공학석사학위논문

Highly Selective Catalytic Hydrogenation and Etherification of 5-Hydroxymethyl-2-furaldehyde for Valuable Chemical Production

5-하이드록시메틸-2-퓨랄데하이드의 선택적 수소첨가 촉매 반응과 이터화 반응을 통한 고부가가치 화학물질 생산

2016년 2월

서울대학교 대학원

화학생물공학부

한주성

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ABSTRACT

Highly Selective Catalytic Hydrogenation and Etherification of 5-Hydroxymethyl-2-furaldehyde for Valuable Chemical Production

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The transformation of lignocellulosic biomass-derived 5-hydroxymethyl-2-furaldehyde (HMF) to fuels and additives is of considerable interest for reducing the dependence on fossil fuels. This study presents an efficient process to produce 2,5-bis(alkoxymethyl)furan (BAMF) as a potential biodiesel. We have synthesized $Ru(OH)_x/ZrO_2$ catalyst for selective hydrogenation of HMF to 2,5-bis(hydroxylmethyl)furan (BHMF). $Ru(OH)_x/ZrO_2$ catalyst showed excellent performance of selective hydrogenation of HMF's aldehyde group to alcohol group under optimized condition. This reaction proceeded well in various n-alcohol solvents in more than 98 % yield. Moreover, the catalyst can be reused 5 times without significant loss of catalytic activity. The resulting solution of BHMF in various alcohol solvents was sequentially etherified to BAMF by Amberlyst-15 catalyst. From this two-step sequential reaction process, the valuable potential biodiesel chemical, BAMF, which has diverse alkoxy groups, can be obtained efficiently. The yields of BAMF were more than 70 % except for 2,5-bis(methoxymethyl)furan (BMMF) which gave 50 % yield.

Keywords: biomass transformation, hydrogenation, etherification, bio-diesel, heterogeneous catalyst, $Ru(OH)_x/ZrO_2$ catalyst, amberlyst, sequential reaction, HMF, BHMF, BAMF

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LIST OF ABBREVIATIONS

AMF	5-(alkoxymethyl)furfural
AMFA	5-(alcoxymethyl) furfuryl alcohol
BAMF	2,5-bis(alkoxymethyl)furan
BBMF	2,5-bis(butoxymethyl)furan
BEMF	2,5-bis(etoxymethyl)furan
BHMF	2,5-bis(hydroxymethyl)furan
BHMTHF	2,5-bis(hydroxymethyl)tetrahydrofuran
BMMF	2,5-bis(metoxymethyl)furan
BMFA	5-(butoxymethyl) furfuryl alcohol
BPMF	2,5-bis(propoxymethyl)furan
DMF	2,5-dimethyl furan
EL	ethyl levulinate
EMF	5-(ethoxymethyl)furfural
FDCA	2,5-furandicarboxylic acid
FID	flame ionization detector
GC	Gas chromatography mass spectra
GC/MS	Gas chromatography mass spectra
GVL	Gamma valerolactone
HMF	5-hydroxymethyl-2-furaldehyde
^{1}H NMR	proton nuclear magnetic resonance

ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma atomic emission spectroscopy
n-alcohol	normal alcohol
n.d.	not detected
Ru(OH)x/ZrO2	Ruthenium hydroxide supported on zirconia
TMS	tetramethylsilane
XPS	X-ray photoelectron spectra
XRD	X-ray diffraction
ZSM-5	Zeolite Socony Mobil-5

Highly Selective Catalytic Hydrogenation and Etherification of 5-Hydroxymethyl-2-furaldehyde for Valuable Chemical Production

I. Introduction

I. Carbohydrate from Lignocellulosic Biomass

Global warming induced by greenhouse gas emissions has led to the development of renewable and sustainable green energy resources for transportation fuels and fine chemical products.[1-4] In this regard, biomass as a green energy resource generated from water, carbon dioxide and sunlight has attracted much research attention. Among various kinds of biomass, lignocellulosic biomass is highly attractive resource because it is extracted from non-food biomass of trees and agricultural residues. It is the most abundant organic compound as well which contains plenty of carbohydrates.[5] The carbohydrate contents of lignocellulosic biomass are 60-80%, which is composed of poly/oligosaccharides such as cellulose, hemicelluloses, and starch.[5] Figure 1 shows the microstructure of lignocellulosic biomass.

So, various transformation methods of lignocellulosic biomass to platform chemicals such as 5-hydroxymethyl-2-furaldehyde (HMF), which can be converted further to polymer building blocks and potential biofuel candidates, have been reported recently.[6-10]

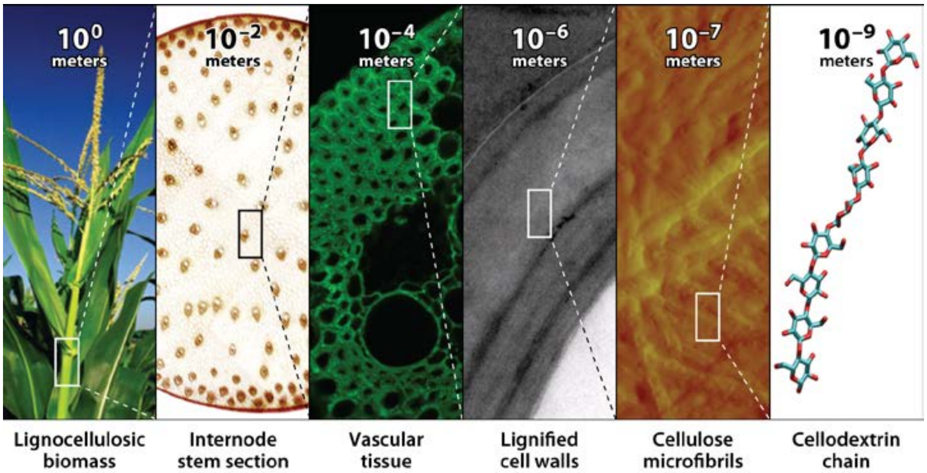


Figure 1. Microstructure of the lignocellulosic biomass.[11] The first two images are courtesy of DOE/ NREL.

I. 1 5-Hydroxymethyl-2-furaldehyde as Platform Chemical

5-Hydroxymethyl-2-furaldehyde (HMF) is a promising platform chemical derived from lignocellulosic biomass because it can be transformed into value added chemicals, such as polymer building blocks (2,5-furandicarboxylic acid (FDCA), 2,5-bis(hydroxy-methyl)furan (BHMF)) and potential biofuel cadidates (2,5-dimethyl furan (DMF), 5-(alkoxymethyl)furfurals (AMF), 2,5-bis(alkoxymethyl)furan (BAMF), ethyl levulinate (EL), gamma valerolactone (GVL)).[7,12,13] Since some HMF derivatives are listed in the “Top 12 valuable chemical” by the US Department of Energy (DOE) and National Renewable Energy Laboratory (NREL), the key issue is to develop manufacturing processes of HMF which could be economically acceptable.[14] Figure 2 shows synthetic process of HMF and its valuable derivatives.

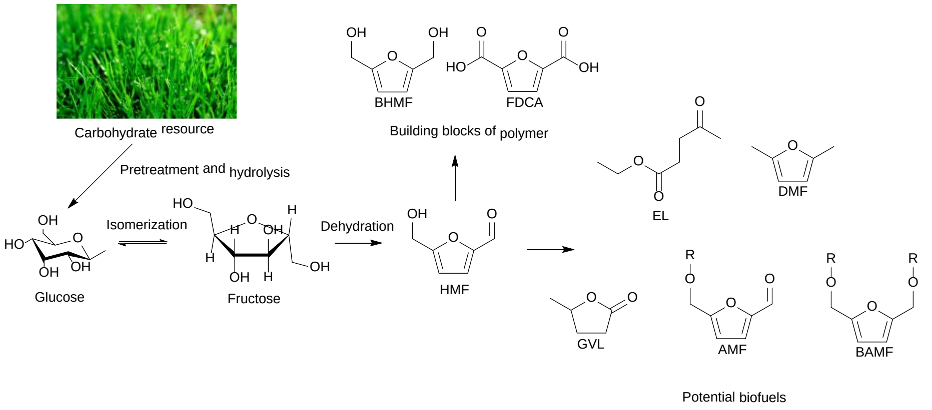


Figure 2. Production of HMF and its valuable derivatives.[7]

I. 2 2,5-Bis(hydroxymethyl)furan as Polymer Building Block

The production of polymer building blocks derived from 5-hydroxymethyl-2-furaldehyde (HMF) such as 2,5-furandicarboxylic acid (FDCA), 2,5-bis(hydroxy-methyl)furan (BHMF) have drawn much attention owing to the apllication of biobased polymer, competing with petroleum based PET, Nylon and PU.

