

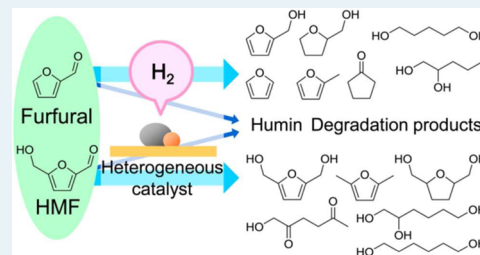
Catalytic Reduction of Biomass-Derived Furanic Compounds with Hydrogen

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ABSTRACT: Furfural and 5-hydroxymethylfurfural (HMF) are important platform chemicals in biorefinery. Reduction of furfural or HMF with H₂ over heterogeneous catalysts is the simplest way to convert the oxygen-rich compounds. However, the process can involve many types of reactions such as hydrogenation of the C=O bond, hydrogenation of the furan ring, C–O hydrogenolysis, rearrangement, C–C dissociation, and polymerization. Hydrogenation reactions are most studied in line with hydrogenations of other α,β -unsaturated aldehydes, and it becomes possible to produce each product selectively: furfuryl alcohol, tetrahydrofurfuryl alcohol, 2,5-bis(hydroxymethyl)furan, or 2,5-bis(hydroxymethyl)tetrahydrofuran. Total reduction of side substituents to give 2-methylfuran or 2,5-dimethylfuran is another well-known reaction. Rearrangement and C–O hydrogenolysis reactions have been recently investigated, and they can give useful products such as cyclopentanone, 1,5-pentanediol, and 1,6-hexanediol. Ongoing studies of the reaction mechanisms are also reviewed.

KEYWORDS: biorefinery, hydrogenation, hydrogenolysis, noble metal, catalyst modification



1. INTRODUCTION

The production of fuel and chemicals from biomass, which is known as the concept of biorefinery, has received much attention in view of the replacement of petroleum-based production.^{1–8} Since biomass is generally a very complex mixture of polymeric compounds with many kinds of components in smaller amounts, biorefinery usually uses platform chemicals that are produced and isolated from biomass via fermentation or chemical conversion.^{9–12} These platform chemicals are further converted into target molecules, playing a similar role to building block molecules in petroleum refinery such as ethylene; propylene; and benzene, toluene, and xylenes (BTX). In 2004, the U.S. Department of Energy (DOE) released a report of potential platform chemicals in biorefinery.¹³ From the initial list of over 300, the report selected the top 30 building block candidates and finally identified 12 sugar-derived platform chemicals. Since the release of the 2004 DOE report, a number of studies focusing on the biorefinery concept have been carried out. In 2010, Bozell and Petersen released a “revised” list of the new top 10 chemical opportunities from biorefinery carbohydrates.¹⁴ However, even today the production of chemicals from biomass is challenged by too-limited technologies of conversion methods of the platform chemicals to have a wide range of target products.

Furfural and 5-hydroxymethylfurfural (HMF) are produced from sugars via acid-catalyzed dehydration (Scheme 1).^{15–18} The raw material of furfural is xylose, which is a main component of hemicellulose. Xylulose with a furanose structure has been proposed as an intermediate in furfural formation, while another reaction route without a furanose intermediate has also been proposed.^{16,18} Production of furfural has already been

commercialized, and the world production is on the order of 10⁵ tons/year. The current commercial production uses agricultural waste such as corn cobs and oat husks as raw materials. Potential resources include black liquor in the pulp process, and coproduction processes of furfural and cellulosic sugars (or ethanol) from lignocellulose have been also proposed.¹⁵ Furfural was included in the 2010 biorefinery building block list¹⁴ and was also included in the 2004 DOE top 30 list,¹³ although it was omitted from the final top 12 list in 2004 because a static market for furfural had already been formed.

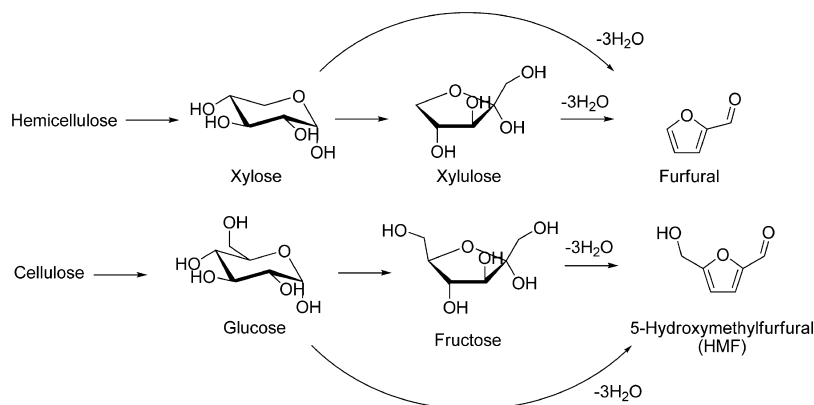
HMF is produced from hexoses. While fructose with a furanose structure is the immediate precursor of HMF, production of HMF from glucose or even cellulose is also possible.^{15,16,19} Because of the much higher boiling point of HMF compared with furfural, isolation of HMF from the reaction mixture is rather difficult. HMF was not included in the 2004 DOE list because of the lack of efficient conversion processes for HMF with high yield at that time, while 2,5-furandicarboxylic acid, an HMF derivative, was included in the 2004 DOE list.¹³ Recently, very much effort has been made to develop efficient processes of HMF production, and the potential of HMF as a platform chemical has been growing. Of course, the 2010 building block list included HMF,¹⁴ and any future list of biomass-derived platform chemicals will not miss HMF (and furfural). There are excellent reviews on the manufacture of furfural and HMF.^{20,21}

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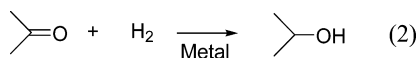
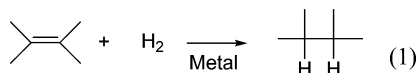
Scheme 1. Formation of Furfural and HMF



Furfural and HMF are highly oxidized organic molecules in comparison with most petrochemical products. In addition, furanic compounds are known to be toxic to many microorganisms.²² Therefore, the conversion of furfural or HMF usually involves catalytic reduction. Both furfural and HMF are multifunctionalized compounds, and many types of reaction can proceed in the catalytic conversions. In this paper, we summarize the potential reactions and products in the catalytic conversions with hydrogen. We focus only on the reactions of furfural, HMF, and their derivatives as the sole substrates using molecular hydrogen and heterogeneous catalysts. The coupling reactions of furfural and HMF with another substrate molecule are excluded for simplicity. Readers may find other reviews that cover all the fields of upgrading furfural or HMF;^{23–25} however, these reviews are best from the viewpoint of synthetic chemistry, and the detailed properties of furfural and HMF reduction, such as the nature of side reactions, are not well explained. This paper will help the future development of catalysts for any type of reductive conversion of furfural and HMF.

2. REACTIONS POTENTIALLY INVOLVED IN THE CONVERSIONS OF FURFURAL AND HMF

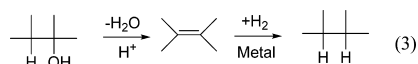
2.1. Hydrogenation. Hydrogenation is the most fundamental reaction in reductive conversions. Furfural and HMF possess both C=C and C=O bonds, both of which can be hydrogenated over proper catalysts (eqs 1 and 2). The products



of the hydrogenation of furfural are furfuryl alcohol (FOL), tetrahydrofurfural, and tetrahydrofurfuryl alcohol (THFA), and those in the hydrogenation of HMF are 2,5-bis(hydroxymethyl)furan (BHF), 5-hydroxymethyltetrahydrofurfural, and 2,5-bis(hydroxymethyl)tetrahydrofuran (BHTHF) (Scheme 2). Hydrogenation proceeds over the surface of metal catalysts.²⁶ The metal surface activates hydrogen molecules to form active hydrogen species, which attack the double bond of the substrate adsorbed on the catalyst surface. Typical active metals include noble metals, Cu, Ni, and Co. Generally, most catalysts can hydrogenate both C=C and C=O bonds. Control of the relative activity in C=O/C=C hydrogenation has been one

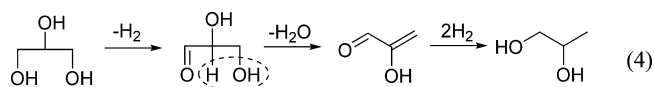
of the most important themes of the design of hydrogenation catalysts.^{27–29}

