

Catalytic hydrogenation of furfural and furfuryl alcohol to fuel additives and value-added chemicals

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Abstract: The selective hydrogenation of furfural and furfuryl alcohol at different temperatures has been studied using several catalysts. The effect of various reaction conditions (pressure, catalyst amount, and solvent) was studied. We have shown that Pd/TiO₂ catalysts can be very effective for the synthesis of 2-methylfuran at room temperature. Using octane as a solvent, the solvent effectiveness was investigated and showed actively high selectivity towards 2-methylfuran and furfuryl alcohol, but there were many byproducts that were still noticed. Although adding Ru to the Pd/TiO₂ catalyst contributed to reducing the catalytic activity, this addition improved the selectivity to 2-methylfuran and furfuryl alcohol with decreased byproduct formation. The Ru/Pd variation demonstrated a considerable influence on the selectivity. While adding a small amount of Ru (1 wt.%) shifted the selectivity towards 2-methylfuran and furfuryl alcohol, increment of the Ru ratio reduced the catalytic activity and revealed very poor selectivity towards 2-methylfuran.

Key words: Hydrogenation, catalysts, furfuryl alcohol, furfural, hydrogenolysis, 2-methylfuran

1. Introduction

Hydrogen is treated through the process of hydrogenation where a chemical reaction occurs between the hydrogen and the chemical compound. For biomass valuation, the performance by the H₂ activation has a vital role, since there is biorenewable feedstock that attains high oxygen concentrations as compared to petroleum-based feedstock.¹ The objective of the reactions of choice is to enhance the H/O and H/C ratio of these biomass-derived oxygenates with the help of hydrogenolysis or hydrogenation.²

Usually, metal catalysts are used for the hydrogenation reactions, like RANEY Ni or supported monometallic noble metal catalysts.¹ The superior catalysts are the supported bimetallic catalysts containing Pd:Pt and Pd:Ru for hydrogenation reactions, since their catalytic activities are excellent compared to the monometallic analogues based on the two-metal synergistic effect.¹ For nitrile to amine, alkadiene to alkene, and alkyne hydrogenation, Pd-based bimetallic catalysts are applied. For alkene hydrogenation, Rh-based bimetallic catalysts are applied. For aromatic hydrogenation, Pd:Pt supported on solid acids is applied.³⁻⁵ Apart from having effi-

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cient catalytic activities, the catalysts also have the ability to remove the monometallic catalysts' less favorable structures, for instance, by leaching and deactivation.

Recently, research studies on bimetallic catalysts' efficient use include aromatic hydrogenation by Pd:Pt supported on solid acids,³⁻⁵ like alkene hydrogenation using Rh-based bimetallic catalysts, such as Rh:Sn (rhodium takes the prize for ethene hydrogenation and the active base metal is nickel)⁶ alkyne hydrogenation; alkadiene to alkene by Pd-based bimetallic catalysts such as Pd:Au and Pd:Pt; nitrile hydrogenation to amines by Pd-based bimetallic catalysts; and hydrogenation of CO to methanol around Pd-based alloys like Pd:Li as catalysts. The current research studies have also indicated that metallic catalysts are useful for biorenewable hydrogenation or in various petroleum fields as substrates, since they can be used further. For instance, in a catalyst, two metals are mixed to bring forward the bimetallic or alloy catalysts' set development. For petroleum refineries, there has been development in the catalysts. For these refineries, bimetallic catalysts are essential, specifically when the gasoline octane number is increased. Furthermore, it helps control the hazardous tetraethyl lead replacement.⁷

2. Hydrogenation of carbohydrates

Compounds such as aldehydes and ketones integrate carbonyl functional groups (C=O) like glucose and xylose that are hydrogenated to create alcohol groups (O-H), so that sugar alcohols like sorbitol and xylitol can be attained by applying metallic catalysts. In specific vegetables and fruits, they are naturally available in minute amounts and, through glucose, mannose, and xylose hydrogenation, they can be formed commercially. Sugar alcohols are produced in a common manner in China. These include sorbitol and xylitol, where an annual increase in the amount is observed, which is at present over 700,000 t/year.⁸ China produces nearly 50% of the entire sugar alcohol total global production, which is why it seems vital to research this specific area.

Due to Ni leaching, RANEY Ni is subjected to deactivation. The alcohol is to be purified even though for the transformation it is applied as the commercial catalyst. To make sure that leaching does not occur, the catalyst includes another nonmetal.¹ The Ni leaching is not significant by the glucose to sorbitol by Ni:B alloy hydrogenation. As compared to the monometallic RANEY Ni catalyst, there is enhancement in the activity.⁹ Moderate activity has been observed for monometallic Ni/SiO₂ compared with Ni:B alloy supported on SiO₂. As compared to the RANEY Ni catalyst, the Ni:B alloy's activity is observed to be higher.

According to researchers, the improved activity is in the catalyst's amorphous phase. The alloy catalyst's higher activity is the result of integration of two aspects, which are the surface electronic state and the structural advantages. The bond distance of Ni:Ni is shorter for the amorphous catalyst and the Ni coordination number is lower when compared to the crystalline catalyst. This crystalline catalyst was created using amorphous material calcination. Furthermore, considering the Ni:B amorphous catalyst's high dispersion, the high activity level would be due to the effective structure and the metallic Ni and alloying B electronic interaction within the Ni:B alloy, making sure it is Ni electron-rich.⁹ The electrons' influence due to the presence of boron and the glucose absorption weakens at the carbonyl functional group (C=O). At Ni:B, at the catalyst surface, the hydrogen absorbed would be higher, which is why it can be stated that the hydrogenation activity is higher. For the glucose to sorbitol hydrogenation analysis, an additional amorphous Ni:P alloy catalyst was taken into account by Li et al.¹⁰ There was an increase in the catalyst's active surface area, which enhanced the catalytic activity using RANEY Ni during alloy development. The RANEY Ni:P alloy catalysis surface area was much lower as compared to the RANEY Ni catalyst. This occurred even after considering the earlier catalyst reported and the turnover frequency (0.4 s⁻¹) of the RANEY Ni:P alloy catalyst was higher. The Ni:P alloy formation on

the surface led to higher catalytic activity.¹⁰ Metals such as Mo, Cr, Fe, and Sn were used for the modification of the RANEY Ni catalyst and metalloids like B or P were not applied. The glucose hydrogenation was then assessed.¹¹