Among HMF derived polymer buiding blocks, BHMF is a highly attractive chemical because it can be used not only as an polymer buiding block but also as an intermediate of drugs and crown ethers.[15] For these reasons, various methods of hydrogenation of HMF to BHMF have been conducted. Among them, hydrogenation of HMF using heterogeneous metal catalysts under H_2 gas shows good performance.[15-17]However, selective hydrogenation of HMF to BHMF is very difficult because HMF can be transformed to over-hydrogenated products.

I. 3 2,5-Bis(alkoxymethyl)furan as Potential BioDiesel

5-(Alkoxymethyl)furfural (AMF) is an attractive biodiesel as it has higher energy density and cetane number than bio-ethanol and gives no adverse effect on engines up to 17 wt % in petroleum-derived diesels.[18] 5-(Ethoxymethyl)furfural (EMF) is a promising second generation bio-diesel, and a variety of synthetic routes to EMF have recently been reported.[19-21] It has 30.3 MJ/L of energy density that is 3 % lower than gasoline and 29 % greater than ethanol and has diverse advantages such as less toxic and soot.[22]

Despite these advantages, the aldehyde group of AMF decreases the cetane number and the stability.[22,23] In this regard, 2,5-bis(alkoxymethyl)furan (BAMF) is more attractive biodiesel due to the absence of aldehyde group. Nevertheless, it is more technically demanding to produce BAMF because the aldehyde group of HMF should be hydrogenated to an alcohol group and etherificated subsequently.[24]

II. Catalytic Conversion of HMF to Valuable Chemicals

II. 1 Catalytic Hydrogenation of HMF to BHMF using Metal Catalyst

In various ways, hydrogenation of HMF to BHMF using heterogeneous metal catalysts gave good performance. Kumalaputri et al. reported that HMF was transformed into BHMF in 99 % yield in ethanol at 100 ℃ in 3 hours over Cu-doped porous metal oxide.[25] Tamura et al. obained BHMF in 99 % yield using Ir-ReO$_x$ in water at mild conditions.[26] Recently, Chatterjee et al. obtained 98.9 % selectivity of BHMF with complete conversion in an auqueous medium using Pt/MCM-41 catalyst at 35 ℃ under 0.8 Mpa of H_2 within 2 hours.[17] In parallel, Pasini et al. reported that HMF was converted to BHMF with a selectivity of 99 % in toluene with Ru-based Shvo’s catalyst.[27]

However, these previous hydrogenation of HMF to BHMF were unsuccessful in various solvents, especially in alcohol solvents.

II. 2 Catalytic Reaction of HMF to BAMF using Metal and Acid Catalyst

Since biodiesels that contain ether groups have high cetane number, high energy density, stability and no adverse effects on engine,[18] etherification reaction is very important reaction to produce high quality diesels. For etherification, acid catalysts such as acidic ion exchange resins, zeolite or p-toluene sulfuric acid have usually been used.[28]

Mixture of metal and acid catalysts have been utilized in the etherification of HMF to BAMF. Balakrishnan et al. reported one pot reductive etherification of HMF by Pt/Al_2O_3, PtSn alloys and Amberlyst-15 catalyst. They obtained 2,5-bis(etoxymethyl)furan (BEMF) and 2,5-bis(butoxymethyl furan (BBMF) in 59 % and 47 % yields respectively.[22] Recently, Quan Cao et al. reported that HMF was converted to 2,5-bis(methoxymethyl furan (BMMF) by using Cu/SiO_2 and zeolite catalyst in 68 % yield.[29]

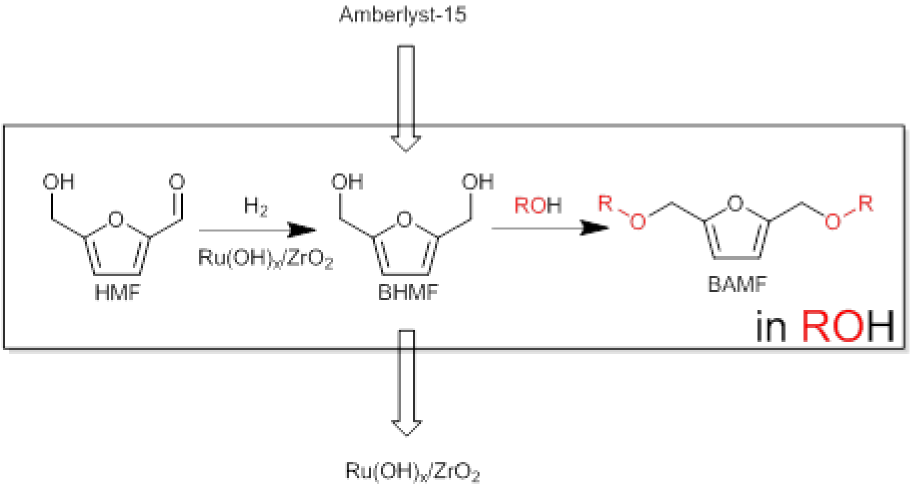
However, these processes are inefficient to obtain a reasonable yield of BAMF or cannot present a general pathway which can be applied in various alcohol solvents for obtaining diverse alkoxy groups of BAMF.

Moreover, the one pot process has a disadvantage in catalyst recycling due to the presence of two types of catalyst.

III. Research Objectives

Herein, we report a more versatile synthetic method of potential biodiesel, BAMF, using a two-step sequential reaction process with previously reported heterogeneous Ru catalyst[30] and heterogeneous acid catalyst. At first, zirconia-supported Ru ($Ru(OH)_x/ZrO_2$) was used as the catalyst for HMF hydrogenation reaction to BHMF. Then, Amberlyst-15 was utilized as a heterogeneous acid catalyst for BHMF etherification reaction. Amberlyst-15 has been reported to have outstanding performance in the BHMF etherification reaction.[22]

Scheme 1 shows the two-stpe sequential reaction process of our method. HMF was hydrogenated to BHMF using $Ru(OH)_x/ZrO_2$ catalyst in various n-alcohol solvents in the presence of H_2 gas. As $Ru(OH)_x/ZrO_2$ catalyst could be removed by simple filtration, BHMF dissolved in various n-alcohol solvents could be obtained easily at high purity. Sequentially, Amberlyst-15 was added to the resulting BHMF solution for the etherification reaction. In this reaction, alcohol solvents acted as both reactant and solvent. By this two-step sequential reaction process, valuable potential biodiesel chemical, BAMF, which has diverse alkoxy groups, can be obtained efficiently.



Scheme 1. Two-step sequential reaction for production of BAMF from HMF.

II. Experimental Section

I. General

I. 1 Materials

5-Hydroxymethyl-2-furaldehyde (HMF) (99 %), ruthenium (III) chloride ($RuCl_3 \cdot H_2O$, anhydrous, 99.99 %), ruthenium (Ⅳ) oxide hydrate, ruthenium 5 % on activated charcoal, amberlyst-15 (H^+ form, 4 mmol/g resin), methanol (anhydrous, 99.8 %), ethanol (anhydrous, 99.5+ %), 2-propanol (anhydrous 99.5 %), and 1-buthanol (anhydrous, 99.8 %) were purchased from Sigma Aldrich. Sodium hydroxide (reagent grade ≥ 98 %), 1-propanol (99.5 %), and tert-butyl alcohol (99.0 %) were purchased from Daejuung Chemical & Metal (South Korea). Zirconium oxide (20-30 m^2/ g) was obtained from STREM and 2,5-bis(hydroxymethyl)furan (BHMF) (98+ %) was purchased from Apollo Scientific Ltd. Ruthenium (IV) oxide (anhydrous, 99.5+ %) was purchased from ACROS ORGANICS. All the NMR solvents were obtained from Cambridge Isotope Laboratories, Inc. All chemicals were used as received without further purification.

I. 2 Characterization

The ^{1}H NMR was obtained on an Ascend^{TM} 400 (Bruker, USA). Mass spectra (GC/MS) were recorded on Hewlett Packard 6850 gas chromatograph system with 5973 MS detector (Hewlett Packard, USA) at an ionization voltage of 70 eV equipped with a DB-5 capillary column (internal diameter=0.25 mm, length=30 m). Gas chromatography (GC) analyses were performed on a Younglin GC-6500 using a flame ionization detector (FID) equipped with a DB-5HT capillary column (internal diameter = 0.25 mm, length = 30 m). The X-ray photoelectron spectra (XPS) was obtained on a SIGMA PROBE (Thermo VG, U.K) equipped with a full 180 degree spherical sector analyzer to examine the chemical composition of the elements. An Al anode was used as photon sources at 15 kV. The X-ray diffraction (XRD) patterns were obtained on a Bruker D8 DISCOVER (Bruker, USA) equipped with a full 180 degree spherical sector analyzer to examine the chemical composition of the elements. The amount of metal loadings on the solid support of catalysts was measured using an inductively coupled plasma emission spectrometer (ICP, Shimadzu ICPS-7510).