2.2. Dehydration and Indirect C–O Hydrogenolysis. Furfural and HMF are produced by dehydration (eq 3), and



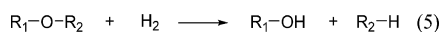
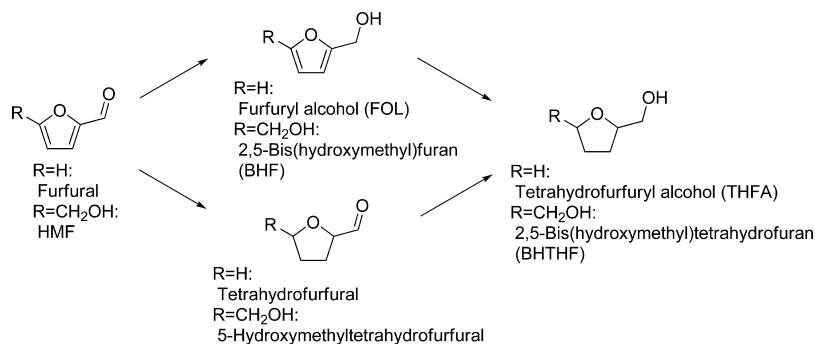
further dehydration does not proceed except under extremely severe conditions such as direct contact with concentrated sulfuric acid.³⁰ However, once they are hydrogenated, they become susceptible to dehydration over acid catalyst. The C=C double bonds produced by dehydration are readily hydrogenated to give saturated alkyl chains, considering that the reactants of dehydration are also produced by hydrogenation. The combination of dehydration and hydrogenation formally transforms a C–OH group to a C–H group and is considered as indirect hydrogenolysis of the C–O bond.¹⁰ This type of reaction has been most investigated for glycerol hydrogenolysis over the combination of acid and metal catalysts. The two-step indirect hydrogenolysis of glycerol produces 1,2-propanediol as the main product.^{31–36} However, in general it is difficult to obtain a high yield of a sole product from a polyfunctionalized substrate via two-step indirect hydrogenolysis because overhydrogenolysis can proceed at high conversions.

It should be noted that Cu-based catalysts without strong acids are very selective in the hydrogenolysis of glycerol to 1,2-propanediol.^{37–39} The selectivities are higher than those obtained with systems using a combination of acid and metal catalysts. This reaction is a variant of indirect hydrogenolysis, and the high selectivities are explained by the presence of a dehydrogenation step before the dehydration step. The aldehyde group produced by the dehydrogenation step activates C–H at the α -position and promotes the dehydration (eq 4).

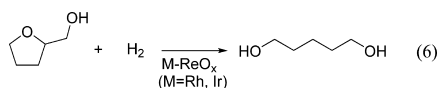


2.3. Other Types of C–O Hydrogenolysis. C–O hydrogenolysis of biomass-related oxygen-rich compounds has been more and more studied in recent years as the importance of biorefinery is growing.^{12,37,40,41} There are other types of C–O hydrogenolysis with a mechanism different from dehydration + hydrogenation. Hydrogenolysis of C–O bonds in ethers such as tetrahydrofuran requires the reaction in this category (eq 5).

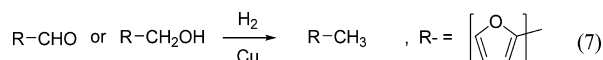
Scheme 2. Hydrogenation of Furfural and HMF



This type of reaction proceeds only over limited catalysts. One typical example is the hydrogenolysis over Rh or Ir catalysts modified with ReO_x, which we discovered recently.⁴² The systems selectively dissociate the C–O bond neighboring another –CH₂OH group in the substrate, enabling the conversion of tetrahydrofurfuryl alcohol to 1,5-pentanediol in high yield (eq 6).^{42–46}

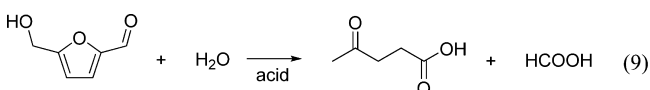
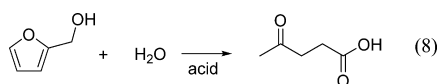


Another type of C–O hydrogenolysis is the Cu-catalyzed conversion of formyl or hydroxymethyl groups attached to a furan ring to methyl groups (eq 7). This reaction was discovered in the 1940s.⁴⁷ Both types of reactions (eqs 6 and 7) will be further explained in later sections.



Nonselective and non-acid-catalyzed C–O hydrogenolysis has also been pointed out but is little discussed in the literature.⁴⁸

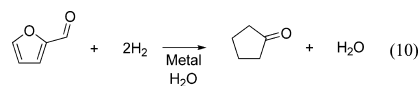
2.4. Rearrangement. The presence of rearrangement is characteristic of the reaction of furanic compounds. Two types of reactions of furfural derivatives involving rearrangement have been reported. One is the formation of levulinic acid (4-ketopentanoic acid) from FOL or HMF (eqs 8 and 9).



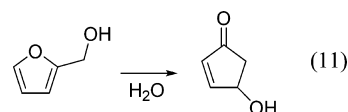
These reactions were discovered long ago⁴⁹ and are known to be catalyzed by strong acids. As the equations show, these reactions involve hydration. When alcohol solvent is used, the product becomes the corresponding ester of levulinic acid.⁵⁰ The proposed pathway of the formation of levulinic acid from HMF is shown in Scheme 3.⁴⁹ As a related reaction, conversion of HMF may be accompanied the formation of 1-hydroxy-2,5-hexanedione and the hydrogenated compound 1,2,5-hexanetriol in the presence of acid, noble metal, and H₂.^{51,52}

According to Scheme 3, 1,2,5-trioxo-3-hexene works as an intermediate of C5 compounds. Hydrogenation of this intermediate gives 1,2,5-trifunctionalized C6 compounds.

The other type of rearrangement reaction is the formation of cyclopentanone from furfural (eq 10), first reported by Hronec

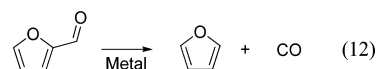


and Fulajtarová very recently.^{53,54} This reaction proceeds over metal catalysts under H₂ in diluted neutral aqueous solution. Xu and co-workers proposed that rearrangement of FOL to 4-hydroxycyclopent-2-en-1-one via the attack of H₂O at the 5-position is the key step in the formation of cyclopentanone (eq 11).⁵⁵

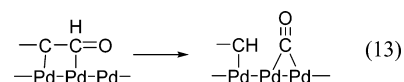


These reactions are side reactions for most purposes, except in the cases that levulinic acid derivatives or cyclopentanone derivatives are the target compounds.

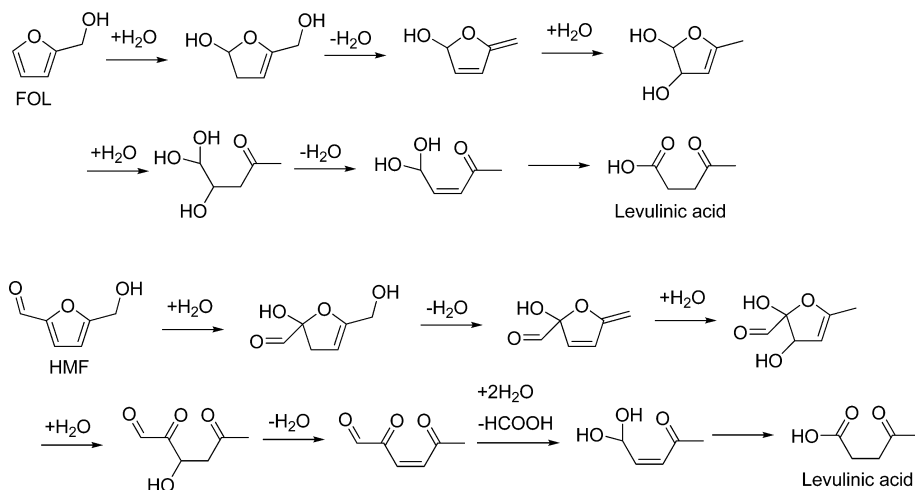
2.5. C–C Dissociation. C–C dissociations are usually regarded as side reactions in the conversion of furfural or HMF because there are other biomass-derived building block molecules with four or fewer carbon atoms, such as erythritol (C₄), succinic acid (C₄), glycerol (C₃), ethanol (C₂), and carbon monoxide in synthesis gas (C₁).^{13,14} C–C dissociations include several types of reactions. Decarbonylation (eq 12) is one



example that is frequently observed in the conversion of furfural over metal catalysts, particularly Pd-based ones.⁵⁶ Decarbonylation proceeds via the adsorbed species on the metal surface, where both the furan ring and the formyl group strongly interact with the metal atoms (eq 13).^{57,58} Decarbonylation



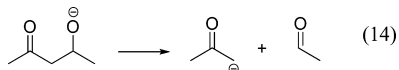
produces carbon monoxide. The adsorption of carbon monoxide on the metal surface is usually very strong: for example, removal of adsorbed CO on Pt/Al₂O₃ or Pt/SiO₂ by evacuation requires temperatures above 553 K, although the adsorption

Scheme 3. Proposed Mechanism of Levulinic Acid Formation from FOL or HMF⁴⁹

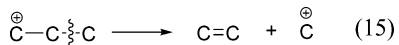
may be weakened by the modification of Pt surface.^{59,60} If decarbonylation takes place as a side reaction in the reduction at lower temperature, the catalyst may be deactivated.

Similarly to decarbonylation, if a carbon chain strongly interacts with the surface of a metal catalyst at multiple carbon atoms, C–C dissociation between these carbon atoms may occur.

