REVIEW

Reductive Conversion of Biomass-Derived Furancarboxylic Acids with Retention of Carboxylic Acid Moiety

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Abstract

Catalytic reduction systems of 2-furancarboxylic acid (FCA) and 2,5-furandicarboxylic acid (FDCA) with H_2 without reduction of the carboxyl groups are reviewed. FCA and FDCA are produced from furfural and 5-hydroxymethylfurfural which are important platform chemicals in biomass conversions. Furan ring hydrogenation to tetrahydrofuran-2-carboxylic acid (THFCA) and tetrahydrofuran-2,5-dicarboxylic acid (THFDCA) easily proceeds over Pd catalysts. Hydrogenolysis of one C–O bond in the furan ring produces 5-hydroxyvaleric acid (5-HVA) and 2-hydroxyadipic acid. 2-Hydroxyvaleric acid is not produced in the reported systems. 5-HVA can be produced as the lactone form (δ-valerolactone; DVL) or as the esters depending on the solvent. These reactions proceed over Pt catalysts with good yields (~70%) at optimized conditions. Hydrogenolysis of two C–O bonds in the furan ring produces valeric acid and adipic acid, the latter of which is a very important chemical in industry and its production from biomass is of high importance. Adipic acid from FDCA can be produced directly over Pt-MoO_x catalyst, indirectly via hydrogenation and hydrodeoxygenation as one-pot reaction using the combination of Pt and acid catalysts such as Pt/niobium oxide, or indirectly via two-step reaction composed of hydrogenation catalyzed by Pd and hydrodeoxygenation catalyzed by iodide ion in acidic conditions. Only the two-step method can give good yield of adipic acid at present.

Keywords Biomass · Hydrogenolysis · Furanic compound · Carboxylic acid

Introduction

Utilization of biomass as source of chemicals has received much attention because of the depletion of fossil resources and global warming issue. Generally, biomass resources have complex structure and contain various minor components. Therefore, the use of "platform chemicals," which can be readily synthesized in pure form from biomass, as intermediates is a typical approach to synthesizing useful chemicals from biomass [1–3]. Typical platform chemicals in biomass utilization include carboxylic acids, sugar alcohols

and furanic compounds. In particular, furanic compounds are very important because they can be synthesized from inedible lignocellulosic biomass and can be converted into various compounds [4–8]. The most basic biomass-derived furanic compounds are furfural and 5-hydroxymethylfurfural (HMF), which are produced by dehydration of pentoses and hexoses, respectively. Furfural has been already industrially manufactured from pentose-rich hemicellulose component of lignocellulose. While fructose dehydration is the easiest method to produce HMF, it is possible to produce HMF from glucose or even cellulose, both of which are more common biomass constituents than fructose, and enormous efforts to investigate such methods have been devoted in these years. Furfural and HMF have reactive unsaturated furan ring and aldehyde group, and the conversion of furfural and HMF has been also intensively investigated by using various reactions such as reduction, oxidation, addition and condensation. While reductive conversion has been the most investigated because of the high unsaturation of furfural and HMF and variety of products [4, 6–10], oxidation of the side chain of furfural and HMF can give furancarboxylic acids, namely 2-furancarboxylic acid (furoic acid; FCA) and 2,5-furandicarboxylic

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acid (FDCA), respectively, relatively easily (Fig. 1). While typical oxidation systems of furfural and HMF with O_2 require excess amount of base which needs neutralization after reaction [11, 12], several recently reported systems using O_2 and catalysts such as Pt [13–15], Au/basic oxides [16–21], Ru [22] and Mn compounds [23–25] can give excellent yield of FCA and FDCA even without base. FDCA has attracted much attention as a monomer of polyester, polyethylene 2,5-furandicarboxylate (PEF) which is an analogue of the most used polyester, polyethylene terephthalate (PET) [26–28]. While furfural and HMF are gradually polymerized during storage, FCA and FDCA are stable solids. However, the utilization of FCA or FDCA as sources of other chemicals