By loading Cr on the Ni catalyst, there was an increase in the glucose hydrogenation rate. The enhancement of glucose hydrogenation rate was mainly due to the integrated influence of the thermodynamically stable and compacted Ni atoms and low valent Cr^{3+} ions on the catalyst's surface (increase in the surface area led to the increase in space for interaction to take place on the catalyst surface using nucleophilic attack upon the carbon atom through the hydride ions). The Lewis acid sites were the Cr^{3+} ions, where the $\text{C}=\text{O}$ bonds were used to absorb the glucose molecules when the lone pair of electrons was donated on the oxygen. The $\text{C}=\text{O}$ bond is polarized and also the H_2 would be separated from the closest Ni atoms along with the $\text{C}=\text{O}$ bond's nucleophilic attack reducing the glucose aldehyde group. The catalytic process activities declined in the case of Cr associating with the Ni catalyst. As a part of this decrease, it can be stated that the organic material remnants adsorbed the active sites' poisoning.¹¹

Li et al.⁸ indicated that the glucose hydrogenation to sorbitol using Co:B alloy catalyst was Ni-based alloy catalyst replacement. Earlier research studies indicated that, compared to Co:B alloy catalysts, there is less activity in the monometallic Co catalysts. The influence of the alloy catalysts was successful in terms of reuse up to five times where the metal ions were not leached or deactivated. Activity levels were higher for the Ni- or Co-based alloy catalyst reactions; however, catalyst deactivation issues occurred due to the leaching of the metal within the reaction solution. This problem has not been resolved as of yet.^{12,13}

On the other hand, the used Ni catalyst alternatives are cobalt, platinum, palladium, rhodium, and ruthenium-based catalysts. For hydrogenation, the active catalysts used are the ruthenium-based catalysts. In this case, the ruthenium catalysts would not leach into the reaction medium.^{14–17} For the RANEY Ni catalysts, the most attractive alternative is ruthenium supported on carbon since higher activity is indicated by the Ru/C catalysts, they are stable, and they would not leach into the reaction solution.^{17,18} The Ru/ SiO_2 stability would be indicated by using glucose hydrogenation conditions through electron microscopy and in situ X-ray absorption spectroscopy.

Furthermore, it is observed that deactivation leads to Ru catalysis sintering. For a longer time period, the catalyst was deactivated with the reactions since the ruthenium nanoparticles in aqueous glucose solution stabilized against sintering for a short reaction time and the ruthenium nanoparticles initiated growth.^{17,19} Analysis has been done for various ruthenium-based catalysts applied for sugar hydrogenation. As compared to the glucose hydrogenation Ni analogues, the Ru-based alloy catalysts' stability and catalytic activities is much higher. The RANEY Ni catalyst and monometallic ruthenium catalysts have not been favored and the ruthenium-based amorphous alloy-based catalysts are used since they are similar to the ones prepared for Ni-based catalysts.²⁰

Initially, due to the amorphous nature, the disordering is long-range and the ordering is short-range. Secondly, the unsaturated ruthenium sites in the alloy are strongly coordinated. Finally, when the ruthenium is alloyed with a nonmetal like B or P in the case where they are electron-deficient, the ruthenium sites would be slightly electron-rich. The ruthenium sites' electron-rich state in both cases, along with the nonmetal sites' electron-deficient state, creates glucose adsorption as it is weaker and the hydrogen absorption becomes stable.

The influence of both Ni and Ru in Ru/NiO- TiO_2 catalysts on the D-glucose to D-sorbitol through the hydrogenation of sugar monosaccharides to sugar alcohols was successfully analyzed by Mishra et al.²¹ Much attention has been paid to this research. The acid hydrolysis of polysaccharides helped attain the sugars. The

two acid functionalities and the metal sites helped mix the two reactions into one (Figure 1). The reaction time declines due to this cascade, also reducing the raw material consumption, waste created, energy, and solvents. Various monometallic (Pd, Pt, Rh, and Ru) indicated support towards the catalysts with nanoparticles since they are tested for the one-reaction conversion of cellobiose (glucose dimer) to C6 alcohols. Furthermore, there was active Ru on poly (N-vinyl-2-pyrrolidone), which was quite selective for sorbitol. Nearly 26% decline was observed in the sorbitol selectivity since 3-b-D-glucopyranosyl-D-glucitol was created when the pH of the solution reached 7. In the case of basic conditions, where the pH equals 10, there was a 24% decline in the sorbitol selectivity since there was creation of another C6-alcohol and dideoxyhexitol.²²