Other types of C–C dissociation include reactions with anionic or cationic intermediates. A typical example with an anionic intermediate is the retro-aldol reaction, which decomposes α,γ -disubstituted substrates (eq 14). While important in



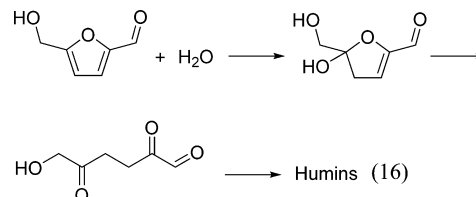
the conversion of sugars and sugar alcohols,^{61,62} retro-aldol reactions are hardly observed in the conversions of furfural and HMF since they do not have oxygen atoms bonded at positions γ to another oxygen atom. Decomposition of carbocations is well-known in the catalytic cracking process of heavier oils, featuring C–C dissociation at the position β to the cationic center (β -scission) (eq 15).⁶³ C–C dissociation via carbocations



generally gives complex mixtures of products because the produced carbocations might be decomposed further. Although rarely discussed in the literature of furfural or HMF conversions, this type of C–C dissociation might take place under severe conditions with strong acid.

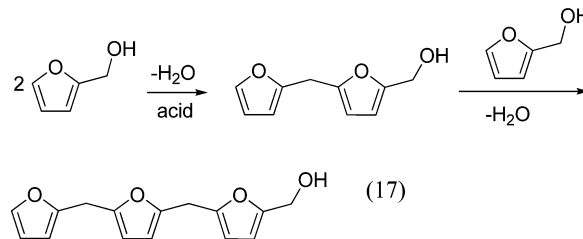
2.6. Polymerization/Oligomerization. Furanic compounds, including furfural and HMF themselves, are easily polymerized. The brown solid products formed by polymerization of furfural or HMF are called humins.⁶⁴ The formation of humins is one of the most severe problems in the production and storage of furfural and HMF. The partial hydrogenation products of furfural and HMF (FOL and BHF) are also very easy to polymerize, especially in acidic aqueous media.⁶⁵ The polymerization or oligomerization reaction is sometimes a considerable side reaction in the reductive conversion of furfural or HMF, especially when hydrogenation of the furan ring is slow.

The mechanism of polymerization of furanic compounds is quite complex, and there is much room for clarification. Horvat et al.⁴⁹ and later Lund and co-workers^{66,67} proposed that the key step in the formation of humins from HMF is the hydration of HMF to give 2,5-dioxo-6-hydroxyhexanal and that polymerization proceeds via aldol condensation (eq 16). HMF itself



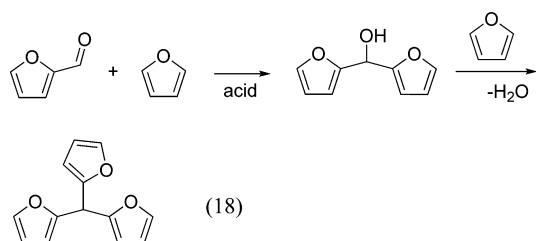
(like furfural) has no hydrogen atom α to the aldehyde group, and thus, aldol condensation of HMF alone is not possible. In contrast, 2,5-dioxo-6-hydroxyhexanal has many α -hydrogen atoms and can make polymer networks via addition or condensation with other 2,5-dioxo-6-hydroxyhexanal molecules and/or HMF.

In the case of FOL polymerization, an acid-catalyzed Friedel–Crafts-type reaction can link one furan ring to another ring with methylene groups at the 2- and 5-positions of the rings (eq 17).⁶⁵

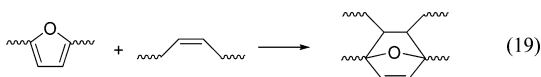


Similar acid-catalyzed additions of furfural or HMF with furan are also known,^{68,69} although these reactions are slower than Friedel–Crafts-type reactions (acid-catalyzed additions of alcohols). These aldehyde substrates produce a hydroxymethylene-bridged structure, and the OH group quickly reacts with another furan ring via a Friedel–Crafts-type reaction to give a trimer (eq 18).

The reaction shown in eq 17 produces chain polymers without large conjugation. In fact, however, polymerization of



FOL usually produces brown or black cross-linked polymers.⁶⁵ One possible mechanism for linking two chains is Diels–Alder cycloaddition of the furan ring (diene) and another double bond (dienophile) (eq 19).⁶⁵ Besides FOL, other furanic



compounds can undergo Diels–Alder cycloaddition. Therefore polymerization of furanic compounds other than FOL may involve Diels–Alder cycloaddition to some extent. The rate of Diels–Alder cycloaddition can be enhanced by the presence of an acid catalyst, which activates dienophile molecules.⁷⁰

As discussed above, most C–C bond formation reactions of furanic compounds are catalyzed by acid, which explains why reduction of furfural or HMF in acidic media is prone to suffer from oligomerization.

3. CATALYST PROPERTIES THAT AFFECT SELECTIVITIES

3.1. Adsorption Structure on the Catalyst Surface.

Hydrogenation of α,β -unsaturated aldehydes has been extensively studied over decades, where acrolein (propenal), crotonaldehyde (2-butenal), and citral (3,7-dimethyl-2,6-octadienal) have been frequently selected as model substrates.^{27,28} The accumulated studies, either experimental or theoretical, indicate that the catalytic performance, especially selectivity, is critically affected by the adsorption structures of the substrates.²⁹ Generally speaking, the atoms directly bonded to the surface metal atoms are more likely to react. For example, hydrogenation of acrolein over a Pt catalyst primarily gives propanal via C=C hydrogenation, as the Pt metal surface strongly adsorbs acrolein at the carbon atoms of the C=C bond (Figure 1a).⁷¹ The

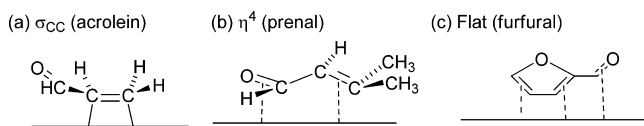


Figure 1. Typical adsorption modes of α,β -unsaturated aldehydes on the Pt(111) surface.

presence of substituents on the C=C bond can affect the adsorption geometry. In the cases of crotonaldehyde and prenal (3-methyl-2-butenal), the presence of methyl groups weakens the adsorption via steric hindrance and makes the adsorption of both C=C and C=O via the π -electrons preferable (Figure 1b).^{72,73} Hydrogenation of α,β -unsaturated aldehydes with larger molecule sizes shows generally higher selectivity for C=O hydrogenation than acrolein, which may be affected by the change in adsorption geometry.⁷¹ Furfural and HMF have two C=C bonds and one C=O bond in the same plane. Therefore, strong adsorption of the two C=C bonds on a flat metal surface orients the plane parallel to the metal surface

(Figure 1c).⁷⁴ In this case, the C=O bond is also located on the metal surface. This may be one reason for the fact that selective hydrogenation of furfural at the C=O bond is relatively easy in comparison with that of acrolein or crotonaldehyde, while the aromatic nature of the furan ring also reduces the C=C hydrogenation reactivity to improve the C=O hydrogenation selectivity.⁷⁵

The adsorption geometry may be also changed by temperature and surface coverage. Higher temperature or higher surface coverage leads to dissociation of weak bonds between the metal surface and the substrate and changes the adsorption mode to the one with only the strongest bond.²⁸ However, the effect of temperature or substrate concentration on the reactivity is not so straightforward because other factors are also affected simultaneously by these parameters.

Adsorptions on Pd and Cu metal surfaces as well as Pt have been most intensively investigated.^{57,76,77} The properties of Pt and Pd surfaces for the adsorption of α,β -unsaturated aldehydes are quite similar: they have a strong affinity for C=C double bonds, and the most stable adsorption mode of furfural is the flat configuration with the furan ring parallel to the metal surface.^{57,58} In contrast, Cu metal surfaces have very weak affinity for C=C bonds, and α,β -unsaturated aldehydes, including furfural, are known to be adsorbed on the Cu surface at the oxygen atom of the C=O bond (Figure 2).⁷⁶ Indeed,

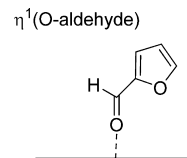


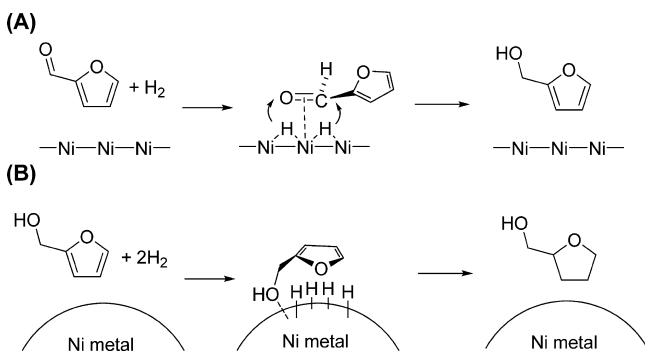
Figure 2. Adsorption of furfural on the Cu surface.