II. Hydrogenation of HMF to BHMF Catalyzed by $Ru(OH)_x/ZrO_2$

II. 1 Preparation of $Ru(OH)_x/ZrO_2$

The supported ruthenium hydroxide ($Ru(OH)_x/ZrO_2$) catalyst was prepared by the previously reported method.[30] Briefly, ZrO_2 (4 g) was stirred in deionized water for a few min and then $RuCl_3 \cdot H_2O$ (263.3 mg, 1 mmol) was added, followed by addition of NaOH solution to raise the pH to 13. The catalyst was removed by filtration and the solid residue was dried in air.

The loading level of Ru in the catalyst was confirmed by ICP-AES. Furthermore, the characteristics of the Ru and O species on the catalyst surface were analyzed by XPS. The surface morphologies of the catalyst were observed by XRD.

II. 2 Hydrogenation of HMF to BHMF Catalyzed by $Ru(OH)_x/ZrO_2$

The HMF (100 ul, 0.97 mmol) was reduced in various solvents (3 mL) by using $Ru(OH)_x/ZrO_2$ (0.31 mol % of Ru) catalyst under H_2 gas (15 bar). The reaction proceeded in a pressure vessel with a Teflon liner (200 mL), equipped with a glass vial (10 mL). After the reaction, the catalyst was filtered and the filtrate was was evaporated by vacuum. The products were analyzed by ^1H NMR (400 MHz, DMSO-d6, TMS): δ (ppm)= 6.2 (s, 2H), 5.2 (t, 2H), 4.4 (d, 4H) and ^1H NMR (400 MHz, D_2O): δ (ppm)= 6.2 (s, 2H), 4.7 (s, 2H), 4.4 (s, 4H). GC/MS analysis was performed to ensure that any by-product was not formed. The separated $Ru(OH)_x/ZrO_2$ catalyst was washed with acetone and aqueous sodium hydroxide (0.1 N) and dried, in air before being recycled.

III. Etherification of BHMF to BAMF Catalyzed by Amberlyst-15

The BHMF (32 mg, 0.25 mmol) was etherificated in various alcohol solvents (1.5 mL) by using Amberyst-15. The reaction proceeded in a glass vial (10 mL) with a cross-shaped magnetic stirring bar. The final products were analyzed by GC/MS and the yields were calculated by GC analysis.

IV. Two-step Sequential Reaction of HMF to BAMF in Various n-Alcohol Solvents

HMF (100 ul, 0.97 mmol) was hydrogenated to BHMF in methanol, ethanol, 1-propanol and 1-butanol solvents (3 mL) by using $Ru(OH)_x/ZrO_2$ (0.31 mol % of Ru) catalyst under H_2 gas (15 bar). The reaction proceeded in a pressure vessel with a Teflon liner (200 mL), equipped with a glass vial (10 mL) at 120 ℃ for 6 h. After the reaction, solvents were added up to 3 mL and then the catalyst was filtered. Subsequently, Amberlyst-15 was added (24.25 mg, 10 mol %) and the solution was stirred for 10 h at 60 ℃. The final products were analyzed by GC/MS and the product yields were calculated by GC analysis.

III. Results and Discussion

I. Characterization of $Ru(OH)_x/ZrO_2$ Catalyst

The loading level of Ru on the ZrO_2 was confirmed by ICP-AES. As a result, $Ru(OH)_x/ZrO_2$ contained 0.2-0.26 mmol of Ru /g.

The surface morphological changes of ZrO_2 during fabrication of $Ru(OH)_x/ZrO_2$ was analyzed by X-ray diffraction (XRD) spectra. Figure 3 shows the XRD patterns of ZrO_2 and $Ru(OH)_x/ZrO_2$ in the range from 10° to 70° (2-theta). From the XRD results, we could confirm that $Ru(OH)_x/ZrO_2$ did not containe Ru(0) or RuO_2 particles.[31,32] (monoclinic phase of ZrO_2 is 28.5°, 34.5° and tetragonal phase of ZrO_2 of ZrO_2 is 50.2°.)[33]

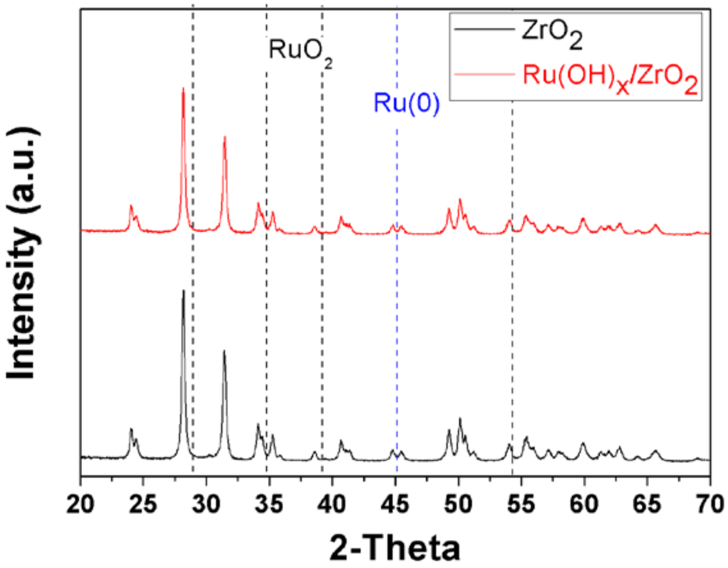
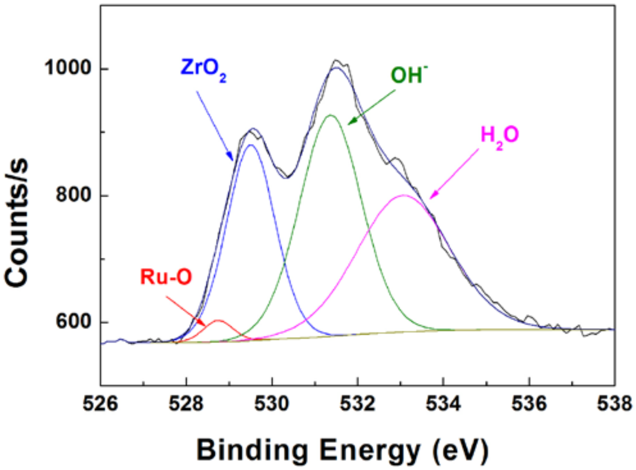


Figure 3. XRD patterns of $Ru(OH)_x/ZrO_2$ (Red) and ZrO_2 (Black).

The surface charateristic of the Ru and O speies on $Ru(OH)_x/ZrO_2$ was analyzed by XPS. Figure 4 (a) shows the O 1s XPS spectra of $Ru(OH)_x/ZrO_2$. Binding energies of 529.5 eV was attributed to ZrO_2, and 531.3 eV corresponded to hydroxide groups from Ru-OH bond or Zr-OH bond. The most important information is the peak at 528.7 eV from Ru-O bond.[30] From this result, we can conclude that Ru was supported on ZrO_2. Figure 4 (b) shows the Ru 3d XPS spectra. As can be seen, three components of the C 1s (284.5 eV, 286.3 eV and 287.8 eV) and 2 pairs of Ru^{3+} peaks were detected. The first pair of Ru 3d peak was Ru_1 ($3d_{3/2}$) and Ru_1 ($3d_{5/2}$) corresponded to 281.0 eV and 285.1 eV respectively, while the second one was Ru_2 ($3d_{3/2}$) and Ru_2 ($3d_{5/2}$), found at 282.8 eV and 286.9 eV. The Ru_1 was the component of Ru (Ⅲ) hydrated oxide and Ru_2 was the hydrated Ru (Ⅲ)-OH incorporated on the ZrO_2.[34] From XRD and XPS resulsts, we can conclude that $Ru(OH)_x/ZrO_2$ fabricated with active sites of Ru were well supported on ZrO_2 without forming Ru(0) or RuO_2 particles.

(a)



(b)

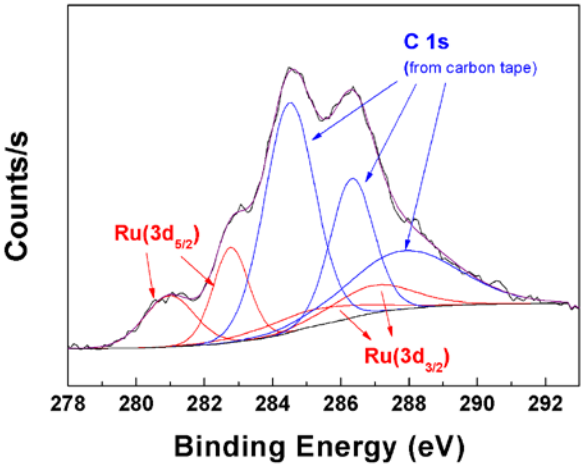


Figure 4. XPS spectra of Ru(OH)$_x$/ZrO$_2$; (a) peaks of O 1s speices from Ru(OH)$_x$/ZrO$_2$, (b) peaks of Ru 3d speices from Ru(OH)$_x$/ZrO$_2$.