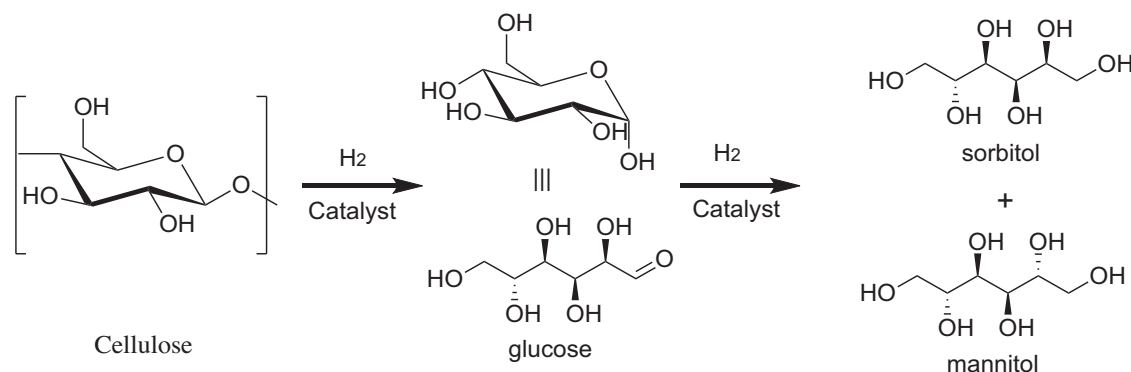


Figure 1. Cellulose hydrogenation into sugar alcohols within a single reaction.²³

In the present example, the needed durability of the supported metal catalyst has been presented. Fukuoka et al.²³ presented an alternative process where a single procedure of cellulose was converted to sugar alcohols (sorbitol and mannitol) with the help of acidic oxides since the monometallic catalysts were supported like the Pt/ γ -Al₂O₃ and Pt/SiO₂-Al₂O₃. According to them, the sugar alcohol yield was 30% at 190 °C in 24 h. Furthermore, analysis was done for the bifunctional catalysts for sugar alcohol's one-step synthesis. Examples include the use of a mixture of Ru/C and H₄SiW₁₂O₄₀,²⁴ Ru/C nanotubes,²⁵ reformed Ni/C nanofibers,²⁶ and Pt/C black.²⁷

There are various research studies conducted to enhance cellulose hydrolysis using support material modification. However, currently, no such research is being conducted. For hexitol formation using direct cellulose, the Ni bimetallic catalysts, as well as Pt, Pd, Ru, Rh, and Ir supported on mesoporous carbon (MC), have been applied.²⁸ For the case of one-pot cellulose conversion, the most effective results are for the complete hexitol yield for greater than 57% (1% Ir – 5% Ni/MC). On the other hand, keeping the same reaction conditions, there was consecutive 10% and 5% hexitol yield for the 5% Ni/MC and 1% Ir/MC.

Moreover, the two monometallic catalysts' physical mixture would be less active as compared to the bimetallic catalysts. Analysis of nickel bimetallic catalysts has been done as well, which indicates that for more than three uses of the same activity there is stability. Table 1 indicates the summarized information for the hydrogenation of glucose, monosaccharides, and polysaccharides using monometallic, bimetallic, and related catalysts. It is found that there are limited catalysts in the biomass reaction hydrogenation.

3. Alcohol and aldehyde hydrogenation

Sustainable energy sources and organic carbons are renewable biomasses. For ages, this has been considered as the primary industrial and consumer feedstock. The renewable biomass resources since the last century are

Table 1. Biomass is hydrogenated with the help of mono- and bimetallic catalysts.

Catalyst	Substrate	T (°C)	P (bar)	t (h)	Conv. (%)	Ref.
Ni:B/SiO ₂	Glucose	100	400	6	30	9
10% Ni/SiO ₂	Glucose	100	400	6	8	9
RANEY Ni	Glucose	120	40	2	38	29
Ni:B	Glucose	120	40	2	85	29
Co _{75.4} B _{24.6}	Glucose	120	40	6	89	13
Co _{73.7} Cr _{1.5} B _{24.8}	Glucose	120	40	6	91	13
Co _{74.8} Mo _{0.5} B _{24.7}	Glucose	120	40	6	92	13
Co _{74.7} W _{1.2} B _{24.1}	Glucose	120	40	6	97	13
Ru _{88.9} B _{11.1}	Glucose	80	40	2	95	30
Ru _{86.8} Cr _{2.6} B _{10.6}	Glucose	80	40	2	99	30
Ru _{86.7} Cr _{3.0} B _{10.3}	Glucose	80	40	2	100	30
Ru _{93.2} P _{6.8}	Maltose	90	20	2	98	31
Ru _{88.9} B _{11.1}	Maltose	90	20	2	45	31
1% Pt:5% Ni/MC	Cellulose	245	60	0.5	100	28
1% Pd:5% Ni/MC	Cellulose	245	60	0.5	100	28
1% Ru:5% Ni/MC	Cellulose	245	60	0.5	100	28
1% Rh:5% Ni/MC	Cellulose	245	60	0.5	100	28
1% Ir:5% Ni/MC	Cellulose	245	60	0.5	100	28
1% Ir/MC	Cellulose	245	60	0.5	90	28
5% Ni/MC	Cellulose	245	60	0.5	86	28
1% Ir/MC+5% Ni/MC ^a	Cellulose	245	60	0.5	92	28
2% Ir:5% Ni/MC	Cellulose	245	60	0.5	99.5	28
3% Ir:5% Ni/MC	Cellulose	245	60	0.5	100	28
4% Ir:4% Ni/MC	Cellulose	245	60	0.5	100	28
1% Ir/AC	Cellulose	245	60	0.5	66	28
5% Ni/AC	Cellulose	245	60	0.5	59	28
1% Ir:5% Ni/AC	Cellulose	245	60	0.5	79	28

Physical mixture, MC = mesoporous carbon , AC = activated carbon.