reduction of furfural over Cu catalysts usually converts only the substituent, producing FOL or 2-methylfuran (sections 4.1 and 4.4). Adsorption on the Ni surface has been less investigated, although Ni is an excellent hydrogenation catalyst. This is probably because the bare Ni metal surface is too highly reactive, leading to breaking of the adsorbed molecules.^{78–80} However, C–C or C–O bond dissociation is usually not so severe in the hydrogenation over Ni catalysts.^{51,81} Coadsorption of hydrogen may change the adsorption behavior. We have reported on the basis of a kinetic analysis that the adsorption of furfural on a Ni/SiO₂ catalyst is much stronger than that of FOL under the hydrogenation conditions, suggesting that furfural is adsorbed at the C=O group (Scheme 4A).⁸¹

The particle size effect has been also investigated to control the selectivity in hydrogenation of α,β -unsaturated aldehydes, and the effect is also partly explained by the change in adsorption geometry.²⁸ For example, larger Pt particles are more selective for unsaturated alcohols, and one of the reasons is that the flat Pt (111) surface can adsorb C=O and C=C bonds in the same plane simultaneously.²⁸ In the case of Ni/SiO₂, smaller Ni particles adsorb FOL more strongly and show higher turnover frequency (TOF; reaction rate per surface Ni atom) for FOL hydrogenation to THFA. The –CH₂OH group in the FOL molecule may assist in the adsorption onto the Ni metal surface, and the configuration of the –OH group outside the furan ring leads to easier adsorption onto rough surfaces, for example, the edge or corner of the particles⁸¹ (Scheme 4B).

The property of the adsorption of substrate on the catalyst can be changed by addition of a secondary metal, especially an

Scheme 4. Proposed Mechanisms for the Hydrogenation of (A) Furfural and (B) FOL over Ni/SiO₂⁸¹ (Reprinted with Permission from Wiley-VCH Verlag GmbH & Co.)



oxophilic metal such as Sn. The oxophilic metal promotes the adsorption of the substrate at the C=O bond. When the oxophilic metal (or metal cation) is located on the noble-metal surface, the hydrogen species formed on the noble metal is transferred to the C=O bond to achieve selective hydrogenation (Figure 3).^{82–84} The use of a secondary additive metal

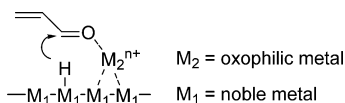
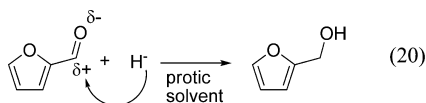


Figure 3. Adsorption and hydrogenation of an α,β -unsaturated aldehyde on a bimetallic catalyst.

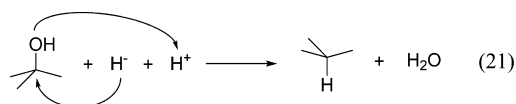
to noble-metal catalysts is a major approach to improve the C=O hydrogenation selectivity in the hydrogenation of α,β -unsaturated aldehydes.²⁷ The use of a reducible oxide support such as TiO₂ is another frequently applied approach.⁸⁵ Under reductive conditions, the oxide support is partially reduced and interacts strongly with the noble-metal surface [strong metal–support interaction (SMSI)]. The same mechanism as shown in Figure 3 can work for the catalysts with SMSI.⁸⁶

The effect of adsorption geometry on other reactions has also been mentioned. As discussed in section 2, C–C dissociation reactions and rearrangement reactions of the C5 ring may take place over metal catalysts. Both types of reactions affect the C–C bond, and the catalysts that strongly adsorb C=C bonds such as Pt- and Pd-based catalysts can promote these reactions.

3.2. Nature of the Hydrogen Species. The hydrogen molecule is also activated on the surface of catalysts by adsorption. In addition to the adsorption structure of the substrate, the nature of the active hydrogen species may affect the overall reductive conversions of substrates. As an extreme case, homogeneous reactions of unsaturated aldehydes (including furfural and HMF) with NaBH₄, where the active hydrogen species is hydride, produce unsaturated alcohols very selectively.⁸⁷ The hydride anion attacks the positively charged C atom in the C=O bond (eq 20). Similarly, more negatively charged hydrogen species can attack C=O bonds more selectively, and hydrogen species with a smaller charge can attack C=C bonds more selectively.^{88,89}

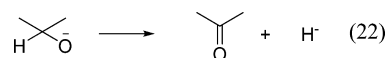


Hydride-like species have also been proposed as active species in direct C–O hydrogenolysis.⁴⁶ The mechanism is a variant of nucleophilic substitution, and hydride works as a nucleophile (eq 21). Ir–ReO_x/SiO₂ is a typical catalyst for



direct hydrogenolysis. This catalyst also shows very high performance for selective hydrogenation of unsaturated aldehydes to give α,β -unsaturated alcohols, which agrees with the formation of hydride-like active species.⁹⁰

The nature of the hydrogen species formed on the catalyst may also affect the dehydrogenation activity. Dehydrogenation of alcohols typically proceeds via hydride abstraction from adsorbed alcohol or alkoxide (eq 22).⁹¹ Catalysts that tend to form hydride-like species can be advantageous for the dehydrogenation reaction.



Because hydrogen species are formed on metal surfaces, the difference in catalytic performance of the active metal elements may be substantially derived from the difference in the nature of the hydrogen species. In spite of the above considerations, the nature of adsorbed hydrogen species is difficult to investigate because of the lack of effective observation methods for hydrogen species, while adsorbed substrates have been investigated in detail with various techniques such as IR spectroscopy.

3.3. Acid/Base Properties. As discussed in section 2, acid can catalyze many types of reactions such as dehydration, rearrangement to levulinic acid, and polymerization. Therefore, strongly acidic conditions or acidic supports are usually avoided in the selective conversions of furfural or HMF to one specific target product. However, once the furan ring is hydrogenated, acid-catalyzed side reactions are not so severe. C–O hydrogenolysis reactions, whether the mechanism is of the indirect type (dehydration + hydrogenation) or not, involve protons in the reaction mechanism. When the target compound is a product of C–O hydrogenolysis, control of the acidity is essential.

Basic conditions have been less investigated in the conversion of furfural or HMF without additional substrates, while coupling of furfural and ketones via base-catalyzed aldol condensation has been reported to produce larger molecules, which are expected to be the intermediates of bio-based kerosene and diesel fuel.^{92–95} Nonetheless, the use of weakly basic supports can be one approach to modify the catalyst performance if the basicity is not strong enough to catalyze undesirable side reactions such as aldol condensation.

4. PRODUCTS IN THE REDUCTION OF FURFURAL OR HMF AND THE REPORTED SYSTEMS

4.1. Furfuryl Alcohol (FOL) and 2,5-Bis(hydroxymethyl)furan (BHF). Hydrogenation of the C=O bond in furfural produces FOL. FOL is industrially used in the production of resins and other applications, and the hydrogenation of furfural to FOL has been operated for decades.⁹⁶ The commercial system uses a copper chromite catalyst. Because of the toxicity of copper chromite and the recent

Table 1. Selected Gas-Phase Systems for Hydrogenation of Furfural

catalyst	substrate	flow conditions	P_{tot} (MPa)	T (K)	conv. (%)	product ^a (selectivity (%))	ref
Hydrogenation of the C=O Bond							
Cu–Cr	furfural	cat. 0.3 g	0.1	533	53	FOL (98)	56
Cu/MgO	furfural	H ₂ /furfural = 2.5, GHSV 0.05 mol h ⁻¹ g _{cat} ⁻¹	0.1	453	98	FOL (98)	97
Cu–Ca/SiO ₂	furfural	H ₂ /furfural = 5, LHSV 0.33 mL h ⁻¹ mL _{cat} ⁻¹	0.1	403	100	FOL (99)	98
CuLa/MCM-41	furfural	H ₂ /furfural = 5, GHSV 0.087 mol h ⁻¹ g _{cat} ⁻¹	0.1	413	98	FOL (>99)	99
Cu–MgO	furfural	H ₂ /furfural = 2.5, GHSV 0.05 mol h ⁻¹ g _{cat} ⁻¹	0.1	453	98	FOL (98)	100
Cu–Cr/TiO ₂	furfural	H ₂ /furfural = 3, GHSV 0.04 mol h ⁻¹ g _{cat} ⁻¹	0.1	413	90	FOL (88)	101
Pt/TiO ₂ –V ₂ O ₅ –SiO ₂	furfural	H ₂ /furfural = 2, LHSV 2 g h ⁻¹ g _{cat} ⁻¹	0.1	423	87	FOL (91)	102
Total Hydrogenation							
NiO/SiO ₂	furfural	cat. 0.3 g	0.1	473	15	THFA (>99)	56
Ni/SiO ₂	furfural	H ₂ /furfural/N ₂ = 36/1/72, GHSV 1.1 mol h ⁻¹ g _{cat} ⁻¹	0.1	413	>99	THFA (94)	81

^aFOL, furfuryl alcohol; THFA, tetrahydrofurfuryl alcohol.