II. Hydrogenation of HMF to BHMF Catalyzed by $Ru(OH)_x/ZrO_2$

II. 1 Optimization of Hydrogenation of HMF to BHMF

The hydrogenation of HMF to BHMF was carried out using zirconia-supported ruthenium hydroxide ($Ru(OH)_x/ZrO_2$) catalyst. The reaction conditions were optimized with $Ru(OH)_x/ZrO_2$ (0.31 mol %).

Table 1 shows the effect of reaction temperature on hydrogenation of HMF to BHMF. The conversion of HMF was found to be increasing with increasing temperature. $Ru(OH)_x/ZrO_2$ selectively hydrogenated HMF to BHMF at 50 ° and 80 °C. However the conversions were very low. A complete conversion of HMF was achieved on raising the temperature to 120 ° and 150 °C for 6 h. Therefore, 120 °C was selected for further HMF hydrogenation reactions.

Table 1. Hydrogenation of HMF to BHMF Depending on Temperature

Entry	**Temperature (℃)**	**Conversion (%)**	**BHMF Selectivity (%)**
1	50	28	> 99
2	80	57	> 99
3	120	> 99	> 99
4	150	> 99	> 99

Reaction condition: HMF (100 uL, 0.97 mmol), $Ru(OH)_x/ZrO_2$ (15 mg, 0.31 mol %), H_2 15 bar, 1-butanol (3 mL), 6 h. Results were analyzed by ^{1}H-NMR spectrum.

Table 2 shows the effect of H_2 pressure on the hydrogenation of HMF. As shown from Table 2, under 10 bar of H_2, most of HMF was hydrogenated to BHMF in 99 % yiled. When the H_2 pressure was increased to 15 bar or 40 bar, the reactions progressed with the same pattern. From these results, we could determine that hydrogen pressure has no significant effect on the hydrogenation reaction of HMF with $Ru(OH)_x/ZrO_2$ catalyst.

Table 2. Hydrogenation of HMF to BHMF Depending on Pressure

Entry	**Pressure (bar)**	**Conversion (%)**	**BHMF Selectivity (%)**
1	10	> 99	> 99
2	15	> 99	> 99
3	40	> 99	> 99

Reaction condition: HMF (100 uL, 0.97 mmol), $Ru(OH)_x/ZrO_2$ (15 mg, 0.31 mol %), temperature 120 ℃, 1-butanol (3 mL), 6 h. Results were analyzed by ^{1}H-NMR spectrum.

Figure 5 shows the effect of time on the conversion of HMF to BHMF. The hydrogenation of HMF to BHMF proceeded rapidly and very selectively within 2 h (87 % conversion). After 2 h, the yield of BHMF increased slowly up to 99 % and no further reaction occurred from 6 h to 12 h. This trend was attributed to an inhibition effect of the BHMF product, which has two CH_2OH groups, and other combination of the inhibiting effect.[27] This result implies that the $Ru(OH)_x/ZrO_2$ catalyst has a higher activity toward the C=O bond than other reactive sites.

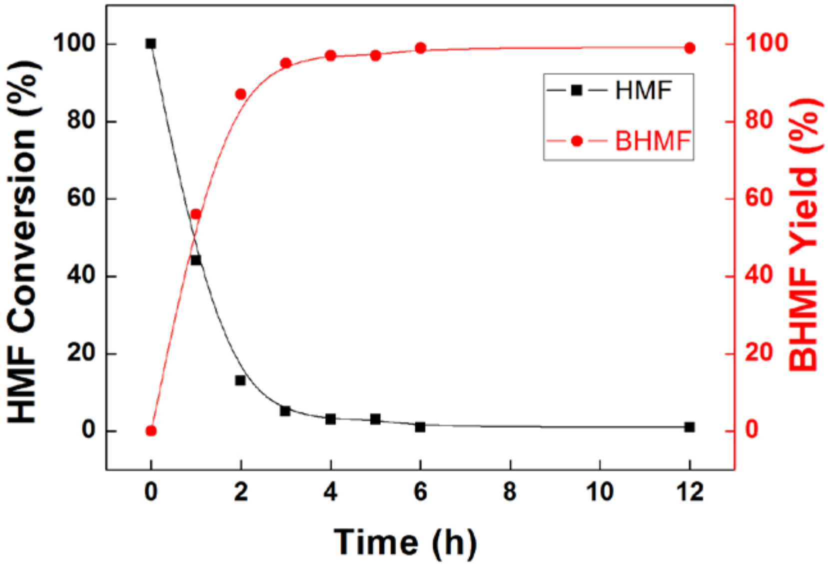


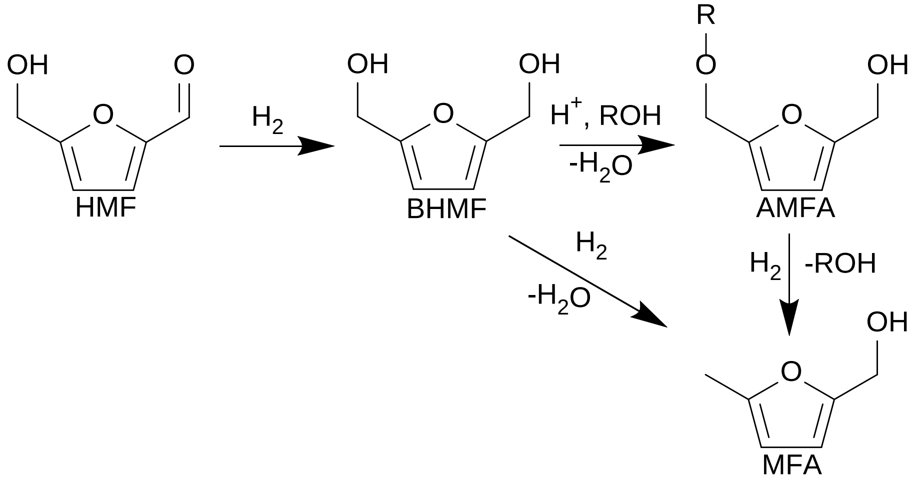
Figure 5. Hydrogenation of HMF to BHMF depending on time. Reaction condition: HMF (100 uL, 0.97 mmol), Ru(OH)$_x$/ZrO$_2$ (15 mg, 0.31 mol %), temperature 120 ℃, H$_2$ 15 bar, 1-butanol (3 mL). Results were analyzed by ^{1}H-NMR spectrum.

Table 1 presents the solvent effect on this reaction. The selectivity of BHMF was very high in various solvents. Especially in aliphatic alcohols (Entries 1, 2, 3, 5), HMF was hydrogenated exclusively to BHMF without any side reactions in more than 98 % yield. In case of 2-propanol and t-butanol (Entries 4, 6), complete convertion of HMF was not achieved and some byproducts such as 5-(alkoxymethyl) furfuryl alcohol (AMFA) and 5-methylfurfuryl alcohol (MFA) were produced (Scheme 2). Moreover, HMF was converted to BHMF in moderate yield in the presence of nonpolar solvent such as toluene (entry 7). These findings suggest that the catalytic ability for the hydrogenation of HMF to BHMF is related to the polarity of the solvents. In highly polar solvents, the C=O bond is more polarized, and H_2 absorbed on the Ru active site can easily attack to the C=O bond of HMF due to the strong interaction between C=O bond and the solvents.[35] Owing to these phenomena, linear alcohols which have relatively high polarity gave superior catalytic performance compared to branched alcohols. Among the solvents tested toluene showed the least conversion yield. It might be due to low solubility of HMF in toluene. However, the solvent effect on the reaction seems to be complex. The polarity of solvents might be one of the activity controlling factors for the hydrogenation of HMF.[36]

Table 3. Hydrogenation of HMF to BHMF Depending on Solvent

Entry	**Solvent (3 ml)**	**Conversion (%)**	**Selectivity (%)**		
			BHMF	**AMFA**	**MFA**
1	Methanol[a]	> 99	> 99	n.d.	Trace
2	Ethanol[a]	> 99	> 99	n.d.	n.d.
3	1-Propanol	> 99	> 99	n.d.	n.d.
4	2-Propanol	82	92	4	4
5	1-Butanol	> 99	> 99	n.d.	n.d.
6	t-Butanol	70	95	1	4
7	Toluene	55	96	n.d.	4

Reaction condition: HMF (100 uL, 0.97 mmol), $Ru(OH)_x/ZrO_2$ (15 mg, 0.31 mol %), temperature 120 ℃, H_2 15 bar, solvent (3 mL), 6 h. Results were analyzed by ^{1}H-NMR spectrum. [a]: H_2 30 bar.