petroleum, natural gas, and coal. Nearly 95% of organic chemicals and 85% of energy are supplied by these. On the other hand, in the past 20 years, it has been found that human needs are not being met by petroleum. At the same time, it would be quite difficult to access natural gas resources.^{32–35} Keeping these points in mind, governments and consumers are interested in renewable products and power as this would positively influence the environment and the CO₂ emissions. There are various advantages related to the technology conversion and it is quite possible that biomass could again become civilization's central feed stock. This is specifically the case for bulk chemicals and transportation fuel renewable carbon sources.³⁶

Within the chemical industry, vital discussion relates to carbon-based compound manufacturing and petroleum. The oil supply has decreased and the cost has increased, which is why much focus is placed on alternatives in terms of biomass fuels, bulk chemicals, and solvents. Fatty acids, lignin, lipids, proteins, and carbohydrates are part of the biomass. Apart from oil and coal, since this is the easily available carbon source,

it is considered as the most attractive alternative feedstock.³⁷ In the past few years, biomass technology has gained vital interest and various research studies have been conducted within the context of application of various chemical production forms converting to natural resources.^{38,39} This is a vital aspect to be analyzed based on the energy requirements at present.

The needs have become quite diverse, which makes it necessary to reduce the fossil fuel resource dependency.⁴⁰ Among the vital intermediates are the furan derivatives, part of the primary renewable feedstock. This is mainly because their chemistry is rich and they can be formed easily from carbohydrates. Carbohydrates seem to be quite promising since they are the largest natural carbon source. There have been various recent developments within carbohydrate conversion into furan derivatives in the form of furfural and furfuryl alcohols.⁴⁰ Various products are created through furfural hydrogenation based on the catalyst being used as part of the vapor phase hydrogenation. For instance, the furfuryl alcohol is created along with 2-methylfuran and tetrahydrofurfuryl alcohol. For the liquid phase, there is need for high pressure, high temperature, and hydrogenation to produce the ring-opening products.⁴¹ A typical method to create furfuryl alcohol is indicated in Figure 2. It is a potential path for the reactions and the furfural. At present, for the manufacturing process, furfuryl alcohol is considered to be quite effective along with derivatives like the chemical intermediates for fragrances, vitamin C, and lysine manufacturing.⁴¹

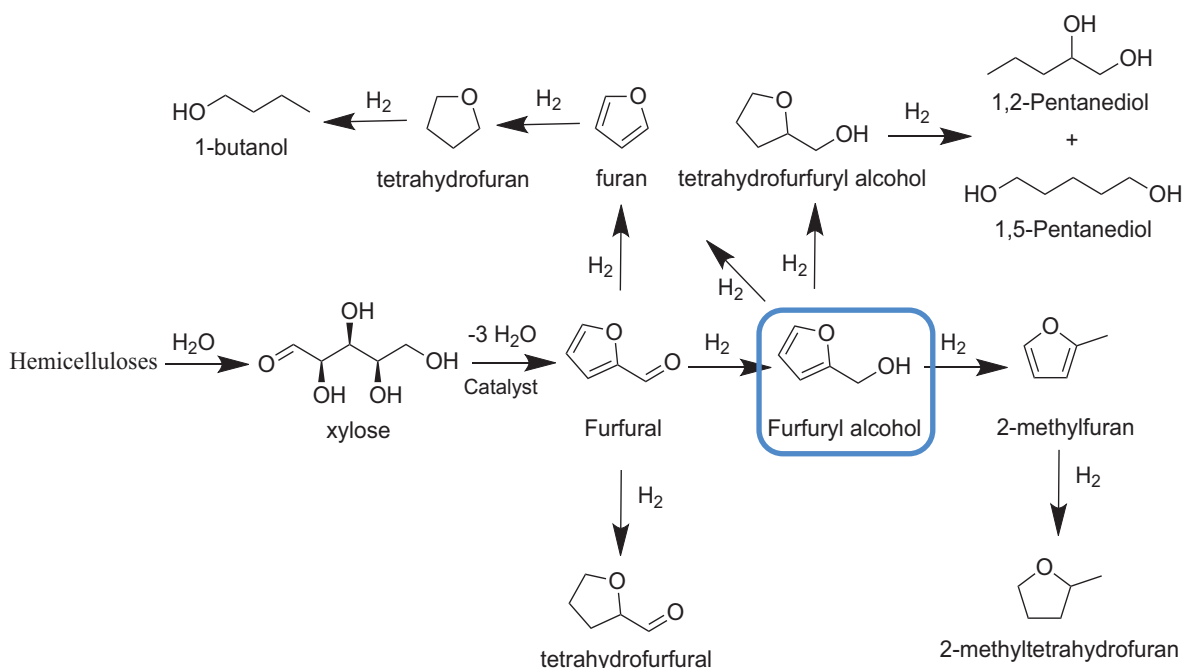


Figure 2. The furfuryl alcohol hydrogenation literature suggests the following reaction pathway.^{41–44}

These can be attained when green conditions are present, like green solvents, low temperature, and low pressure. Within the chemical industry, there are various applications carried out by compounds like furfural, furfuryl alcohol, and attractive biofuels like 2-methylfuran and 2-methyltetrahydrofuran.^{45–47} They are considered as vital initial manufacturing materials for resin production. In 1906, Padoa and Ponti wrote the first report regarding furfuryl alcohol formation as the primary product through the process of hydrogenation upon furfural. The furfural vapors were passed using hydrogen upon the nickel catalyst at 190 °C.^{48–50} Furfuryl

alcohol hydrogenolysis was analyzed in 1931 to the 1,2- and 1,5-pentandiol over copper chromite. The reaction took place during the liquid phase and conditions were kept at 11.5 h, 175 °C, and gauge pressure of 100 to 150 bar H₂. The catalyst used, 3 g, was in large amounts. There was only 70% yield and tetrahydrofurfuryl alcohol and methyltetrahydrofuran had 10% yield.⁵¹ Toxicity is the most important issue of the copper chromite catalysts as it leads to environmental pollution in a severe manner.