Table 2. Selected Liquid-Phase Systems for Hydrogenation of Furfural and HMF

catalyst	substrate	solvent	substrate/solvent/catalyst (g)	P_{H_2} (MPa)	T (K)	t (h)	conv. (%)	product ^a (selectivity (%))	ref
Hydrogenation of C=O Bond									
Cu–Zn–Cr–Zr oxide	furfural	iPrOH	14/88/1.5	2	443	3.5	>99	FOL (96)	103
Raney Ni–CuPMo ₁₂	furfural	EtOH	12/8/0.5	2	353	1	98	FOL (99)	104
Co–Mo–B alloy	furfural	EtOH	12/71/2	1	373	3	>99	FOL (nearly 100)	105
Pt–Sn/SiO ₂	furfural	iPrOH	2.3/40/0.25	1	373	8	90	FOL (98)	106
Ni–Ce–B alloy	furfural	EtOH	12/24/1	1	353	3	97	FOL (almost 100)	107
Ni–Fe–B alloy	furfural	EtOH	12/24/1	1	373	4	>99	FOL (>99)	108
Ir–ReO _x /SiO ₂	furfural	water	0.3/3/0.05	0.8	303	6	>99	FOL (>99)	90
Ir–ReO _x /SiO ₂	HMF	water	0.38/3/0.05	0.8	303	6	>99	BHF (>99)	90
PVP–NiB	furfural	EtOH	5.8/59/0.2	1.8	353	3	59	FOL (96)	109
Ni–Sn/TiO ₂	furfural	iPrOH	0.1/2.4/0.05	3	383	1.25	>99	FOL (>99)	110
Cu–Fe oxide	furfural	octane	2.4/3.5/0.2	9	433	5	91	FOL (98)	111
Au/Al ₂ O ₃	HMF	water	0.5/1.5/0.01	6.5	393	2	>96	BHF (>96)	112
Total Hydrogenation									
Raney Ni–Al(OH) ₃	furfural	iPrOH	0.1/2.4/0.05	3	383	1.25	>99	THFA (>99)	110
Raney Ni	HMF	MeOH	50/1200/38	0.48	333	4	>95	BHTHF (>99)	120
Ni–Pd/SiO ₂	furfural	water	0.48/9.5/0.1	8	313	2	99	THFA (96)	87
Ni–Pd/SiO ₂	HMF	water	0.63/9.4/0.1	8	313	2	99	BHTHF (96)	87
Ru/CeO ₂	HMF	1-butanol/water (2:1)	1.2/24/0.2	1.8	403	12	>99	BHTHF (91)	113
RuO ₂	furfural	MeOH	26/55/2	4	393	1	>99	THFA (76)	121

^aHMF, 5-hydroxymethylfurfural; FOL, furfuryl alcohol; THFA, tetrahydrofurfuryl alcohol; BHF, 2,5-bis(hydroxymethyl)furan; BHTHF, 2,5-bis(hydroxymethyl)tetrahydrofuran.

development of selective hydrogenation catalysts for α,β -unsaturated aldehydes, a number of catalytic systems for selective hydrogenation of furfural to FOL have been recently reported (Tables 1 and 2).^{56,90,97–112} Very high selectivities (>95%) have been obtained in a number of systems in both the gas and liquid phases. Copper catalysts have been most used for gas-phase hydrogenation of furfural to FOL. Alcohol solvents are generally used in the liquid-phase hydrogenation because the rearrangement side reactions proceed more rapidly in water.¹¹³

The product obtained from HMF is BHF, which can be used in the manufacture of polyurethane foams.¹¹² Although HMF hydrogenation has been less investigated than furfural hydrogenation, liquid-phase systems for furfural hydrogenation to FOL are expected to be applicable to HMF hydrogenation. Gas-phase hydrogenation of HMF is difficult because of the very high boiling point of HMF.

Liquid-phase selective hydrogenations of the C=O bond have been studied mostly with catalysts with two or more

components. As mentioned in section 3.1, the combination of an active metal and an oxophilic metal, which adsorb hydrogen and the substrate, respectively, is effective, and the two metals should closely interact. Therefore, revealing the interaction between the components is a main subject in catalyst characterization. Traditional characterization methods are adsorption studies using CO or small model substrates as probe molecules.²⁸ The adsorption amount, adsorption strength (determined by temperature-programmed desorption), and vibrational frequencies of adsorbed molecules are measured and discussed. Extended X-ray absorption fine structure (EXAFS) analysis has recently become a powerful tool to characterize multicomponent catalysts because it can directly detect the chemical bonds between the components. We have characterized an Ir–ReO_x/SiO₂ (Re/Ir = 1) catalyst, which shows excellent performance for selective hydrogenation under exceptionally mild conditions (Table 2).^{114–116} The characterization used various techniques. After reduction, the presence of Ir metal particles with a size of ~2 nm was confirmed by

X-ray diffraction (XRD) and transmission electron microscopy (TEM). All of the Ir species were reduced to the metal state, as shown by Ir L₃-edge XAFS [both EXAFS and X-ray absorption near-edge structure (XANES)]. The Re species were partially reduced to low-valent Re oxides (ReO_x), as shown by temperature-programmed reduction (TPR), XPS, and Re L₃-edge XAFS. To see the interaction between Ir metal and ReO_x species, CO adsorption and curve fitting of Re L₃-edge EXAFS were conducted. The amount of CO adsorption was significantly lower than the value expected from the particle size. Curve fitting of Re L₃-edge EXAFS showed the presence of Re–metal bonds with a coordination number of ~6 as well as Re–O bonds. We concluded that the Ir metal particles were covered with ReO_x clusters via direct Ir–Re bonds.

It is very difficult to distinguish between Ir and Re as a backscattering atom in EXAFS. The catalysts with components in different rows in the periodic table are more definitively characterized with EXAFS. We have characterized Rh–ReO_x/SiO₂ in a similar way as for Ir–ReO_x/SiO₂.^{117,118} The data obtained from techniques other than EXAFS were similar to those in the case of Ir–ReO_x/SiO₂: Rh metal particles and partially reduced ReO_x species were present on reduced Rh–ReO_x/SiO₂ (Re/Rh = 0.5), as shown by XRD, TPR, and Re L₃-edge XANES. The amount of CO adsorption was lower than the value expected from the particle size. On the other hand, the EXAFS curve fitting gave a clear indication of the presence of Rh–Re bonds. In the curve fitting of Rh K-edge EXAFS, both Rh–Rh and Rh–Re bonds were present with coordination numbers of 10 and 1.8, respectively. In the curve fitting of Re L₃-edge EXAFS, Re–Re bond, Re–Rh bond, and Re–O single bond were present with coordination numbers of 3.7, 2.7, and 1.4, respectively. The high ratio of the coordination number of Rh–Rh to that of Rh–Re and the small coordination numbers of the Re–metal bonds (Re–Rh and Re–Re) indicated that Re atoms are located on the surface of Rh metal particles. The presence of Re–Re bonds showed that ReO_x species formed a cluster. These data indicate a structure in which Rh metal particles are partially covered with ReO_x clusters via direct Rh–Re bonds.

We also conducted similar characterizations for Pt–ReO_x/SiO₂,⁶⁰ Rh–ReO_x/C,⁴⁴ and Rh–MoO_x/SiO₂.⁴³ All of these catalysts have a similar structure. Noble-metal particles are partially covered with low-valent metal oxide species via direct noble metal–additive metal bonds, while the structures of the low-valent metal oxide species may be different: MoO_x has a monomeric structure, while ReO_x forms clusters. However, when these catalysts were applied to hydrogenation of crotonaldehyde, only Ir–ReO_x/SiO₂ showed high selectivity for crotyl alcohol.⁹⁰ The higher selectivity of the Ir–ReO_x/SiO₂ catalyst may be related to the low activity of the monomeric Ir catalyst. Monomeric Rh and Pt catalysts are very active and not selective for C=O hydrogenation. The activity of unmodified Rh or Pt sites in the modified catalyst can lower the selectivity.

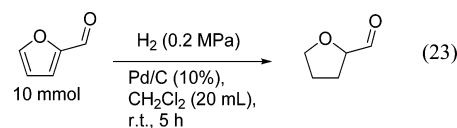
Similar to the Ir–Re pair, the use of metals that are usually inactive is a promising approach to develop very selective catalysts. Ohyama et al.¹¹² reported supported Au sub-nanoparticle catalysts for HMF hydrogenation.

4.2. Tetrahydrofurfuryl Alcohol (THFA) and 2,5-Bis-(hydroxymethyl)tetrahydrofuran (BHTHF). Total hydrogenation of furfural and HMF produces THFA and BHTHF, respectively. Both products are much more stable than the furanic compounds. THFA is used as an environmentally benign solvent.¹¹⁹ BHTHF can be used as a monomer for polyester.²⁴

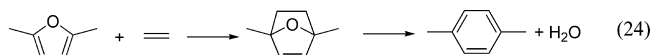
In addition, both compounds can be converted to useful straight-chain polyols by hydrogenolysis, as explained in a later section. Above all, THFA and BHTHF are very useful compounds.