has been much less investigated. Because FCA and FDCA are in a high oxidation level, the reduction of FCA and FDCA is an important reaction in the utilization. However, if the carboxyl groups of FCA or FDCA are reduced, the advantage of the use of FCA or FDCA as a reactant is lost because the products can be also synthesized from furfural or HMF with smaller amount of reducing agent. Therefore, the reduction of the furan ring of FCA and FDCA with retention of the carboxyl groups is more important. Recently, our group and several other research groups have reported such reductive conversions of FCA and FDCA. In this paper, we review the chemical reductive conversions of FCA and FDCA with retention of the carboxyl groups in three categories: hydrogenation of the furan ring,
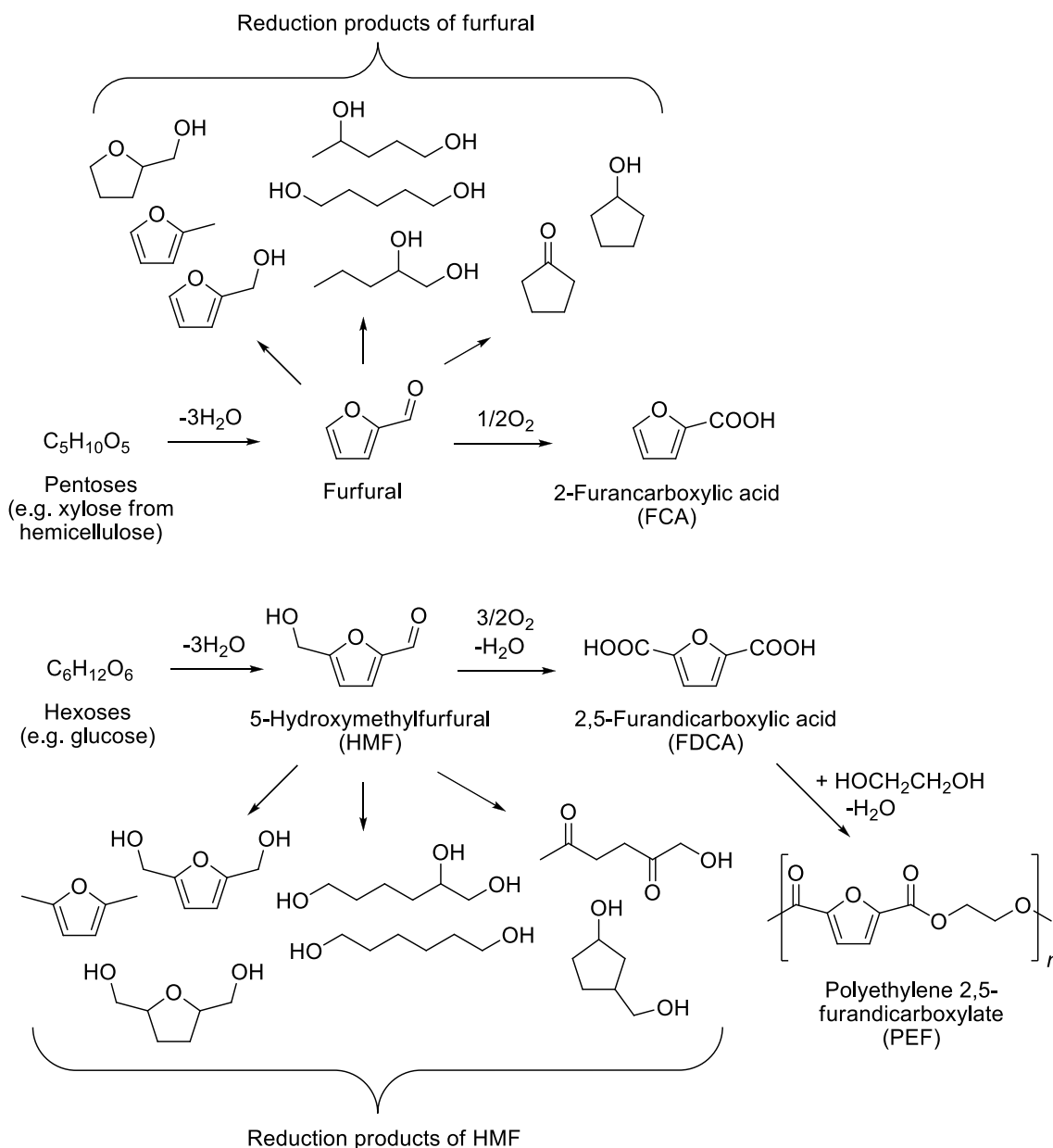

Fig. 1 Utilization of furfural and HMF including oxidation to FCA and FDCA

C–O hydrogenolysis in the furan ring and C–O hydrogenolysis after hydrogenation of the furan ring. The systems for the most important products, adipic acid, 5-hydroxyvaleric acid and valeric acid, are compared with other production methods from biomass.