A new method was developed by Dunlop et al.⁵² for the transformation of furfural and furfuryl alcohol into a high-yielding tetrahydrofurfuryl alcohol through the hydrogenation within the availability of nickel-based catalysis. During the vapor phase, furfuryl alcohol hydrogenolysis was conducted. The temperature maintained was 120–150 °C with a gauge pressure of 2 to 3 bar.⁵³ Using catalytic hydrogenation, furfuryl alcohol can be altered to tetrahydrofurfuryl alcohol by applying supported catalysts like noble metals (Ni, Ru, Rh, Pd, and Pt). This would be in addition to the mixtures of the copper-supported catalyst. The most effective and active results were presented by catalysts supported by Ni, as they made use of 59% Ni/SiO₂-Al₂O₃ catalyst providing 99% yield. There was selectivity to tetrahydrofurfuryl alcohol, and the conversion was above 99%. Additionally, furfuryl alcohol hydrogenation was observed to be the most appropriate method for tetrahydrofurfuryl alcohol generation. There is common use of catalysts that are nickel-supported. As compared to nickel-supported catalysts, the group VIII (Pd, Rh, and Pt) supported catalysts are not efficient.⁵⁴ Furthermore, the liquid phase was used for the reaction in the group VIII supported catalysts. Also, there was need for pressure and temperature.^{53,54}

An autoclave was present for conducting the hydrogenation reactions for the transformation of furfuryl alcohol into tetrahydrofurfuryl alcohol using nickel-supported catalyst. When analyzing the reaction conditions, 1000 rpm would be the stirring rate, 180 °C would be the temperature, and gauge pressure of 40 bar would be the hydrogen pressure. There was a selectivity of over 98.3%, and the catalyst presence was 99.9% when the furfuryl alcohol was converted to tetrahydrofurfuryl alcohol within a time period of 3.5 h.⁵⁴ A slurry reactor was used to carry out the conversion of the liquid phase hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol over various ruthenium-supported catalysts (5% Ru/TiO₂, 5% Ru/Al₂O₃, and 5% Ru/C). The solvent should be 2-propanol, with temperature of 60 °C within 5% Ru/TiO₂ catalyst, and a hydrogen gauge pressure of 27 bar needs to be present to attain optimum hydrogenation of furfuryl alcohol conditions. There was nearly 95% conversion, and after 2 h, the tetrahydrofurfuryl alcohol selectivity was 97%.⁵⁵

Furfuryl alcohol gas phase hydrogenation was carried out by Sitthisa et al.⁵⁶ in 2011. The conditions maintained were 250 °C and a hydrogen pressure of reaction at 1 bar over Ni-Fe/SiO₂ bimetallic catalysts. Furthermore, the methylfuran and furan were the main products for the furfuryl alcohol hydrogenolysis over the monocatalyst Ni/SiO₂. On the other hand, the bimetallic catalyst, Fe, is enhanced, the furan yield decreases, and 2-methylfuran yield increases. For the case of furfuryl alcohol and hydrogenolysis of furfural, the products attained were similar. As compared to furfuryl alcohol, the vital change was the low furfural conversion to 2-methylfuran. Through furfuryl alcohol, it was possible to attain higher yield as compared to other furfural catalysts with 5 wt.% Ni:Fe/SiO₂. Significant change is observed with an increase of Fe/Ni ratio.⁵⁶ Furfuryl alcohol hydrogenation, as stated by Zhang et al.,³⁴ was conducted at 120 °C and hydrogen gauge pressure of 30–60 bar for 4 h in an aqueous phase over Ru-supported catalysts and MnOx-supported Pd, Pt, and Rh catalysts. Using the Pd/MnOx and Rh/MnOx catalysts, it was possible to attain high selectivity levels of furfuryl alcohol hydrogenation to tetrahydrofurfuryl alcohol hydrogenation.

However, for the Ru/MnOx catalysts, the 1,2-pentanediol indicated high selectivity. The furfuryl alcohol

polymerization was decreased and 1,2-pentanediol selectivity was increased through MnOx in the Ru/MnOx catalysts. At high temperature and low pressure, with water as the solvent, the 1,2-pentanediol formation increased. For instance, the 1,2-pentanediol yield was 42.1% over Ru/MnOx catalyst at 6 h, 150 °C, and gauge pressure of 15 bar. Lately, many studies have been conducted to investigate the selective hydrogenation of furfuryl alcohol to 2-methylfuran using palladium-supported catalysts at room temperature. These studies proved that Pd/TiO₂ catalysts have a powerful effect on the synthesis of 2-methylfuran under two conditions: at room temperature, and at a low pressure of hydrogen (1–3 bar).

Additionally, the effectiveness of several reaction conditions, which are pressure, catalyst amount, and solvent, was examined.⁴³ Some examples are present regarding furfuryl alcohol hydrogenation/hydrogenolysis through bimetallic or metal-metalloid alloys even though they can be utilized effectively through biomass valorization (Table 2). Renewable biomass research (celluloses and hemicelluloses) has indicated reaction development where the solid catalysts used for the process and included with other reactions for feedstock can be utilized effectively. Lignocellulosic biomass is the best pentose sugars source where there is no competition with food supply.

Table 2. Alloy catalysts used for the furfuryl alcohol hydrogenation/hydrogenolysis.