Total hydrogenation to THFA and BHTHF readily proceeds over Ni catalysts.^{56,81,110,120} The gas-phase total hydrogenation of furfural over a Ni/SiO₂ catalyst with 94% THFA yield has been reported.⁸¹ In the liquid-phase reaction, a Raney Ni catalyst can convert both furfural and HMF to the total hydrogenation products, although the activity is not high.^{87,110,120} Alloy catalysts composed of Ni and another metal are generally less selective for furan ring hydrogenation than monometallic Ni catalysts. However, a silica-supported Ni–Pd alloy catalyst (Ni–Pd/SiO₂) can convert HMF to BHTHF in 96% yield, and the activity is much higher than those of Raney Ni and Ni/SiO₂.⁸⁷ One problem with Ni catalysts in liquid-phase hydrogenation is the leaching of Ni metal into the reaction solution.⁸⁷ Noble-metal catalysts are generally more stable than Ni catalysts in terms of leaching. Ru catalysts have been reported to be active for total hydrogenation.^{113,121} Dumesic and co-workers reported that a Ru catalyst supported on oxides with isoelectric points >7 such as CeO₂, magnesia–zirconia, and γ-Al₂O₃ shows a good yield of BHTHF (88–91%).¹¹³ Pt and Pd catalysts are much less selective, and large amounts of unidentified products are formed.^{87,113}

4.3. Tetrahydrofurfural and 5-Hydroxymethyltetrahydrofurfural. As mentioned in section 3.1, selective hydrogenation of the C=O bond of furfural or HMF is relatively easy among α,β-unsaturated aldehydes. In other words, selective hydrogenation of the C=C bond of furfural or HMF is rather difficult. The C=C hydrogenation products, tetrahydrofurfural and 5-hydroxymethyltetrahydrofurfural, are usually not observed or observed only with low selectivity.^{87,106} However, the use of a less polar solvent may destabilize ionic active species, intermediates, and transition states to suppress C=O hydrogenation. The synthesis of tetrahydrofurfural using Pd/C catalyst and CH₂Cl₂ solvent at room temperature (eq 23) was reported by García Liñares and Nudelman.¹²²



4.4. 2-Methylfuran, 2,5-Dimethylfuran, 2-Methyltetrahydrofuran, and 2,5-Dimethyltetrahydrofuran. Complete reduction of the side substituents in furfural and HMF produces 2-methylfuran and 2,5-dimethylfuran, respectively. Further hydrogenation of the furan ring produces 2-methyltetrahydrofuran and 2,5-dimethyltetrahydrofuran, respectively. These types of transformations have gained attention in view of biofuel production because of the good stability and good research octane number (RON) of these products (119 for 2,5-dimethylfuran, 131 for 2-methylfuran).¹²³ 2,5-Dimethylfuran has also been investigated as a source of biobased *p*-xylene production via Diels–Alder cycloaddition with ethylene and subsequent dehydration (eq 24).^{124–126}



The recently reported systems for complete reduction of the side substituents^{99,123,127–129} are summarized in Table 3.

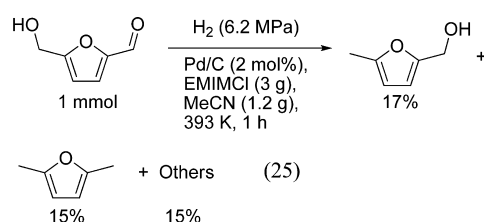
Table 3. Selected Systems for Side-Chain Hydrogenolysis of Furfural, HMF, and Related Compounds

catalyst	substrate	flow conditions	P_{tot} (MPa)	T (K)	conv. (%)	products (selectivity (%))	ref
CuLa- β -zeolite	furfural	H ₂ /furfural = 5, GHSV 0.087 mol h ⁻¹ g _{cat} ⁻¹	0.1	453	9.5	2-methylfuran (82), FOL (18)	99
Cu-Zn-Al oxide	furfural	H ₂ /furfural = 10, LHSV 0.3 g h ⁻¹ g _{cat} ⁻¹	0.1	523	99	2-methylfuran (87)	127
Cu-Zn-Al-Ca-Na oxide	furfural	H ₂ /furfural = 25, LHSV 0.3 g h ⁻¹ g _{cat} ⁻¹	0.1	523	>99	2-Methylfuran (87)	128
Cu-Zn-Al-Ca-Na oxide	FOL ^a	H ₂ /substrate = 25, LHSV 0.3 g h ⁻¹ g _{cat} ⁻¹	0.1	523	98	2-methylfuran (93)	128
CuRu/C	HMF ^a	H ₂ /HMF/1-butanol = 6/1/15, LHSV 0.98 g h ⁻¹ g _{cat} ⁻¹	1.7	493	>99	2,5-dimethylfuran (76)	123
NiFe/SiO ₂	furfural	H ₂ /furfural = 25, W/F 0.1 h	0.1	523	96	2-methylfuran (41), C4 products (29)	129
Pd/HY	furfural	cat. 0.3 g	0.1	623	50	furan (>99)	56
Pd/SiO ₂	furfural	H ₂ /furfural = 25, W/F 0.2 h	0.1	503	74	furan (65), FOL (17), tetrahydrofuran (16)	77
Ni/SiO ₂	furfural	H ₂ /furfural = 25, W/F 4.8 g _{cat} mol ⁻¹ h	0.1	503	72	furan (43), butanal (12), butane (10)	131

^aHMF, 5-hydroxymethylfurfural; FOL, furfuryl alcohol.

Cu-based catalysts are known to be active in the reduction of the side substituents to methyl groups.⁴⁷ Under milder conditions, Cu-based catalysts are selective for alcohols (furfuryl alcohol from furfural), as shown in section 4.1. Complete reduction of the side substituents is usually conducted in the gas phase because of the high reaction temperature.

Chidambaram and Bell¹³⁰ reported the reduction of HMF to 2,5-dimethylfuran in an ionic liquid solvent, 1-ethyl-3-methylimidazolium chloride (EMIMCl), over a Pd/C catalyst, and addition of acetonitrile cosolvent was effective in improving the 2,5-dimethylfuran yield (eq 25). The reaction rate



was much decreased at longer reaction times. At 1 h, 2,5-dimethylfuran was formed with 35% selectivity, and at that time the conversion of HMF was 47%. Prolonging the reaction time to 12 h increased the conversion a little bit to 63%, and the selectivity for 2,5-dimethylfuran was decreased to 28%.

4.5. Furan and Tetrahydrofuran. Furan is formed by the decarbonylation of furfural. Tetrahydrofuran is formed by hydrogenation of furan. While furan and tetrahydrofuran formations are usually regarded as side reactions, the selective

formation of furan from furfural is possible at very high temperature (>473 K). Typical results are also shown in Table 3. Pd catalysts are selective for decarbonylation.^{56,77} Ni catalysts are also active in the formation of furan, although the activity and selectivity are lower.¹³¹ Tetrahydrofuran formation is suppressed under these harsh conditions, probably because of the equilibrium limitations.

4.6. Straight-Chain Rearrangement Products (Levulinic Acid, 1,4-Pentanediol, γ -Valerolactone, 1-Hydroxy-2,5-hexanedione, and 1,2,5-Hexanetriol). Table 4 summarizes the reported systems for rearrangement reactions of furfural or HMF under reductive conditions. As shown in section 2.4, levulinic acid can be formed from furfural or HMF under acidic conditions. Under reductive conditions, levulinic acid or the precursors are reduced, and various 1,4-functionalized C5 compounds such as 1,4-pentanediol and γ -valerolactone may be produced.^{132,133} These compounds are usually not regarded as target compounds in reductive conversion of furfural or HMF because they can be produced by the reduction of levulinic acid obtained directly from carbohydrates.^{134,135} HMF hydrogenation may accompany the formation of 1,2,5-trifunctionalized C6 compounds such as 1-hydroxy-2,5-hexanedione and 1,2,5-hexanetriol.^{51,52} These compounds are usually also regarded as byproducts, while good yields of these compounds (>80%) can be obtained with appropriate catalysts and conditions.

4.7. Cyclopentanone and Cyclopentanol. Cyclopentanone is currently produced by decarboxylation of adipic acid or the esters and is a useful intermediate in organic syntheses.¹³⁶

Table 4. Selected Systems for Reduction/Rearrangement Reactions of Furfural, HMF, and Related Compounds

catalyst	substrate	solvent	substrate/ solvent/catalyst (g)	P_{H_2} (MPa)	T (K)	t (h)	conv. (%)	products (selectivity (%))	ref
Ru/C	furfural	water	5/300/0.4	2.5	438	5	>99	1-hydroxy-4-pentanone (30), cyclopentanol (16), cyclopentanone (11), pentanediols (8), THFA (7)	132
Ru/C + ionic liquid ^a	FOL ^b	EtOH	3.7/75/0.3 + 0.5	3.4	403	5	99	γ -valerolactone (58), methyl levulinate (12)	133
Ru/C	HMF ^b	water, pH 2	2/150/0.02	7	413	1	>99	1,2,5-hexanetriol (96)	51
Rh-Re/SiO ₂	HMF	water	0.1/2/0.025	8	293	17	>99	1-hydroxy-2,5-hexanedione (81), 1,6-hexanediol (7)	52
Pt/C	furfural	water	1/20/0.1	8	448	1	>99	cyclopentanone (40), cyclopentanol (36), 2-methylfuran (5)	53
Pd/C	furfural	water	1/20/0.1	3	433	1	98	cyclopentanone (67), 2-methyltetrahydrofuran (6)	53
NiCu/SBA-15	furfural	water	0.5/9.5/0.2	4	433	4	>99	cyclopentanone (62), 2-methyltetrahydrofuran (17)	55

^aIonic liquid = 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate. ^bHMF, 5-hydroxymethylfurfural; FOL, furfuryl alcohol.