Scheme 2. Possible side reaction pathways of HMF to other chemicals.

II. 2 Active site of Ru catalyst for hydrogenation of HMF to BHMF

The catalytic activity and selectivity for the hydrogenation of HMF to BHMF was compared for various Ru catalysts (Table 4). Among them, $Ru(OH)_x/ZrO_2$ showed the excellent catalytic activity than the conventional Ru catalysts under the similar reaction conditions (entries 2-6). Comparing the hydrogenation reaction of HMF with $Ru(OH)_x \cdot nH_2O$ to that of $RuCl_3 \cdot xH_2O$, Ru-OH active site seem to be more favorable than Ru-Cl because $Ru(OH)_x \cdot nH_2O$ gave higher yield and better selectivity for BHMF (entries 3 & 4). The results of entry 5 and 6 strongly support this hypothesis because RuO_2 hydrate has a crystal water structure, and it can hold more Ru-OH active sites than RuO_2 anhydrous. Commercially available heterogeneous Ru/C catalyst gave lower yield and selectivity for BHMF (entry 7), while no yield was obtained in the absence of the catalyst as well as with pristine ZrO_2 and base treated ZrO_2 under the same reaction conditions (entries 1, 9 & 10).

From the results with $Ru(OH)_x/ZrO_2$ and $Ru(OH)_x \cdot nH_2O$, it can be concluded that the solid support ZrO_2 enhanced the catalytic ability of

Ru-OH in HMF hydrogenation and the selectivity toward BHMF (entries 2 & 3). Based on the electronic metal-support interactions theory, catalytic performance of metal active site can be enhanced by the metal oxide support.[37] In this regard, the electron density of $Ru(OH)_x/ZrO_2$ flows from the Ru-O bond to the Zr-O bond. Owing to these phenomena, ZrO_2 supported Ru possesses higher Lewis acidity than the other Ru catalysts. Therefore, the H_2 molecules can be easily absorbed on the active site of Ru and then transferred to C=O bond for the hydrogenation of HMF to BHMF. The catalytic ability of calcined $Ru(OH)_x/ZrO_2$ for the hydrogenation reaction of HMF decreased significantly (entry 8), which also supports the aforementioned electronic effect in the $Ru(OH)_x/ZrO_2$ catalyst. It is due to the fact that the interface characteristics between ZrO_2 and the Ru active site (Ru-OH) might be altered by the calcination process. Recently, zirconia hydroxide was reported to have an excellent catalytic activity for the hydrogenation of HMF to BHMF.[38] However, this activity was only reported in ethanol solvent.

Table 4. The Results of Hydrogenation of HMF to BHMF using Various Catalysts

Entry	**Catalyst**	**Conversion (%)**	**BHMF Selectivity (%)**	**BHMF Yield (%)**
1	None	n.d.	n.d.	n.d.
2	$Ru(OH)_x/ZrO_2$	> 99	> 99	> 99
3	$Ru(OH)_x \cdot nH_2O$	72	80	58
4	$RuCl_3 \cdot xH_2O$	92	17	16
5	RuO_2 anhydrous	78	54	42
6	RuO_2 hydrate	57	81	46
7	Ru/C	79	53	42
8	$Ru(OH)_x/ZrO_2$[a]	43	>99	43
9	ZrO_2	6	n.d.	n.d.
10	NaOH treated ZrO_2	8	n.d.	n.d.

Reaction condition: HMF (100 uL, 0.97 mmol), $Ru(OH)_x/ZrO_2$ (15 mg, 0.31 mol %), Temperature 120 ℃, H_2 15 bar, 1-butanol (3 mL), 6 h. Results were analyzed by GC/MS. [a]: Calcination at 700 ℃.

II. 3 Recycling test of $Ru(OH)_x/ZrO_2$ in HMF hydrogenation reaction

The stability of heterogeneous catalyst is of considerable important in a continuous catalytic process. Therefore, reusability test of catalyst in the system was investigated. Figure 6 shows the result of recycling $Ru(OH)_x/ZrO_2$ catalyst for the HMF hydrogenation to BHMF. The catalyst was recovered, washed with acetone and 0.1 N NaOH solution, and reused after drying in air overnight. During five recycling, no significant loss of catalytic activity was observed and $Ru(OH)_x/ZrO_2$ catalyst gave almost the same conversion for HMF and selectivity for BHMF. At 5th recycling of $Ru(OH)_x/ZrO_2$ catalyst, the conversion of HMF was 91 % and the selectivity of BHMF is more than 99 %. The decrease of HMF conversion rate is due to the slight leaching of Ru in $Ru(OH)_x/ZrO_2$ catalyst.

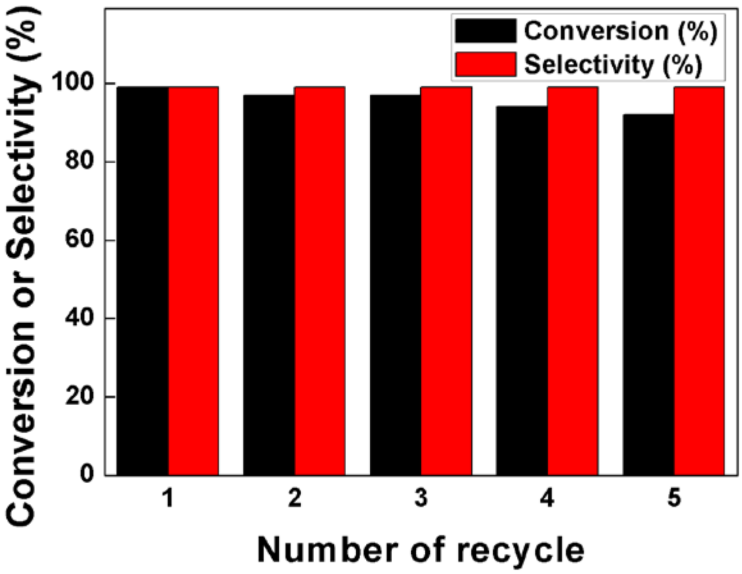


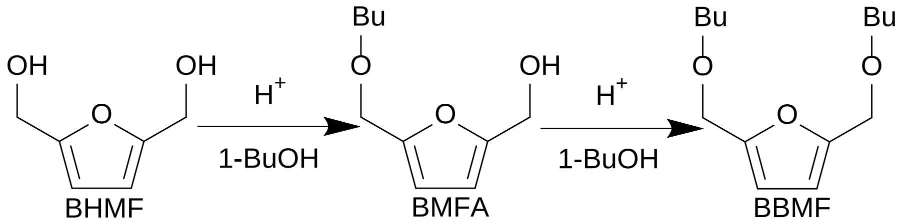
Figure 6. Catalyst recycle test in hydrogenation reaction of HMF to BHMF**.** Reaction condition: HMF (100 uL, 0.97 mmol), $Ru(OH)_x/ZrO_2$ (15 mg, 0.31 mol %), Temperature 120 ℃, H_2 15 bar, 1-butanol (3 mL), 6 h. Results were analyzed by ^{1}H-NMR spectrum.

III. Etherification of BHMF to BAMF Catalyzed by Amberlyst-15

Etherification of BHMF was performed in 1-butanol with Amberlyst-15 catalyst and the reaction conditions such as temperature, time, the amount amount of catalyst were optimized. Furthermore, the reactions in various n-alcohol solvents were conducted to obtain furfurylether with diverse alkoxy groups.

Scheme 3 shows the possible reaction steps. At first step, one of the hydroxyl groups of BHMF is etherificated with n-alcohol to give 5-(butoxymethyl)furfuryl alcohol (BMFA) and then the remaining hydroxyl group reacts to give the final product, 2,5-bis(butoxy-methyl)furan (BBMF).

Table 5 shows the results of the etherification of BHMF according to temperature. The yield of BBMF was increased from 64 % to 74 % as the reaction temperature was increased from 40 ℃ to 60 ℃. Further increase of the temperature to 80 °C had no effect on the yield of BBMF.



Scheme 3. Etherification of BHMF to BBMF.

Table 5. Etherification of BHMF to BBMF Depending on Temperature

Entry	**Temperature (℃)**	**Conversion (%)**	**BMFA Yield (%)**	**BBMF Yield (%)**
1	40	>99	11	64
2	50	>99	4	70
3	60	>99	2	74
4	80	>99	0	73

Reaction condition: BHMF (32 mg, 0.25 mmol), Amberlyst-15 (6.25 mg, 10 mol %), 1-butanol (1.5 mL), 10 h. Results were analyzed by GC.