Catalyst	Phase	T (°C)	P (bar)	t (h)	Conv. (%)	Selec. (%)	Ref.
Cu ₂ Cr ₂ O ₅	Liquid	175	100–150	11.5	70 %	Pediols	51
59% Ni/SiO ₂ -Al ₂ O ₃	Vapor	120–150	20–30	1.5	>99%	THFA 99%	53, 54
Ni-Cu	Liquid	40	130	3	>99%	THFA 98.3%	53, 54
Ni-supported	Liquid	130	50	3.5	99%	THFA 97%	54
Ni-Fe/SiO ₂	Gas	250	1	0.1	80%	2-MF	56
5% Rh/C	Liquid	120	20	26 min	53%	THFA 57%	54
5% Pd/C	Liquid	120	20	1/3	29%	THFA 100%	54
5% Pd/C	Liquid	130	50	1.5	81%	THFA 79%	54
5% Pd/CaCO ₃	Liquid	120	20	1/4	19%	THFA 100%	54
5% Pd/Al ₂ O ₃	Liquid	120	20	13 min	17%	THFA 100%	54
5% Ru/TiO ₂	Liquid	60	27.2	2	95%	THFA 97%	34, 55
Ru/MnOx	Liquid	120	60	4	100%	THFA 79%	34
Ru/MnOx	Liquid	120	30	4	100%	THFA 79%	34
Ru/MgOx	Liquid	120	60	4	63%	THFA 74%	34
Pd/MnOx	Liquid	120	30	4	45%	THFA 100%	34
Rh/MnOx	Liquid	120	30	4	32%	THFA 96%	34
Ru/MgAlO ₄	Liquid	120	60	4	100%	THFA 84%	34
Ru/NaY	Liquid	120	60	4	100%	THFA 77%	34
Pd/TiO ₂	Liquid	25	1	3	65%	2MF 85%	43

THFA = Tetrahydrofurfuryl alcohol, 2-MF = 2-methylfuran, Pediols = 1,2- and 1,5-pentanediols.

Present research indicates that chemical transformation is quite promising.⁵⁷ Carbon-based compound manufacturing and petroleum are two aspects that require attention in the chemical industry. Oil costs are increasing and the supply is decreasing, creating a focus on the development of bulk chemicals, fuels, and solvents with biomass being the alternative. Fatty acids, lignin, lipids, proteins, and carbohydrates are included

as a part of biomass that acts as an alternative and attractive feedstock since it is widely available, like oil and coal. In the past few years, much interest has been paid to biomass technology and various benefits have been brought forward regarding the chemical production of natural sources.^{38,39} It is essential to meet the vast energy requirements through methods that replace fossil fuel resources.⁴⁰

To attain fuel from renewable feedstock sources, pretreatment through hydrolysis of the cellulosic and hemicellulosic components to produce sugar alcohols, such as sorbitol, xylitol, mannitol, lactitol, or maltitol, can be applied since they are converted to fuel components using chemical reactions (for example, furfural, furfuryl alcohol, 5-hydroxymethylfurfural, 2-methyl-furan, 2,5-dimethylfuran, and 2-methyltetrahydrofuran).^{58,59} In 1921,^{60,61} Quaker Oats Company found that furfural, on an industrial level, is a common chemical attained through lignocellulosic biomass.⁶² Using dehydration and hydrolysis, furfural can be created from xylan present in the lignocelluloses and then converted to various components.⁴⁵ On a commercial level, furfural is used for the upgrading of fuels like 2-methylfuran and 2-methyl-tetrahydrofuran^{63,64} using hydrogenation and acid/base catalyzed reactions (Figure 3).

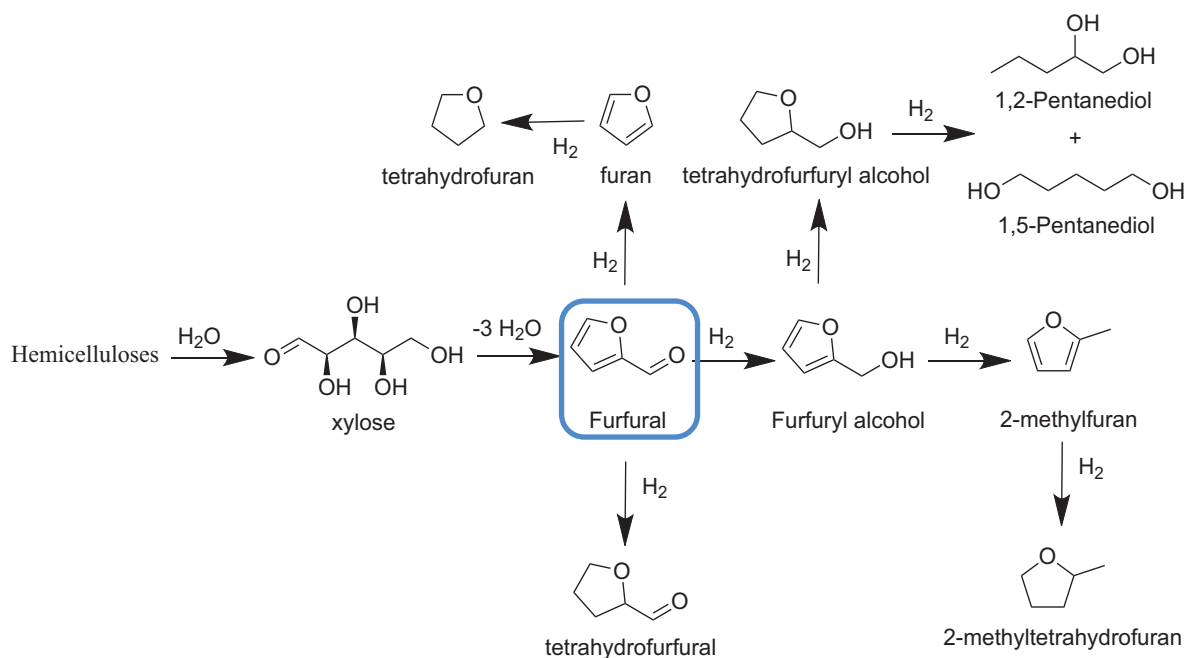


Figure 3. The furfural hydrogenation reaction pathway presented by the literature.^{1,57,61}