Table 5. Selected Systems for C–O Hydrogenolysis Reactions of Substrates Derived from Furfural or HMF

catalyst	substrate ^a	solvent	substrate/solvent/ catalyst (g)	P _{H₂} (MPa)	T (K)	t (h)	conv. (%)	products (selectivity (%))	ref
Rh-ReO _x /SiO ₂	THFA	water	1/19/0.1	8	393	24	96	1,5-pentanediol (80), 1-pentanol (16)	42
Rh-MoO _x /SiO ₂	THFA	water	1/19/0.1	8	393	24	94	1,5-pentanediol (90), 1-pentanol (9)	43
Rh-ReO _x /C	THFA	water	1/19/0.1	8	373	24	99	1,5-pentanediol (95), 1-pentanol (4)	44
Rh-ReO _x /C	THFA	water	1/19/0.1	3.4	393	4	47	1,5-pentanediol (97), 1-pentanol (3)	45
Rh/SiO ₂	THFA	water	1/19/0.1	8	393	4	5.7	1,2-pentanediol (62), 1,5-pentanediol (18), 1-pentanol (6)	42
Rh-ReO _x /SiO ₂	BHTHF	water	0.1/2/0.025	1	393	20	81	1,2,6-hexanetriol (61), 1,6-hexanediol (28), 1,5-hexanediol (10)	52
Rh-ReO _x /SiO ₂ + Nafion	BHTHF	water	0.1/2/0.025 + 0.015	1	393	20	>99	1,6-hexanediol (86), 1,5-hexanediol (14)	52
Ir-ReO _x /SiO ₂	THFA	water	1/4/0.15	8	373	8	94	1,5-pentanediol (87), 1-pentanol (12)	46
Rh/MCM-41	THFA	scCO ₂	0.4/14 MPa/0.1	4	353	24	81	1,5-pentanediol (91), pentanols (9)	139
Pd-Ir-ReO _x / SiO ₂	furfural	water	1/9/0.1	6	313 + 373	8 + 72	>99	1,5-pentanediol (71), 1-pentanol (13), 1,4-pentanediol (6)	146
Pt/Co ₂ AlO ₄	FOL	EtOH	0.4/7.9/0.2	1.5	423	24	>99	1,5-pentanediol (35), 1,2-pentanediol (16), THFA (31)	147
Ru/MnO _x	FOL	water	4/36/0.2	1.5	423	6	>99	1,2-pentanediol (42), THFA (37)	148
Cu–Cr	FOL	none	81/–/3	10–15	448	11.5	NR ^b	1,2-pentanediol (40% yield), 1,5-pentanediol (30% yield)	149

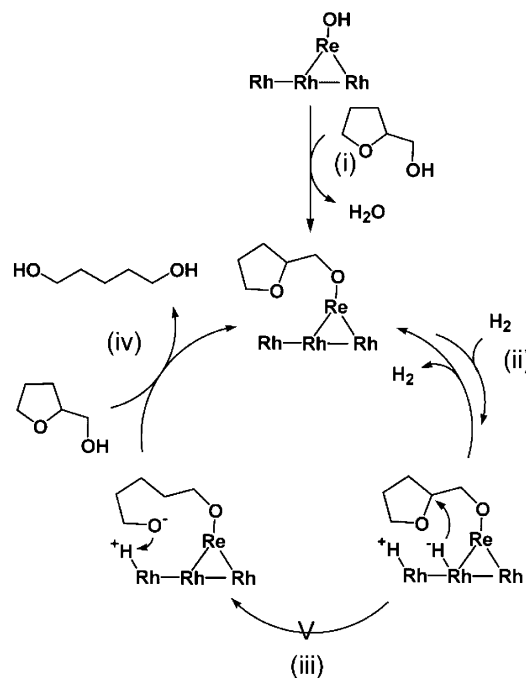
^aFOL: furfuryl alcohol; THFA: tetrahydrofurfuryl alcohol; BHTHF: 2,5-bis(hydroxymethyl)tetrahydrofuran. ^bNot reported.

As mentioned in section 2.4, production of cyclopentanone by the reduction of aqueous furfural was discovered very recently. Around 80% combined yield of cyclopentanone and cyclopentanol has been obtained by using Pt/C^{53,54} and NiCu/SBA-15 catalysts.⁵⁵ High temperature (433 K) and high H₂ pressure (3–8 MPa) are necessary to suppress side reactions such as polymerization.

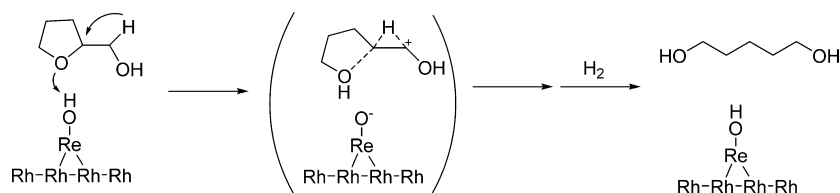
4.8. Hydrogenolysis Products (1,2-Pentanediol, 1,5-Pentanediol, 1,2,6-Hexanetriol, and 1,6-Hexanediol). Useful polyols can be produced by hydrogenolysis of the total hydrogenation products, namely, THFA and BHTHF, over Rh or Ir catalysts modified with a secondary metal such as Re or Mo (Table 5). Aqueous THFA can be converted into 1,5-pentanediol, which can be used as a monomer for polyester, in high yield.^{42–46} Overhydrogenolysis to give 1-pentanol is the sole side reaction. Buntara and co-workers reported similar reactions that convert HMF to 1,2,6-hexanediol or 1,6-hexanediol over Rh-ReO_x/SiO₂.^{52,137,138} Surprisingly, overhydrogenolysis to give 1-hexanol was not observed in this system. Unmodified Rh/SiO₂ can catalyze the hydrogenolysis of THFA to give 1,2-pentanediol, although the activity is much lower than for the modified catalysts.⁴² Kawanami and co-workers reported the use of supercritical CO₂ (scCO₂) as the solvent in hydrogenolysis of THFA.¹³⁹ Monometallic Rh supported on SiO₂-based materials (commercial SiO₂ and MCM-41) gave high selectivity for 1,5-pentanediol in scCO₂, while the addition of water to the solvent changed the main product to 1,2-pentanediol.

As discussed in section 4.1, all of the modified Rh and Ir catalysts have a similar structure in which noble-metal particles are partially covered with low-valent metal oxide species. Monometallic catalysts (Rh, Ir, Re, and Mo) have much lower activities in hydrogenolysis. Therefore, the interface between the noble-metal particle and low-valent metal species may be the catalytically active site. We have proposed a C–O hydrogenolysis mechanism based on the reactivity of related substrates, kinetic analyses, and deuterium-label experiments^{42–44,46,114,115,117,140–145} (Scheme 5). First, the substrate is bound to the surface of the metal oxide species at the

Scheme 5. Proposed Mechanism of Direct C–O Hydrogenolysis of THFA over Rh–ReO_x Catalyst¹⁴² (Reprinted with Permission from Elsevier)



–CH₂OH group to form terminal alkoxide. Next, a hydride species activated on the Rh or Ir metal attacks the 2-position of the alkoxide to break the C–O bond via an S_N2 reaction. Hydrolysis of the reduced alkoxide releases the product. In this mechanism, the C–O bond neighboring a –CH₂OH group is selectively dissociated: THFA to 1,5-pentanediol, glycerol to 1,3-propanediol, 1,2-hexanediol to 1-hexanol, erythritol to 1,4-butanediol, and 2-ethoxyethanol to 2 equiv of ethanol. Hydrogenolysis of a C–O bond neighboring a secondary OH group can be also possible, although the activity is low because of the low adsorption ability of a secondary OH group on the