The amount of catalyst was also optimized. As shown in Table 6, the BBMF yield was improved from 60 % to 74 % as the amount of catalyst was increased from 5 mol % to 10 mol %. With 20 mol % of catalyst, the BBMF yield was not improved further and the ratio of by-product to BBMF was slightly increased compared to the case with 10 mol % catalyst.

Table 6. Etherification of BHMF to BBMF Depending on Amount of Catalyst

Entry	**Amount of Catalyst (mg)**	**Conversion (%)**	**BMFA Yield (%)**	**BBMF Yield (%)**
1	3.125(5 mol %)	> 99	14	60
2	6.25(10 mol %)	> 99	2	74
3	12.5(20 mol %)	> 99	1	73

Reaction condition: BHMF (32 mg, 0.25 mmol), Temperature 60 ℃, 1-butanol (1.5 mL), 10 h. Results were analyzed by GC.

Figure 7 shows the reaction profile of etherification of BHMF to BAMF. The reaction was fast at the beginning, but slowed down as the time passes. In 1 h, most of BHMF was converted to BBMF with some amount of intermediate 5-(butoxymethyl)furfuryl alcohol (BMFA) and unidentified by-products, such as oligomers of BHMF[39] or ring opening products[16]. It is interesting to note that after 1 h, side reactions rarely occured further until the BMFA was transformed to BBMF in 10 h. These results might be related to higher polarity of BHMF than BMFA. BHMF has two hydroxymethyl groups, favorably interacting with the active site of Amberlyst-15, compare to BMFA. Because of that, BHMF formed the undesired products with intermediate product BMFA, which has relatively lower polarity owing to one hydroxymethyl group.[18]

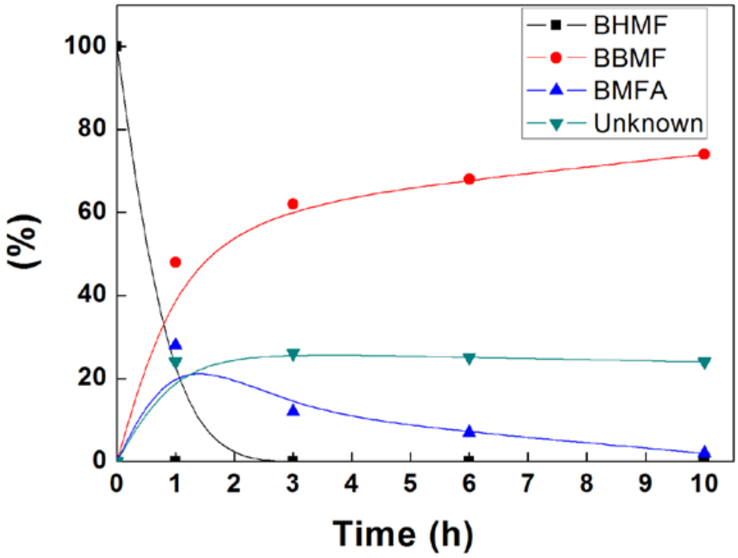


Figure 7. Etherification of BHMF to BBMF depending on time. Reaction condition: BHMF (32 mg, 0.25 mmol), Amberlyst-15 (6.25 mg, 10 mol %), Temperature 60 ℃ 1-butanol (1.5 mL). Results were analyzed by GC.

Table 7 shows the results of etherification reaction of BHMF in various alcohols to obtain furfurylethers with diverse alkyl chains. Reasonable yields of BAMF (70 %, 72 % and 74%) were obtained in ethanol, 1-propanol and 1-butanol, respectively. However, in methanol solvent, a relatively low BAMF yield (57 %) was obtained. These results were attributed to the high polarity of methanol. In methanol, BHMF and methanol favorably solvated the active site of Amberlyst-15 so that undesirable reactions might occur more easily than with other solvents. Because of these phenomena, Zeolite catalyst has been chosen to obtain high yield of BMMF.[29]

Table 7. Etherification of BHMF to BAMF Depending on Solvent

Entry	**Solvent (1.5 mL)**	**Conversion (%)**	**BAMF Yield (%)**
1	Methanol	> 99	57
2	Ethanol	> 99	70
3	1-Propanol	> 99	72
4	1-Butanol	> 99	74

Reaction condition: BHMF (32 mg, 0.25 mmol), Amberlyst-15 (6.25 mg, 10 mol %), temperature 60 ℃, 10 h. Results were analyzed by GC.

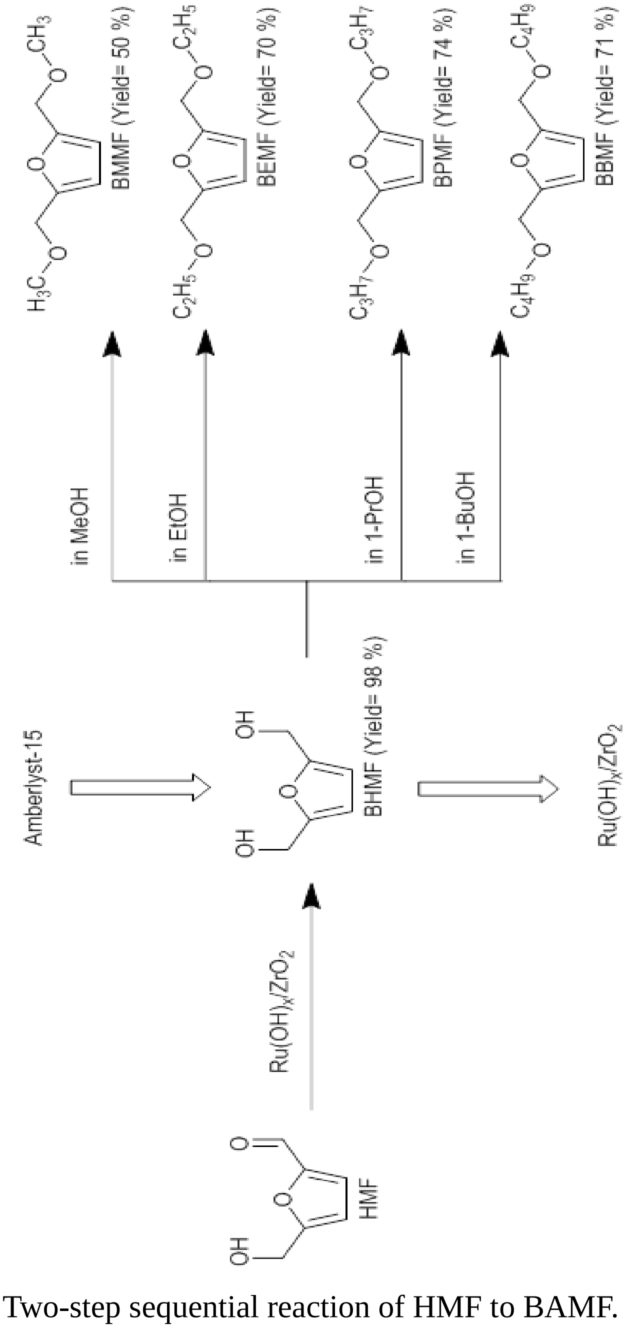
IV. Two-step Sequential Reaction of HMF to BAMF in various n-alcohol solvents

The aforementioned results encouraged us to investigate the two-step sequential reaction process: hydrogenation of HMF with $Ru(OH)_x/ZrO_2$ to obtain BHMF, followed by etherification of BHMF with Amberlyst-15 to get BAMF in various alcohol solvents under the similar conditions (Scheme 4). As shown in Table 8, BAMFs were obtained in 50%, 70%, 74% and 71% yields for methanol, ethanol, 1-propanol and 1-butanol, respectively.

Table 8. Two-step Sequential Reaction of HMF to BAMF

Entry	**Solvent (3 mL)**	**Conversion (%)**	**BAMF Yield (%)**
1	Methanol	> 99	50
2	Ethanol	> 99	70
3	1-Propanol	> 99	74
4	1-Butanol	> 99	71

Reaction condition: HMF (100 ul, 0.97 mmol), $Ru(OH)_x/ZrO_2$ (15 mg, 0.31 mol %), 120 ℃, 6 h (hydrogenation reaction) and Amberlyst-15 (24.25 mg, 10 mol %), 60 ℃, 10 h (etherification raction). Results were analyzed by GC.



Scheme 4. Two-step sequential reaction of HMF to BAMF.