Hydrogenation of Furan Ring

Hydrogenation of the furan ring in FCA and FDCA produces tetrahydrofuran-2-carboxylic acid (THFCA; Eq. 1) and tetrahydrofuran-2,5-dicarboxylic acid (THFDCA; Eq. 2), respectively. While hydrogenation of C=C bonds is easy over various noble metal catalysts, Pd is known to be less active in hydrogenation of C=O bonds than other noble metals [29]. Indeed, simple Pd catalysts are effective in C=C hydrogenation of FCA and FDCA to THFCA and THFDCA, respectively, with very high selectivity (e.g., > 99%) [30–33]. For FDCA, only *cis*-isomer is produced because of the general syn hydrogenation mechanism catalyzed by metal surfaces [32, 34]. Wide range of solvents can be used, including H_2O, alcohols, acetic acid and toluene. However, at high reaction temperature (e.g., 373 K), alcohol solvents lead to esterification of the hydrogenated products [35, 36]. Since FDCA has low solubility in H_2O, acetic acid has been typically used as solvent in Refs. [31, 32]. A typical run of FDCA hydrogenation is shown in Eq. (3) [32]. Our group [36] and Liu et al. [33] reported the effect of noble metal type on the catalytic FCA reduction, and both groups reported that Pd catalyst has higher selectivity to THFCA than other noble metal catalysts (Pt, Ru, Rh and Ir). The main side reaction over the non-Pd noble metal catalysts is the ring opening to 5-hydroxyvaleric acid or its derivatives, which will be discussed in the next section.
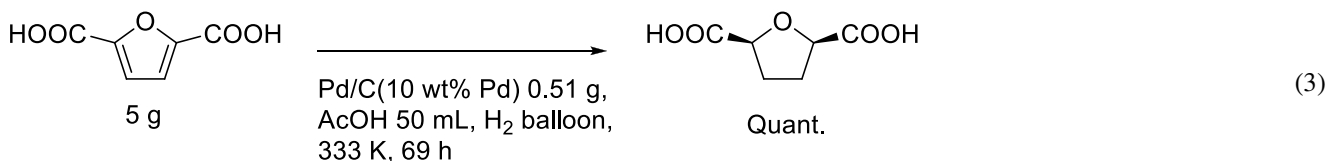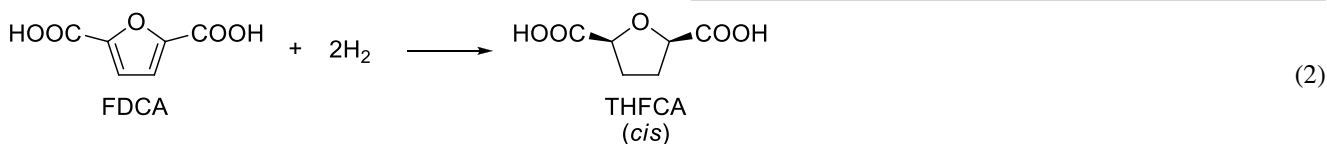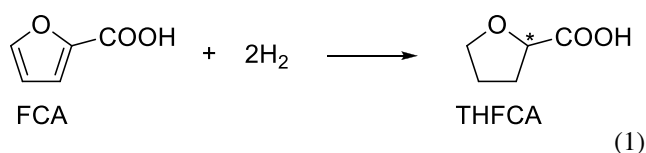
THFCA has an asymmetric carbon atom at 2-position, and therefore, asymmetric hydrogenation of FCA was also investigated. Baiker et al. [30, 37] tested the combination of Pd/Al_2O_3 catalyst and various chiral additives; however, the reported enantioselectivity was not satisfactory (maximum ee 42%, with cinchonidine as a chiral additive). There is another report using Rh complex catalyst with a chiral ferrocenyl diphosphine ligand; however, the reported enantioselectivity was also low (ee 24%) [38].

Ring-Opening Hydrogenolysis

Hydrogenolysis is the reaction composed of bond dissociation and the addition of H atoms to both the produced terminal atoms, although the positions of H atoms incorporated to the products from H_2 might not be the same as that of the dissociated bond. C–O hydrogenolysis of furan compounds initially opens their ring and subsequently C=C bonds in chain structure undergo hydrogenation to be saturated structure, since C=C bonds in chain structure are more easily hydrogenated than those in aromatic ring structure. The possible products of C–O hydrogenolysis of FCA and FDCA are summarized in Fig. 2. Hydrogenolysis of one C–O bond in FCA produces 5-hydroxyvaleric acid (5-HVA) or 2-hydroxyvaleric acid (2-HVA). 5-Hydroxyvaleric acid can be reversibly converted to the lactone form, δ-valerolactone (DVL). Only the hydrogenolysis to 5-HVA and its derivatives (DVL, ester of 5-HVA and solvent) has been reported, and there is no report describing the FCA hydrogenolysis to 2-HVA at present. This is in contrast to a related reaction, furfuryl alcohol hydrogenolysis to pentanediols where both 1,5-pentanediol and 1,2-pentanediol are the main products depending on the catalyst [8, 39–41]. One explanation for the preferential C–O dissociation at 1,2-position to 5-HVA is that the carbonyl (carboxyl) group adsorbed on the catalyst directs the position of hydrogen atom addition to the neighboring