According to the literature, using catalytic hydrogenation at 95%, it is possible to convert furfural to 2-methylfuran. A high temperature (200–300 °C) would be maintained, with conditions of a H₂/furfural molar ratio of 5–8, using furfuryl alcohol as an intermediate with copper catalysts.⁶⁵ Hydrogenation of furfural has made furfuryl alcohol (yield, >96%) within the liquid phase over copper chromite (CuCr₂O₄•CuO). High hydrogen gauge pressure of 69–104 bar and temperature of 180 °C were maintained to carry out the reaction.⁶⁶ Similar activities are indicated by copper-chromite, RANEY copper, and Cu/Al₂O₃; however, stability and activeness are only observed in copper-chromite. Rapid deactivation of the catalyst occurs with regeneration at a temperature of 400 °C. For 2-methylfuran (yield, >95%), there was selective Cu₂Cr₂O₅/C.⁶⁷ At present, within the gas phase, there was 98% selectivity and 99% conversion for furfural hydrogenation making use of

a zeolite catalyst (Cu/Fe). This was at 252 °C and 1 bar pressure.⁶⁸ There was hydrogenation of the furfural over the Cu-based catalyst within the vapor phase and based on the same conditions.⁶⁹ However, within the gas phase, the 2-methylfuran can be attained using a rapid deactivation of the catalyst. This refers to the requirement of the liquid phase and lower temperature. A strong acid is now available after the hydrogenation of furfural into ethyl levulinate over copper-based catalysts, and subsequent ethanolysis of furfuryl alcohol took place. Furfuryl alcohol was created from furfural, which was then changed to ethyl levulinate by applying various solid acid catalysts like strong acids and zeolites.⁷⁰ Within the vapor phase, various furan products and 2-methylfuran were created from furfural hydrogenation. Additionally, 2-methyltetrahydrofuran with a 2-methylfuran yield over the Cu/Zn/Al/Ca/Na catalyst of 87% at 250 °C was also established.⁷¹ Similarly, 2-methylfuran at 90% and 2-methyltetrahydro-furan at 82% were attained after the commercial catalysts were mixed, like supercritical carbon dioxide (scCO₂) mediated continuous hydrogenation by Pd/C and copper chromite.

An analysis was carried out recently of furfural conversion in the vapor phase over the Ni/SiO₂ and Ni:Fe/SiO₂ catalysts within H₂ at 1 bar and in the 210–250 °C temperature range. 2-Methylfuran (38%) was formed using a bimetallic (Ni:Fe/SiO₂) catalyst, which was the major product. The primary products were the C–O hydrogenolysis of furfural, with furfuryl alcohol at 31% and furan at 32%, using hydrogenation and decarbonylation for the monometallic nickel catalyst. For this purpose, the Fe promoted C–O hydrogenolysis carried out at high temperature along with low temperature C=O hydrogenation present during the monometallic nickel catalyst decarbonylation activity suppression. The selectivity difference observed is that surface species are stable and this is less in the case of pure Ni than Ni:Fe.

Usually, furfuryl alcohol is created through the furfural hydrogenation applying H₂ gas on metal catalysts. It is mainly used for chemical manufacturing but can also be applied as a solvent.⁷² For furfural hydrogenation, usually a metal catalyst is applied since it can dissociate H₂. Therefore, hydrogenation is ensured. The choice of the catalyst support is according to the ability to manage and stabilize the metal particles where the active surface area is also increased. An aromatic furan ring is included with the furfural, which also has the ability to be hydrogenated. The carbonyl group, in comparison to the aldehydes, is also included.

The furan ring is aromatic with high stability, which is why it is recommended to use the carbonyl group hydrogenation. The ring can be saturated by the unsaturated C=C bonds, which are strongly associated with the metal catalyst. Hence, the use of metal catalyst determines the aromatic alcohol selectivity. The selectivity and hydrogenation activity are both affected by various metals' geometrics and electronic properties. This is done when the kind of absorption is intermediate.

Various research studies have analyzed the furfural hydrogenation process's differences for various metals like Cu, Ag, Au, Fe, Ru, Co, Ni, Pd, and Pt. The metal that has been analyzed the most as a furfural hydrogenation catalyst is copper. There are some reports where silver has also been analyzed, but gold has not been analyzed yet. As compared to copper group metals, other metals, like silver, are much more active. For the copper group metals, significant selectivity is observed in hydrogenation for the carbonyl group, making sure there is no reaction in the furan ring C=C double bonds. Furthermore, it was the copper catalyst that was found to be the selective one among all tested metal catalysts. Over the monometallic Cu/SiO₂ catalysts, furfuryl alcohol from furfural hydrogenation with 60% yield has been attained. Moreover, the C=O group of furfural has been hydrogenated by the monometallic silver catalysts with selectivity (79%) that is excellent over Ag/SiO₂. However, it is not as high as the monometallic copper catalyst. Also, a 91% yield of hydrogenation of furfural to furfuryl alcohol over Rh:Sn/SiO₂ was achieved.^{73–75}