IV. Conclusion

A two-step sequential reaction (hydrogenation followed by etherification) process from HMF to produce BAMF was developed. $Ru(OH)_x/ZrO_2$ catalyst revealed excellent performance for the hydrogenation reaction of HMF to BHMF in various n-alcohol solvents in more than 98 % yields. Due to the active sites of Ru-OH and the metal-support interaction between Ru and ZrO_2, $Ru(OH)_x/ZrO_2$ gave these outstanding results. The resulting solution of BHMF in various n-alcohols (methanol, ethanol, 1-propanol and 1-butanol) was then etherified by using Amberlyst-15. From the two-step sequential reactions, HMF was transformed to BAMF in more than 70 % yields, except for BMMF, which was obtained in 50 % yield. We proved that BAMF which contains various alkoxy groups could be produced by simple two-step sequential reaction.

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Abstract in Korean

목질계 바이오매스 유래 HMF를 변환시켜 연료를 얻는 것은 석유화학기반 의존도를 줄이기 위한 매우 중요한 연구 주제이다. 본 연구에서는 잠재적 바이오 디젤인, 2,5-비스(알콕시메틸)퓨란의 효율적인 생산 공정실험을 진행하였다. 우선, 수소첨가 반응을 위해 지르코니아에 담지된 불균일계 루테늄 촉매를 제작하였으며, 이를 이용하여 5-하이드록시메틸-2-퓨랄데하이드를 선택적으로 수소첨가 반응시켜 2,5-비스(하이드록시메틸)퓨란을 높은 수율로 얻을 수 있었다. 이 촉매는 최적화된 조건에서 HMF의 알데하이드 그룹만을 선택적으로 수소첨가반응하여 2,5-비스(하이드록시메틸)퓨란으로 변환시켰다. 이 반응은 다양한 노말-알코올 용매에서 잘 진행되었으며, 그 결과 다양한 알코올 용매에서 2,5-비스(하이드록시메틸)퓨란을 98 % 이상의 수율로 얻을 수 있었다. 또한 사용한 불균일계 루테늄 촉매는 큰 활성 저하 없이 5번 재사용이 가능하였다. 이어서, 수소첨가반응에 사용한 불균일계 루테늄 촉매를 간단한 여과를 통해 제거해 준 다음, 불균일계 산 촉매인 앰버리스트-15를 넣어주어 2,5-비스(하이드록시메틸)퓨란의 에터

형성반응을 진행하였다. 그 결과, 2,5-비스(메톡시메틸)퓨란의 경우 50 % 의 수율로 얻을 수 있었으며 에톡시, 프로폭시, 부톡시 그룹을 갖고 있는 2,5-비스(알콕시메틸)퓨란을 각각 70 % 이상의 수율로 얻을 수 있었다. 본 연구 결과들은 바이오매스를 전환하여 그린케미칼들을 얻는 공정 개발에 큰 도움이 될 것이라 기대한다.

주요어 : 바이오매스 전환, 수소첨가반응, 이써 형성 반응, 바이오디젤, 불균일계촉매, $Ru(OH)_x/ZrO_2$, 앰버리스트-15, 순차반응, 5-하이드록시메틸-2-퓨랄데하이드, 2,5-비스(하이드록시메틸)퓨란, 2,5-비스(알콕시메틸)퓨란

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Appendix

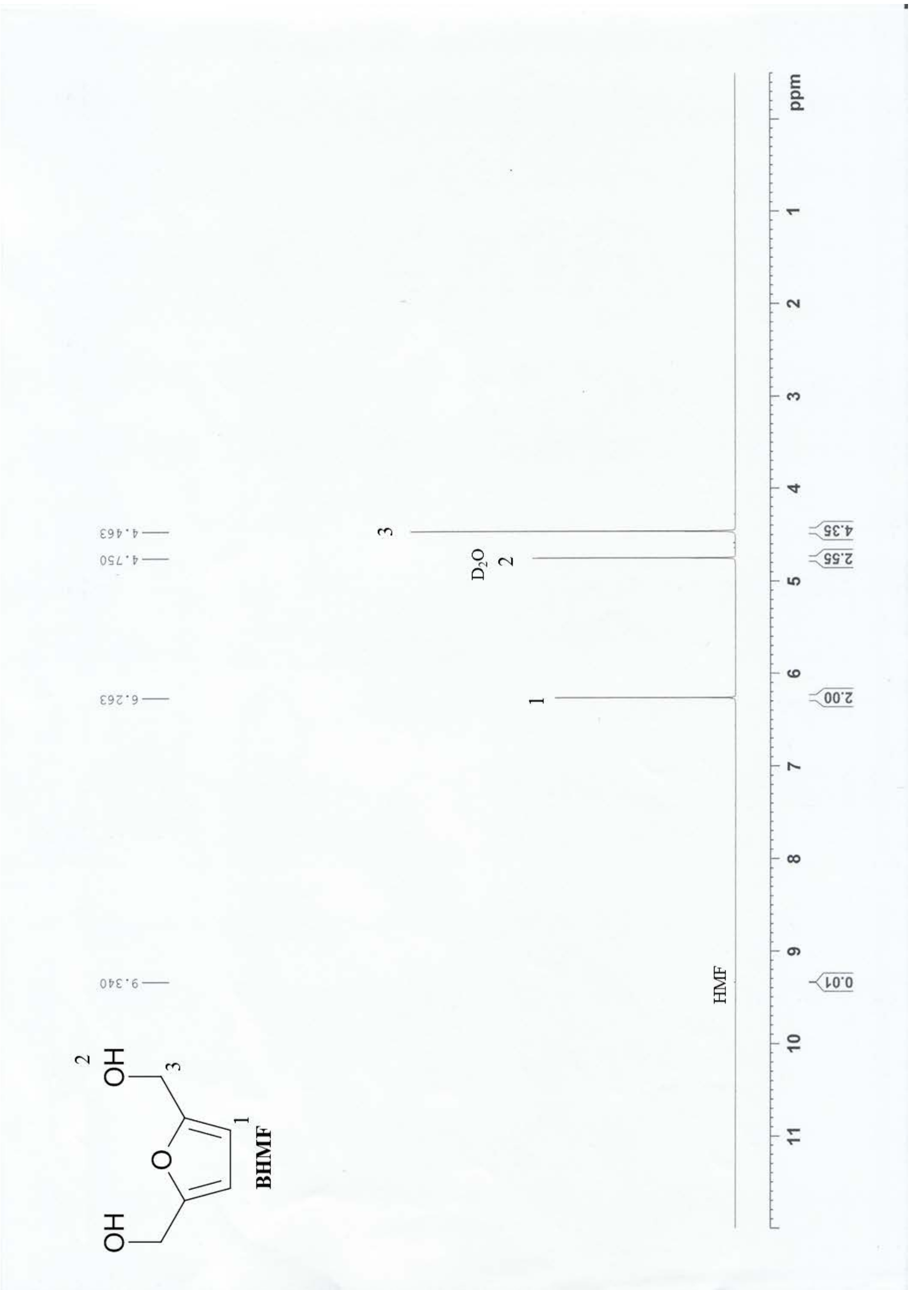

Figure A.1. Hydrogenation reaction mixture of HMF in 1-butanol analyzed by ^{1}H NMR.