$$(1)$$

$$(2)$$

$$(3)$$

Fig. 2 Hydrogenolysis products of FCA and FDCA. Reduction products of the carboxyl groups are omitted. Arrows represent C–O hydrogenolysis unless otherwise noted
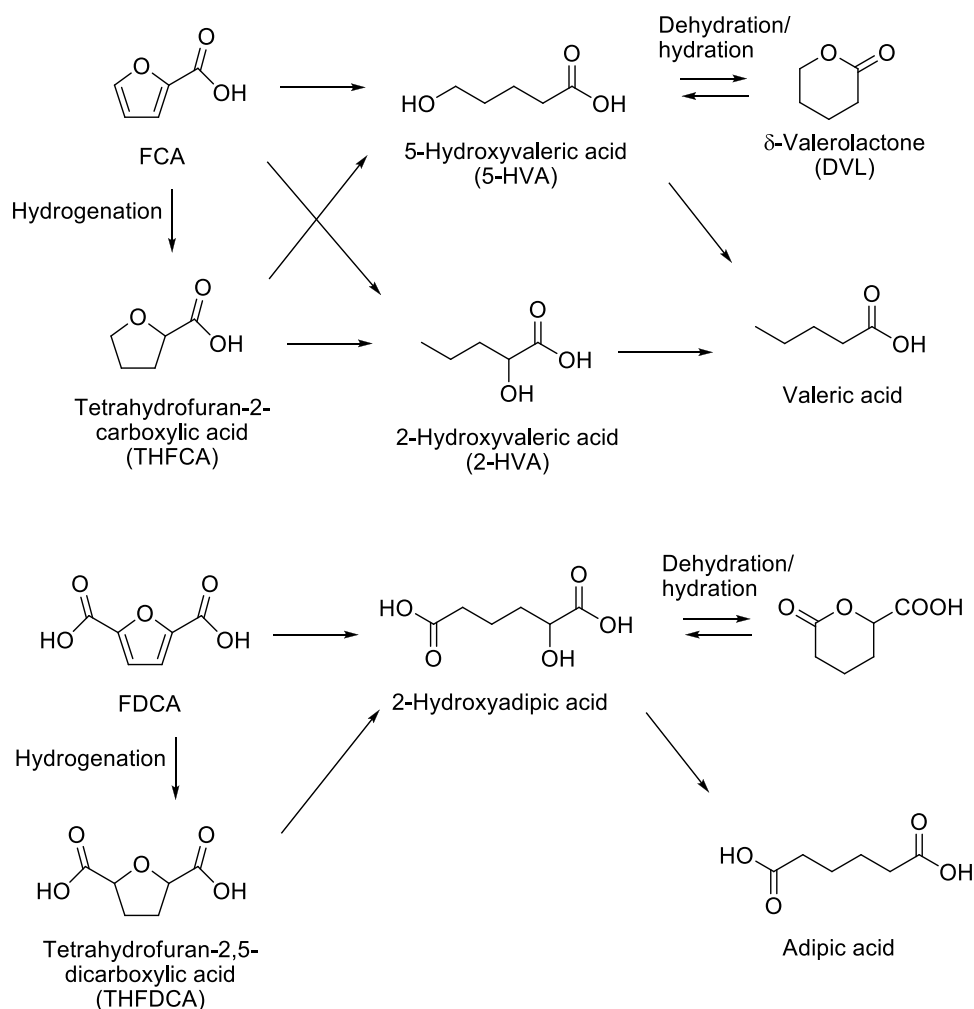
position of the carbonyl group. The mechanism for the selective C–O hydrogenolysis will be discussed later. In the case of FDCA, hydrogenolysis of one C–O bond produces 2-hydroxyadipic acid. The lactone form of 2-hydroxyadipic acid is also probably generated, although such formation has not yet been confirmed because the literature studies for FDCA hydrogenolysis used water solvent that suppresses the formation of lactones.

An old report [42] in 1949 describing the effectiveness of Adams catalyst (PtO₂) in hydrogenation of various substrates showed that the reduction of FCA with Adams catalyst and H₂ in acetic acid solvent produced DVL. However, the detailed procedure and yield and selectivity values were not described in this report, and this reaction had not received attention for long time until the recent days when biomass conversion has great importance. Very recently, our group [36] and Liu et al. [33] reported the detailed study of Pt-catalyzed C–O hydrogenolysis of FCA to 5-HVA and its derivatives (DVL and ester of 5-HVA) almost at the same time. Our group investigated the effects of support and solvent (Table 1) as well as reaction conditions. Although both

the effects of support and solvent are not large, Pt/Al₂O₃ catalyst shows relatively high activity and selectivity to 5-HVA derivatives, and polar solvents such as methanol give higher selectivity. Ester of 5-HVA becomes the main product when smaller alcohols such as methanol are used as the solvent. The highest combined yield of 5-HVA and its derivatives is 62% (methyl 5-hydroxyvalerate 55%, DVL 7%, 5-HVA < 0.1%). Acetic acid solvent, which was used in the old report using Adams catalyst [42], surely gives good selectivity to DVL (66%); however, the reaction rate in acetic acid is lower than that in alcohols. Liu et al. [33] reported Pt-catalyzed FCA hydrogenolysis in water solvent. Although water solvent was less effective to obtain high selectivity than methanol solvent in our study [36], high selectivity to 5-HVA was reported with Pt/SiO₂ catalyst with relatively large Pt particle sizes (> 4 nm) [33]. The highest yield of 5-HVA reached 78%. The stability of the catalysts was investigated in these two studies. The catalysts (Pt/Al₂O₃ and Pt/SiO₂) can be reused without large loss of activity or selectivity when the catalyst is calcined at 573 K as regeneration, although the direct reuse of Pt/Al₂O₃ without calcination