With reference to furfural hydrogenation over Ni, Pd, and Pt metals (group VIII), analyses have been done for the liquid and vapor phases for various supports. All have indicated activity and selectivity.⁷⁵ For instance, in the liquid phase, at 100 °C, the Ni catalysts have a selectivity to furfuryl alcohol of over 95%.^{76,77} High selectivity is observed for the Pt catalysts doped with transition metal oxides, like selectivity to furfuryl alcohol over a Pt/TiO₂/SiO₂ catalyst that was nearly 94%, and over a Pt/ZrO₂/TiO₂ catalyst that was nearly 95%.⁷⁸ However, when other reactions arise, at >200 °C, the group VIII metals' alcohol selectivity declines. There was 25% furfuryl alcohol selectivity for nickel catalysts, like at 230 °C over a Ni/SiO₂ catalyst. Hence, it is also present in hydrogen excess.⁷⁹ Furfuryl alcohol selectivity was only 1% and at 230 °C over Pd/SiO₂ catalyst for the palladium catalysts like at 350 °C over Pd-Y catalysts,⁸⁰ and selectivity was 14%. For the group VIII metals, when high temperature is present, selectivity decreases, and this is because of the decarbonylation reactions and ring opening. Also, saturated alcohol was attained with the help of group VIII metal catalysts and the ring of furfural hydrogenation since the metal surface strongly reacted with the furan ring as compared to other copper group metals.⁸¹ Hence, for furfuryl alcohol from furfural for high selectivity, the favored catalysts are Cu and Ag. As compared to copper group metals, the group VIII metals have higher furfural hydrogenation essential activity due to the d-orbital included in the copper group reducing the bond strength.⁸² For furfural decarbonylation, analysis has been done on active metals like Pd,⁸³ Pt, and Ni.⁸⁴ By including an alloy formation or second metal, the palladium metal's high decarbonylation activity would be modified.⁸⁰ As compared to other catalysts, the Pd catalyst is more active, which is why the decarbonylation activity was lost and faster deactivation was present for Pd/Al₂O₃ catalyst.⁸² The carbon deposition is attributed to the deactivation mainly because of side reactions like decomposition and/or condensation of furfural. The Pd/Al₂O₃ loses activity in a quick manner when hydrogen is not available, but when the hydrogen pressure is increased, the activity is recovered.^{83,84}

The solvent's influence was analyzed by Hronec et al., along with the furfural reaction under the 30–80 bar hydrogen pressure and 160–175 °C reaction temperatures. Cyclopentanone is the main furfural hydrogenation product when water is the solvent and 96.5% over 5% Pt/C is the conversion at 30 bar hydrogen gauge pressure and 160 °C.⁸⁵ Recently, the selective hydrogenation of furfural at room temperature has been examined with a Pd/TiO₂ catalyst. Using octane as a solvent, the solvent effectiveness was investigated and it showed actively high selectivity towards 2-methylfuran and furfuryl alcohol. The addition of Ru to the Pd/TiO₂ catalyst decreased the catalytic activity but improved the selectivity towards 2-methylfuran and furfuryl alcohol with decreased byproduct formation (Table 3).

4. Conclusion

This review has discussed the composition of hemicellulose and the hydrolysis results of lignocellulosic biomass to get xylose as a feedstock for furfural production on an industrial scale. Regarding the use of a catalyst and an extraction solvent, a number of catalyzed process approaches for converting xylose were examined. Significant improvement has been carried out with the materials, syntheses, and their applications for dehydrating xylose to furfural aqueously and organically. Generally, more focus should be placed on extensively utilizing lignocellulosic biomass that contains an amount of hemicellulose. Xylose dehydration into furfural has activation difficulty and hence it is only achieved with strong conditions.

However, there is still an urgent need for processes that are in accordance with the principles of green chemistry and have higher furfural selectivity. A new and effective catalyst structure for converting furfuryl

Table 3. The alloy catalyst applied for furfural hydrogenation/ hydrogenolysis.

Catalyst	Phase	T (°C)	P (bar)	Yield (%)	Ref.
Cu-Al	Liquid	193	1	FA (90%)	65
Cu-Al	Liquid	253	1	2-MF (66%)	65
Cu ₂ Cr ₂ O ₅	Liquid	250	1	2-MF (87%)	65
CuCr ₂ O ₄ ?CuO	Liquid	<180	1	FA (96%)	66
Cu ₂ Cr ₂ O ₅ /C	Vapor	>200	1	2-MF (95%)	67
(Cu/Fe)	Gas	260	55	2-MF (98%)	68
Cu/Zn/Al/Ca/Na	Vapor	250	1	2-MF (87%)	71
Ni/SiO ₂	Vapor	210	1	FA (31%), F (32%)	56
Ni:Fe/SiO ₂	Vapor	250	1	2-MF (38%)	56
Cu/SiO ₂	Vapor	230–290	1	FA (60%)	73
Ag/SiO ₂ , Rh:Sn/SiO ₂	Gas	160–200	2	FA (67%), FA (91%)	75
Ni-Fe-B amorphous alloy	Liquid	100	10	FA (100%)	76, 77
Pt/TiO ₂ /SiO ₂	Liquid	150	1	FA (64%)	79
Pd/SiO ₂	Liquid	230	1	F (43%)	80
Pd:Cu/SiO ₂	Liquid	250	1	F (75%)	80
Pt/C,Pd/C,Ru/C	Liquid	160–175	30	CPON	85
5% Ru:Pd	Liquid	25	3	FA	43

F = Furan, FA = furfuryl alcohol, 2-MF = 2-methylfuran, 2-MTHF = 2-methyltetrahydrofuran, Pediols = 1,2- and 1,5-pentandiols, CPON = cyclopentanone.

alcohol and furfural into beneficial organic molecules (2-MF and FA) at room temperature and low hydrogen pressure has been highlighted. Finally, it has been concluded that the most influential catalyst for this reaction is Ru:Pd/TiO₂. This catalyst is considered as the best, transforming the compromise of FFR and selectivity into the required products, 2-MF and FA.

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