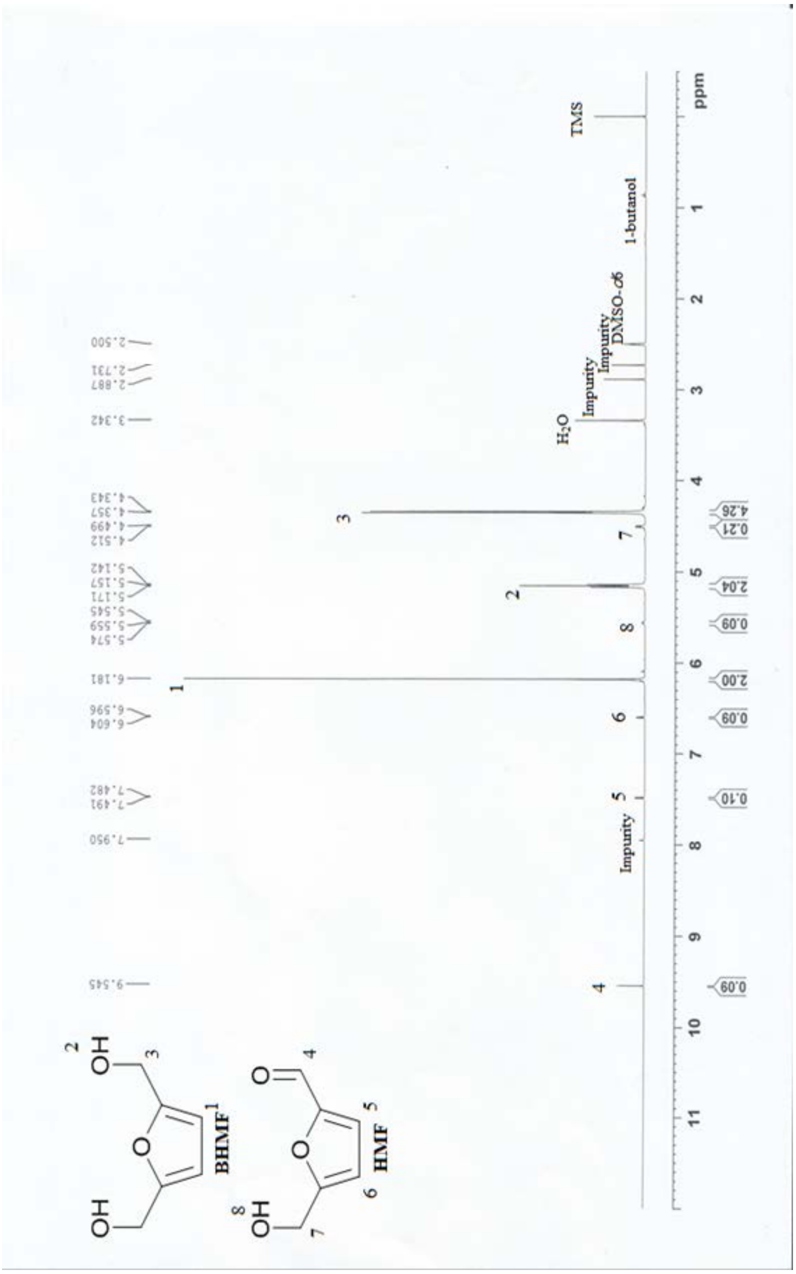

Figure A.2. Hydrogenation reaction mixture of HMF after 5times catalyst recycling analyzed by ^{1}H NMR (Impurity is DMF).

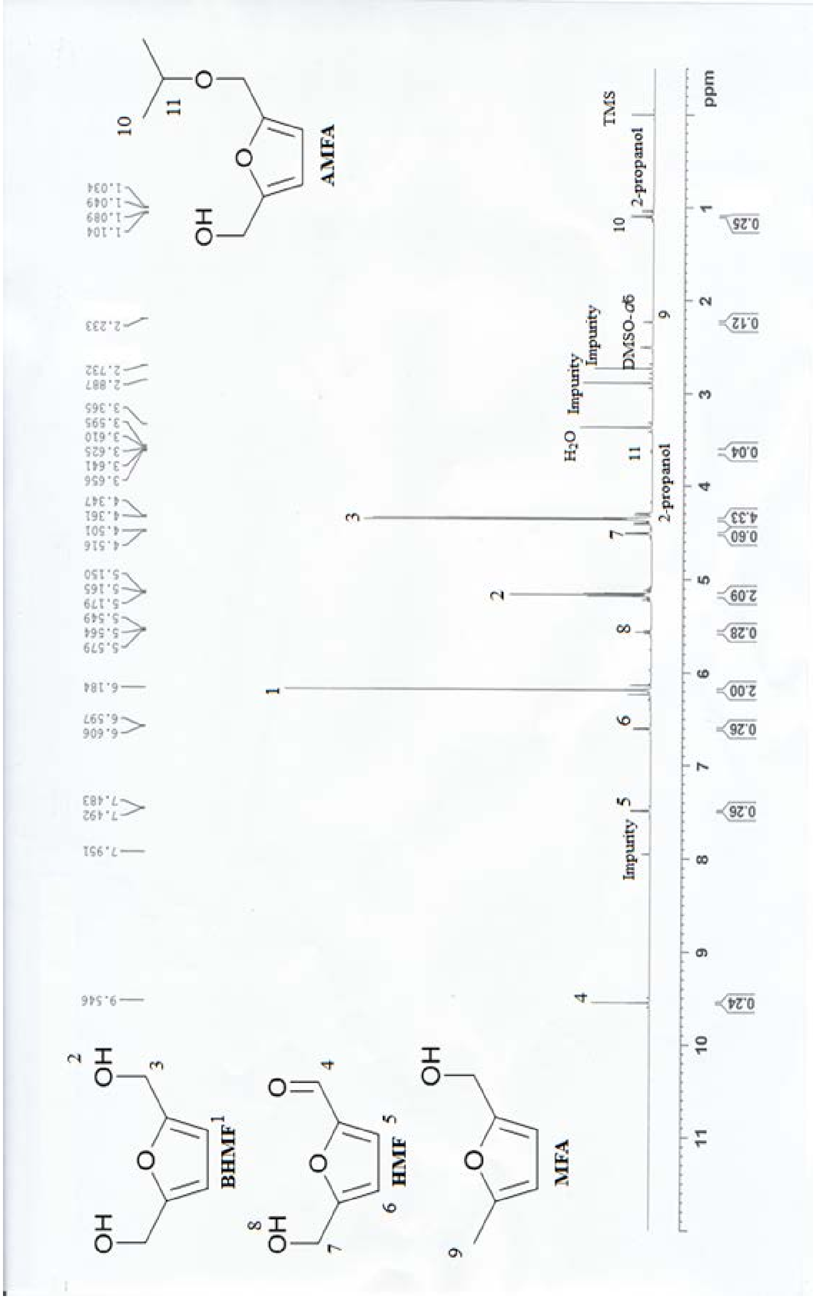

Figure A.3. Hydrogenation reaction mixture of HMF in 2- propanol analyzed by ^{1}H NMR (Impurity is DMF).

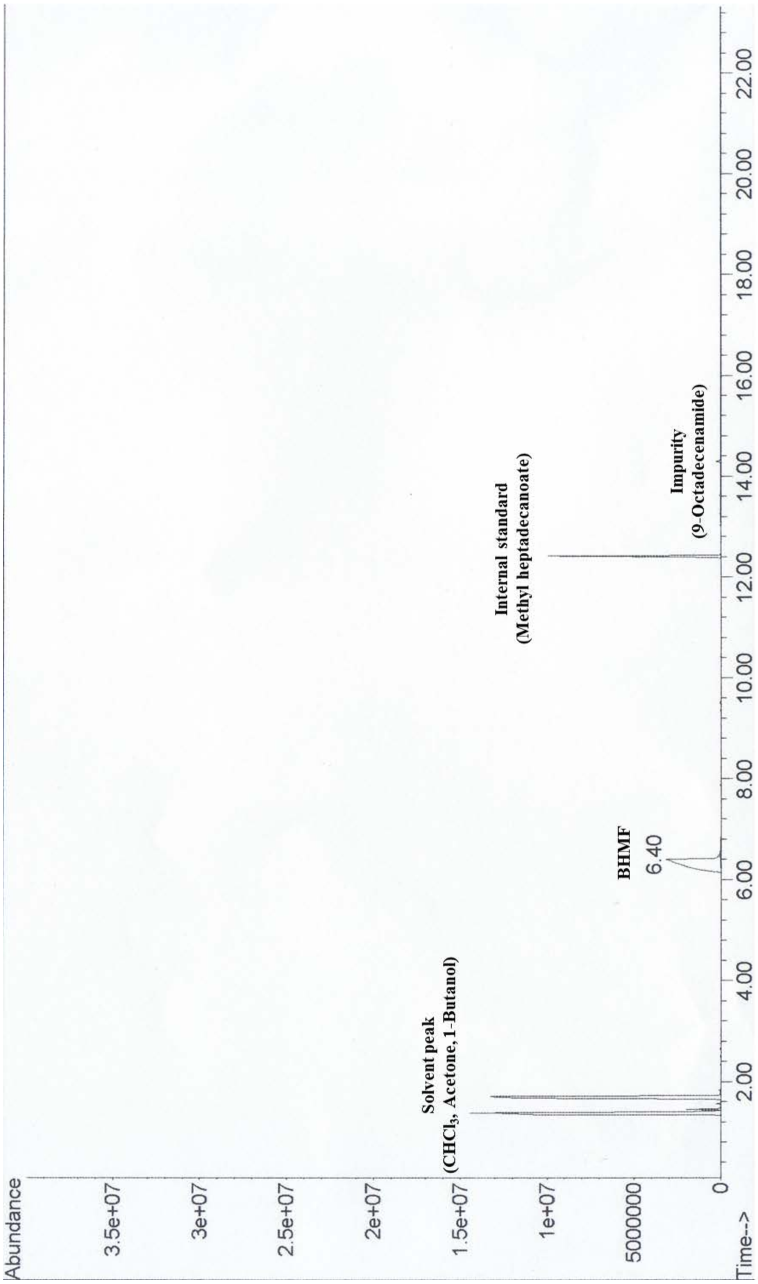

Figure A.4. Hydrogenation reaction mixture of HMF in 1-butanol analyzed by GC/MS.