**Table 1** Reduction of FCA over various catalysts and solvent [36]

Catalyst	Solvent	Conv. (%)	Selectivity (%)					
			Ester of 5-HVA	5-HVA	DVL	Ester of THFCA	THFCA	Others
Pt/Al$_2$O$_3$	Methanol	91	51	< 0.1	6	12	10	< 1
Pt/Al$_2$O$_3$[a]	Methanol	> 99	55	< 0.1	7	20	2	1
Pt/ZrO$_2$	Methanol	58	46	< 0.1	4	13	6	< 1
Pt/CeO$_2$	Methanol	91	37	< 0.1	7	10	24	< 1
Pt/TiO$_2$	Methanol	25	38	< 0.1	5	8	8	3
Pt/SiO$_2$	Methanol	34	34	< 0.1	6	5	23	< 1
Pt/C	Methanol	16	24	< 0.1	6	5	25	1
Rh/C	Methanol	> 99	6	< 0.1	< 1	26	60	< 1
Ru/C	Methanol	> 99	6	< 0.1	< 1	23	61	< 1
Pd/C	Methanol	93	< 0.1	< 0.1	< 0.1	8	89	< 1
Pt/Al$_2$O$_3$	Ethanol	90	44	< 1	13	3	19	< 1
Pt/Al$_2$O$_3$	1-Propanol	96	27	3	24	1	23	< 1
Pt/Al$_2$O$_3$	2-Propanol	97	4	5	42	< 1	27	< 1
Pt/Al$_2$O$_3$	1,4-Dioxane	88	–	5	34	–	35	< 1
Pt/Al$_2$O$_3$	Acetic acid	55	–	< 0.1	66	–	27	1
Pt/Al$_2$O$_3$	Water	99	–	4	33	–	30	6

Reaction conditions: catalyst (4 wt% noble metal) 50 mg (for noble metal/C: 40 mg of 5 wt% noble metal catalyst), FCA 10 mmol, solvent 29 g, H$_2$ 4 MPa (at room temp.), 373 K, 1 h. [a] 4 h. FCA = 2-furancarboxylic acid, HVA = hydroxyvaleric acid, DVL = δ-valerolactone, THFCA = tetrahydrofuran-2-carboxylic acid
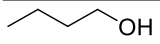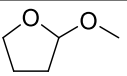
gradually decreases the activity due to deposition of organic compounds on the catalyst surfaces.

The reaction mechanism was discussed based on the reactivity of various related substrates over Pt/Al$_2$O$_3$ in methanol [36]. The control reaction of THFCA does not give C–O hydrogenolysis products but only gives methyl tetrahydrofuran-2-carboxylate which is the ester of THFCA and methanol solvent. This result indicates that the C–O hydrogenolysis which opens the furan ring occurs before total hydrogenation of the furan ring. The reactivity of methyl 2-furancarboxylate, which is the ester of FCA and methanol, is similar to that of FCA: conversion and selectivity to methyl 5-hydroxyvalerate are similar to those from FCA. This result shows that the carboxyl proton in FCA does not play a critical role in the hydrogenolysis. In the case of furan-3-carboxylic acid, the reactivity is much lower than that of FCA; nevertheless, the C–O hydrogenolysis product is formed to some extent as the lactone form (Eq. 4): 22% conversion and 8% yield of 2-methyl-γ-butyrolactone was obtained, while in the same conditions FCA was converted to methyl 5-hydroxyvalerate with 47% yield at 91% conversion. The position of the carboxyl group much affects the reactivity.

(4)
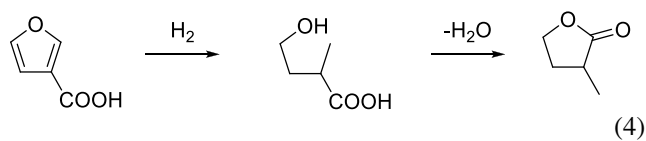
In order to determine whether dihydrofuran derivatives are involved in the catalysis, the reactions of furan, 2,3-dihydrofuran and 2,5-dihydrofuran over Pt/Al$_2$O$_3$ were tested (Table 2) [36]. The reactions were carried out by introducing H$_2$ after heating to the reaction temperature (373 K) because the hydrogenation of these substrates to THF is very fast and completed during heating in the presence of H$_2$. In the reaction of furan, the C–O hydrogenolysis product, 1-butanol, is obtained in moderate yield (41%) as well as the total hydrogenation product THF (40% yield). From dihydrofurans, the 1-butanol yield is much lower, and 2-methoxytetrahydrofuran, which is the product of methanol addition, and THF are mainly produced from 2,3-dihydrofuran and 2,5-dihydrofuran, respectively. These results suggest that C–O hydrogenolysis of furan mainly occurs before addition of two hydrogen atoms. The C–O hydrogenolysis starts with addition of one hydrogen atom to the furan ring, and then, the C–O bond is dissociated. From 2,5-dihydrofuran, significant amount of the C–O hydrogenolysis product (1-butanol) is formed, although it is much lower than that from furan. This result suggests that the C–O hydrogenolysis can occur after addition of one hydrogen atom to 2,5-dihydrofuran, i.e., formation of 2,3,5-trihydrofuran intermediate which possesses a radical at 3-position. Altogether, we assume that C–O hydrogenolysis of furan and furancarboxylic acids occurs after addition of one hydrogen atom at the 2-position, which produces intermediates containing radical at the 3-position. The proposed mechanism [36] is shown in

