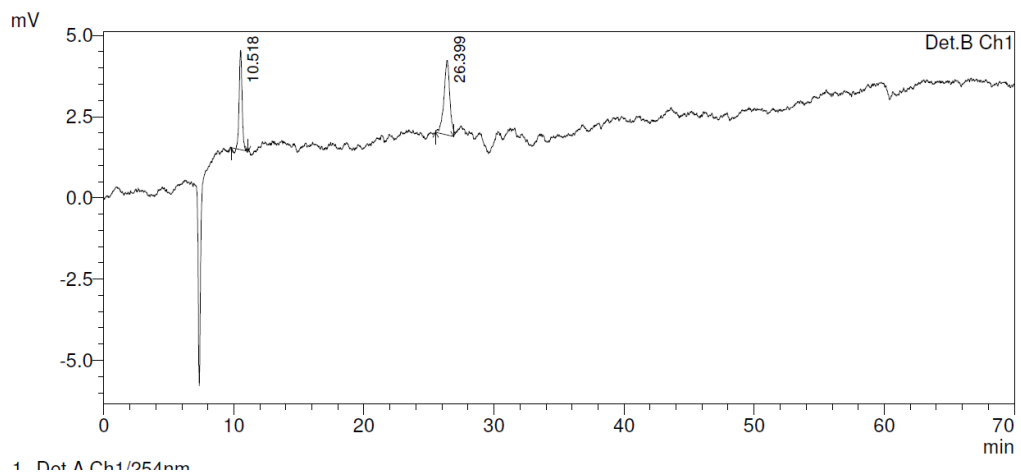

Figure 27 Calibration Curve for Glucose

Figure 28 Data for Glucose form HPLC

APPENDIX C

Data of HPLC

The concentration of 5-HMF and all of byproducts were quantified using HPLC with uv in wavelength 195 nm for detect sugar, 210 nm for detect acid and 285 nm for detect the product using column Agilent Hi-Plex H, 7.7 × 300 mm, 8 m and using 0.005 M H_2SO_4 as a mobile phase. The data of samples were injected in HPLC to get area of peak that appeared as follow:
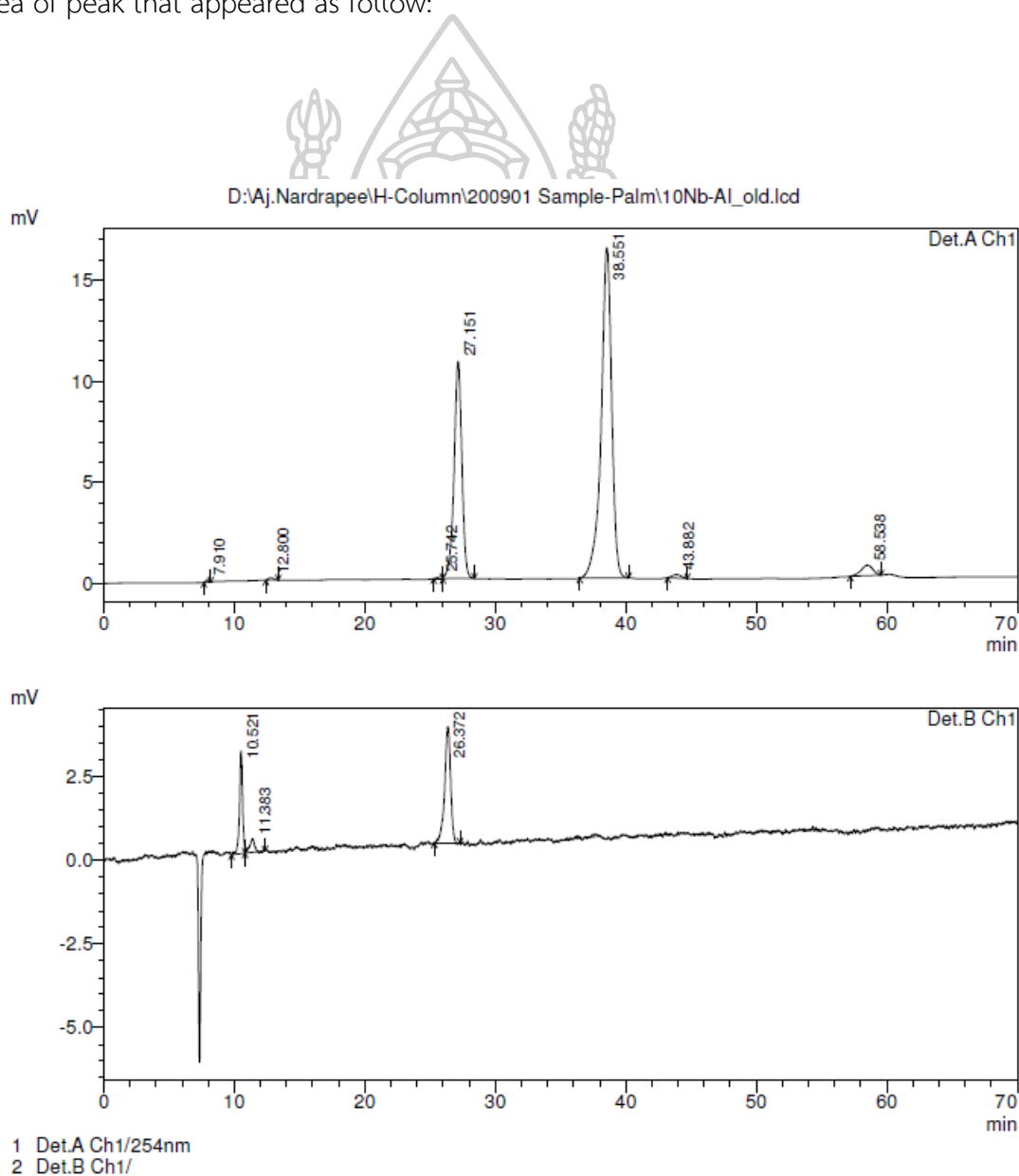

Figure 29 Data form HPLC of 10Nb-Al

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