Scheme 6. “Concerted” Mechanism of THFA Hydrogenolysis over Rh–ReO_x Catalyst Proposed by Dumesic and Co-workers⁴⁵

catalyst surface. The mechanism features first-order kinetics with respect to H₂ pressure. On the other hand, over these Ir- and Rh-based catalysts, hydrogenolysis of other alcohols such as monoalcohols also proceeded to some extent, but different kinetics was observed: zeroth-order or negative order with respect to H₂ pressure. Zeroth-order kinetics is typical for the indirect hydrogenolysis composed of dehydration and hydrogenation (section 2.2). Therefore, these Ir- and Rh-based catalysts can catalyze other mechanisms in addition to the “direct” hydrogenolysis. Dumesic and co-workers investigated the catalysis of Rh–ReO_x/C for THFA hydrogenolysis, and they proposed another mechanism (“concerted” mechanism; Scheme 6).⁴⁵ Acidic Re–OH formed on Rh metal particles gives the proton to the tetrahydrofuran ring, and the α -hydrogen of the alcohol is transferred concertedly to the β -position (2-position of the tetrahydrofuran ring). This step breaks the O–C bond between the 1- and 2-positions to open the ring. Hydrogenation of the produced protonated aldehyde gives 1,5-pentanediol. Buntara et al.¹³⁸ very recently proposed a similar mechanism for the hydrogenolysis of BHTHF over Rh–ReO_x/SiO₂. The reactivity trends of various substrates were explained by stabilization of the resulting cation structures that form upon ring opening or dehydration. However, some selectivities cannot be explained: hydrogenolysis of 1,2-hexanediol gives 1-hexanol as the main product, while the precursor of 1-hexanol (protonated hexanal) is less thermodynamically stable than that of 2-hexanol (protonated 2-hexanone). In addition, it is difficult to explain the reaction order with respect to H₂ pressure (typically 1 for THFA hydrogenolysis) by the “concerted” mechanism. The results of a deuterium-labeling study of THFA hydrogenolysis over Ir–ReO_x/SiO₂ also disagreed with the “concerted” mechanism.⁴⁶ After all, the mechanism of hydrogenolysis is pretty complex, and two or more types of mechanisms can be involved even with the same catalyst. There is much room for clarification of the mechanism of C–O hydrogenolysis.

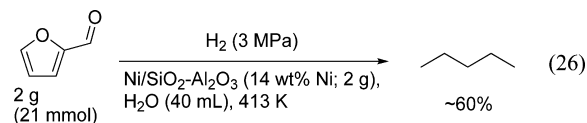
The direct conversion of furfural or HMF to polyols over these modified Rh or Ir catalysts is difficult because these hydrogenolysis catalysts have low activity in hydrogenation of the furan ring. We very recently reported that a Pd–Ir–ReO_x/SiO₂ catalyst can convert furfural to 1,5-pentanediol in 71.4% yield.¹⁴⁶ Addition of Pd to Ir–ReO_x/SiO₂ increased the hydrogenation activity. The reaction was conducted in two steps at different temperatures, first 313 K and then 373 K. The step at lower temperature is necessary to suppress the side reactions during the hydrogenation of furfural to THFA.

There are some reports of direct conversion of furanic compounds to 1,2- or 1,5-pentanediol using catalysts different from those for hydrogenolysis of saturated compounds. These systems are also included in Table 5. Lu and co-workers reported a Pt/Co₂AlO₄ catalyst that can convert furfural to 1,5-pentanediol with a maximum yield of 35%.¹⁴⁷ Zhu and co-workers reported a Ru/MnO_x catalyst that converts furfuryl alcohol to 1,2-pentanediol in 42.1% yield.¹⁴⁸ In the 1930s,

Adkins and Conner reported that a Cu–Cr catalyst can convert furfuryl alcohol to a mixture of products containing 40% 1,2-propanediol and 30% 1,5-pentanediol.¹⁴⁹ In contrast to Rh- and Ir-based catalysts, these catalysts did not convert THFA to diols, indicating that the furan ring was opened before C=C hydrogenation. Optimization of the reaction conditions is necessary because total hydrogenation and/or other side reactions such as 1,4-pentanediol formation can proceed over these catalysts.

4.9. Deep Deoxygenation Products (Pentanol, Hexanol, Pentane, and Hexane). Deep deoxygenation produces monoalcohols and finally alkanes. The key reaction is indirect C–O hydrogenolysis composed of acid-catalyzed dehydration and metal-catalyzed hydrogenation.¹⁰ The total deoxygenation products are *n*-pentane and *n*-hexane. When isomerization or C–C cracking reactions accompany this process, other \leq C6 alkanes can also be produced. Deep deoxygenation products are usually regarded as byproducts, since deep deoxygenation requires a large amount of hydrogen, and the competitiveness against petroleum refinery is weaker than the cases of the production of multifunctionalized compounds. In addition, the deep deoxygenation products have low RONs (62 for *n*-pentane, <30 for *n*-hexane)¹⁵⁰ unless they undergo isomerization, and they are unsuitable for use directly as transportation fuels.

Literature regarding the deep deoxygenation of furfural or HMF is limited. Tiejun and co-workers reported the production of pentane from aqueous furfural over Ni catalysts in combination with solid acid supports.¹⁵¹ About a 60% yield of pentanes with 96% selectivity was observed when 14 wt % Ni/SiO₂–Al₂O₃ catalyst was used at 413 K (eq 26). Higher

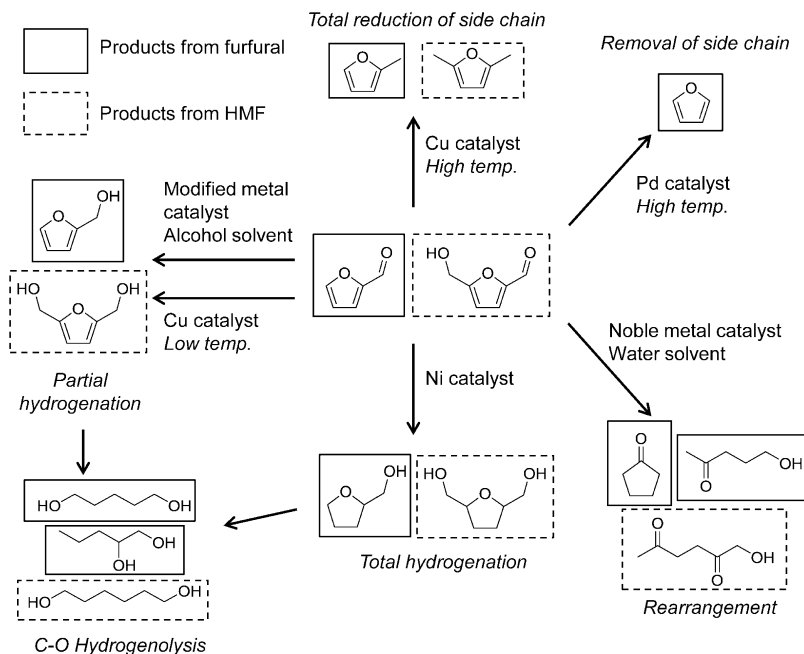


temperatures led to degradation and significant amounts of lighter alkanes, especially methane. A considerable amount of coke or polymer was formed on the catalyst, and deactivation of the catalyst was observed. The deoxygenation reaction probably proceeds via indirect hydrogenolysis (section 2.2).

5. CONCLUSIONS AND OUTLOOK

Catalytic reduction of furfural or HMF is carried out using a simple procedure: only heating the mixture of substrate, solvent, and catalyst under H₂ (liquid-phase reduction) or only passing the mixed gas of substrate, H₂, and inert balance gas through the catalyst (gas-phase reduction). Among the controllable parameters, there is a limited choice among solvents: water or alcohols are usually selected. In spite of the limited parameters (i.e., the choice of catalyst and reaction conditions), there are many possible products: even the simpler furfural has products that might seem to be difficult to give, such as

Scheme 7. Representative Systems for Furfural or HMF Conversions



cyclopentanone, and HMF has even more. The reduction of furfural and HMF has rich chemistry far beyond the hydrogenation of simple α,β -unsaturated aldehydes. The representative systems are summarized in Scheme 7. Promising future works include selective syntheses of one rearrangement product and direct syntheses of C–O hydrogenolysis products such as 1,5-pentanediol and 1,6-hexanediol. Suppression of various types of undesirable side reactions is necessary to obtain high yields of these products. On the other hand, good yields have already been reported with appropriate systems for partial hydrogenation, total hydrogenation, and total reduction of side chains. However, the stability of the catalyst is essential from a practical point of view, although this aspect has not been discussed in this paper. The catalyst should have tolerance to polymeric impurities that are formed inevitably during storage of furfural or HMF. Trace impurities such as phosphorus and sulfur may also poison the catalyst during high turnovers. The development of catalysts that can use crude furfural or HMF is a further challenging task. Anyway, the development of efficient catalytic conversion systems will give us other biomass-derived platform chemicals, broadening the scope of biorefinery. We hope that many catalysis researchers will work together to draw the total picture of furfural and HMF reduction.

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Notes

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ABBREVIATIONS

BHF, 2,5-bis(hydroxymethyl)furan; BHTHF, 2,5-bis(hydroxymethyl)tetrahydrofuran; BTX, benzene, toluene, and xylenes; DOE, U.S. Department of Energy; EMIMCl, 1-ethyl-3-methylimidazolium chloride; EXAFS, extended X-ray absorption fine structure; FOL, furfuryl alcohol; GHSV, gas hourly space volume; HMF, 5-hydroxymethylfurfural; LHSV, liquid hourly space volume; RON, research octane number; scCO₂, supercritical carbon dioxide; SMSI, strong metal–support interaction; TEM, transmission electron microscopy; THFA, tetrahydrofurfuryl alcohol; TOF, turnover frequency; TPR, temperature-programmed reduction; XANES, X-ray absorption near-edge structure; XRD, X-ray diffraction.

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