Table 2 Reduction of furan and dihydrofurans over Pt/Al$_2$O$_3$ [36]

Substrate	Conv. (%)	Yield (%)		
		1-Butanol	2-MethoxyTHF	THF
Furan	93	41	2	40
2,3-Dihydrofuran	95	2	82	1
2,5-Dihydrofuran	> 99	14	10	64

Reaction conditions: Pt/Al$_2$O$_3$ (4 wt% Pt) 50 mg, substrate 10 mmol, methanol 29 g, 1 MPa Ar + 3 MPa H$_2$ (H$_2$ was introduced at 373 K), 373 K, 1 h

Fig. 3. FCA molecule is adsorbed on Pt with the carbonyl C=O group (step (i)), as suggested by the similar reactivity of FCA and methyl 2-furancarboxylate. One hydrogen atom is added to the 2-position of the furan ring (step (ii)), and the position is directed by the carboxylate group: the carboxylate group is adsorbed on the catalyst surface, and the hydrogen atom on the catalyst surface can more easily approach positions near the carboxylate group. The idea that hydrogen addition occurs at the carbon atom which is bonded to the carboxyl group can explain the higher reactivity of FCA than that of furan-3-carboxylic acid. Next, the C–O bond at the 1,2-position is dissociated to give the dienolate species (step (iii)). The dienolate species is protonated and hydrogenated (steps (iv) and (v)) to give 5-HVA. The direction of the position of hydrogen addition and C–O bond dissociation by the carboxylate group can be also related to the absence of the product of C–O hydrogenolysis at 1,5-position, 2-HVA.

On the other hand, Liu et al. [33] proposed another mechanism based on kinetic modeling and density functional theory (DFT) calculations. The first addition of one hydrogen atom to the furan ring is also suggested to be the kinetically relevant step from the kinetic modeling. The difference is that the FCA molecule is adsorbed with the furan ring and the first hydrogen addition occurs at the 4-position. The carbon atom at the 2-position is still strongly bonded to Pt surface, and the C–O bond is dissociated before addition of hydrogen atom to this carbon atom. One problem of this reaction mechanism is that it cannot be applied to 2,5-dihydrofuran where the carbon atoms in the C–O structure cannot be bonded to Pt surface.

The reaction mechanism may be related to that of furfuryl alcohol hydrogenolysis to 1,2- and 1,5-pentanediols, because hydrogenolysis of furfuryl alcohol and FCA has several common features [39–41]. These two substrates are both furans substituted at the 2-position. Both reactions are catalyzed by Pt [42–49]. Both systems cannot open the ring after total hydrogenation (THFCA and tetrahydrofurfuryl alcohol). Alcohols and water are effective solvents for both systems. Although there is no widely accepted mechanism for Pt-catalyzed furfuryl alcohol hydrogenolysis, further mechanistic studies of FCA hydrogenolysis or furfuryl alcohol hydrogenolysis will give useful insights for both the reactions.

When the Pt-catalyzed reaction is applied to FDCA substrate, the product will be 2-hydroxyadipic acid. Wang et al. [50] reported Pt-catalyzed FDCA hydrogenolysis, and actually 2-hydroxyadipic acid was produced over various Pt catalysts. Because the target product of this paper is adipic acid rather than 2-hydroxyadipic acid, the production of 2-hydroxyadipic acid was not investigated in detail (no optimization of reaction conditions). Nevertheless, 2-hydroxyadipic acid yield reaches 73% which is obtained over Pt/HZSM-5 catalyst (Eq. 5).
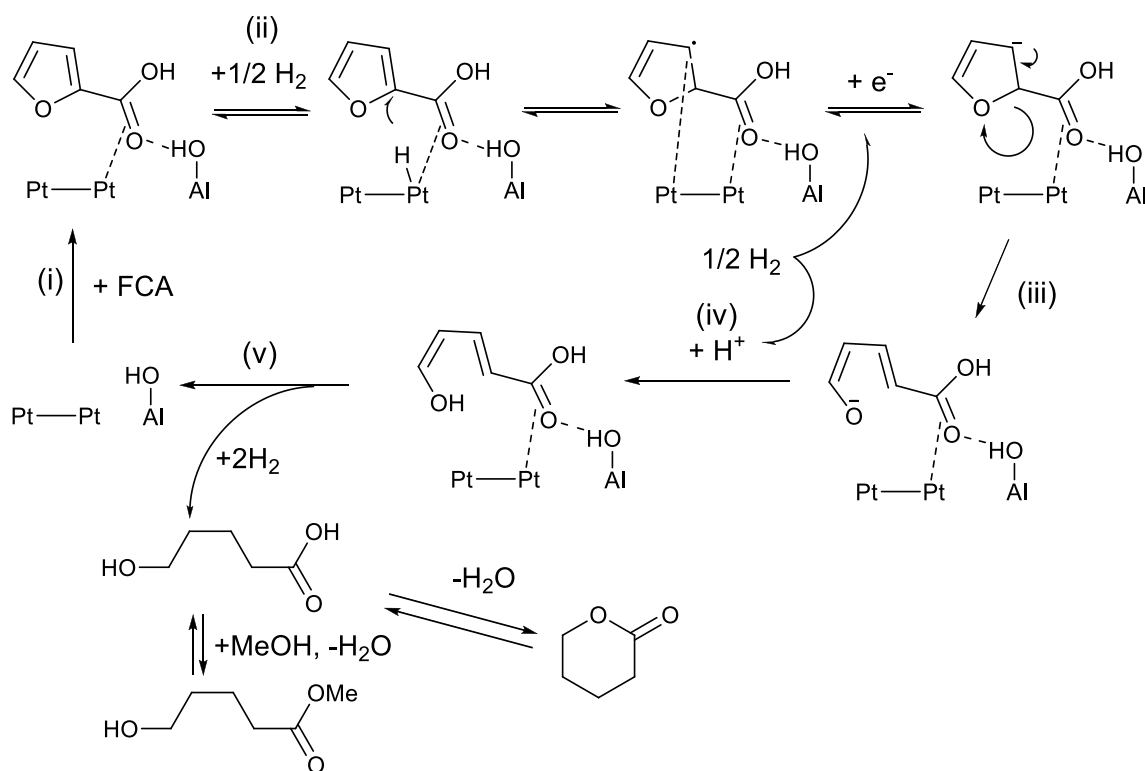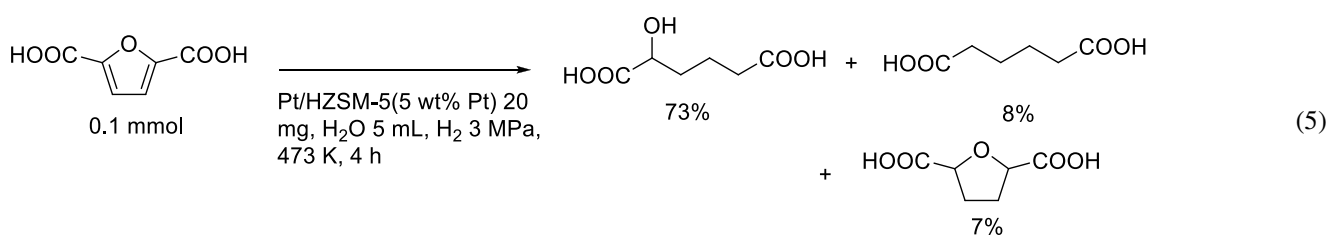
Fig. 3 Proposed reaction mechanism of the reduction of FCA to 5-HVA derivatives over Pt/Al$_2$O$_3$ catalyst. Reprinted with permission from Ref. [36] by Royal Society of Chemistry

Our group [51, 52] reported a variant of the Pt-catalyzed C–O hydrogenolysis. When the Pt/TiO$_2$ catalyst is modified with MoO$_x$, the activity in water solvent is much improved, and the main product becomes valeric acid which is the product of the hydrogenolysis of both the C–O bonds in the furan ring. The dependence of performance on the Pt and Mo loading amounts shows that the highest activity in valeric acid formation is obtained at around Mo 0.5 wt% for any Pt loading [52]. With enough amount of catalyst, all Pt-MoO$_x$/TiO$_2$ catalyst with Mo 0.5 wt% and Pt 1 wt%–20 wt% show similar valeric acid yield of about 60%. However, the stability of Pt-MoO$_x$/TiO$_2$ catalyst is not good, even in comparison with Pt catalysts for 5-HVA production. The Pt-MoO$_x$/TiO$_2$ catalysts gradually lose activity during reuses regardless of the presence/absence of regeneration [51]. The necessity of enough

amount of catalyst to obtain good valeric acid yield is due to the deactivation. Characterization results with X-ray diffraction (XRD), transmission electron microscopy (TEM), CO adsorption and X-ray absorption fine structure (XAFS) suggest that Mo species are mainly located on the TiO$_2$ support surface as Mo(IV) species and not on the Pt metal surface. Pt particles are located on MoO$_x$/TiO$_2$ and a direct bond between Pt and Mo is formed at the interface, as detected by extended X-ray absorption fine-structure (EXAFS) spectroscopy. This interface site between MoO$_x$ and Pt is suggested to be catalytically active (Fig. 4) [52]. After catalytic use, the coordination number of Pt–Mo direct bond in EXAFS is decreased, which can be connected to the deactivation.

The reaction results of related substrates over the Pt-MoO$_x$/TiO$_2$ catalyst are summarized in Table 3 [51, 52]. The
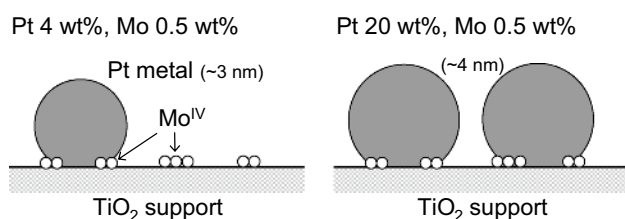
Pt 4 wt%, Mo 0.5 wt%   Pt 20 wt%, Mo 0.5 wt%

Fig. 4 Model structure of Pt-MoO$_x$/TiO$_2$ catalysts after reduction. Oxygen atoms in Mo^{IV} species are omitted. Reprinted with permission from Ref. [52] by American Chemical Society

hydrogenolysis of FDCA to adipic acid is possible; however, the reactivity and selectivity are much lower than those of FCA to valeric acid. The reactivity of furan-3-carboxylic acid is also very low, and very small amount of deoxygenation product (hydrogenolysis product of the two C–O bonds; 2-methylbutyric acid) is formed. This is similar trend to the Pt/Al$_2$O$_3$ catalyst for the hydrogenolysis of one C–O bond in the furan ring. The reactivity of THFCA is similarly low to the case of Pt/Al$_2$O$_3$ catalyst system, and no deoxygenation product (valeric acid) is formed. While small amount of deoxygenation product is formed from furan (butane), such deoxygenation product is hardly formed from dihydrofurans. These similar trends to those of the Pt/Al$_2$O$_3$-catalyzed hydrogenolysis system [36] suggest that there are common reaction steps between Pt-MoO$_x$/TiO$_2$– and Pt/Al$_2$O$_3$-catalyzed systems. We proposed a reaction mechanism for Pt-MoO$_x$/TiO$_2$–catalyzed hydrodeoxygenation (Fig. 5) [52]. This is composed of FCA coordination on Pt site (same as step (i) in Fig. 3), addition of one hydrogen atom to the 3-position of the furan ring (same as step (ii) in Fig. 3), C–O dissociation promoted by Mo species (similar to step (iii) in Fig. 3, the difference is the involvement of Mo

species), further C–O dissociation by the reduction with the Mo(IV) species to pentadienoic acid and Mo(VI) species, and hydrogenation of pentadienoic acid to valeric acid. The Mo(VI) species is also reduced with hydrogen to Mo(IV).

Hydrodeoxygenation of Tetrahydrofurancarboxylic Acids

One-step hydrodeoxygenation of FCA or FDCA is a difficult reaction; the Pt-MoO$_x$/TiO$_2$ catalyst system discussed above has problems of low yield (especially for FDCA to adipic acid) and low stability. The multistep method composed of hydrogenation of furan ring and hydrodeoxygenation of the saturated tetrahydrofuran ring is another approach to the deoxygenation of FCA or FDCA. Typically, hydrodeoxygenation (C–O hydrogenolysis) of alcohols or ether can proceed with the combination of metal and strong acid catalysts via E1 type acid-catalyzed dehydration (or de-alkoxylation in the case of ethers) and metal-catalyzed hydrogenation [53, 54]. However, the dissociation of C–O bond at α-position of carbonyl groups such as 2-position of carboxylic acids is difficult because of the electron-withdrawing effect of the carbonyl group, while C–H bond is easily dissociated at this position. Effective systems for the C–O dissociation of α-functionalized carboxylic acids such as tetrahydrofurancarboxylic acids and lactic acid [55, 56] are very limited.

Wang et al. [50] reported Pt/Nb$_2$O$_5$•xH$_2$O catalyst for the production of adipic acid from FDCA. Niobium oxides are well known solid acids which can work in water solvent [57]. In water solvent under 3 MPa H$_2$ at 473 K, Pt/Nb$_2$O$_5$•xH$_2$O catalyst converts FDCA first to THFDCA. Some amount of 2-hydroxyadipic acid is probably formed via the ring-opening hydrogenolysis discussed in the above section. THFDCA is

Table 3 Reduction of various substrates over Pt-MoO$_x$/TiO$_2$ [51, 52]

Substrate	Conv. (%)	Products (yield (%))
FCA	97	Valeric acid (51), THFCA (4), DVL (5), 5-HVA (7), 5-oxyvaleric acid (9)
FCA[a]	> 99	Valeric acid (61), THFCA (2), DVL (3), 5-HVA (3), 5-oxyvaleric acid (5)
FDCA[b]	> 99	Adipic acid (5), THFDCA (20)
FDCA[c]	> 99	Adipic acid (21), THFDCA (1)
THFCA	18	1,5-Pentanediol (4), DVL (1)
3-Furancarboxylic acid	9	2-Methylbutyric acid (3), γ-valerolactone (3)
Furan	> 99	1-Butanol (35), THF (15), Butane (9)
2,3-Dihydrofuran	> 99	THF (47), 1-butanol (20), 1,4-butanediol (14)
2,5-Dihydrofuran	> 99	THF (46), 1-butanol (24), 1,4-butanediol (14), butane (1)

Reaction conditions: Pt-MoO$_x$/TiO$_2$ (4 wt% Pt, 0.5 wt% Mo) 0.1 g, substrate 10 mmol, water 19 g, H$_2$ 1.5 MPa, 413 K, 4 h

[a]Pt-MoO$_x$/TiO$_2$ (20 wt% Pt, 0.5 wt% Mo) 0.1 g

[b]FDCA 5 mmol

[c]FDCA 5 mmol, 473 K. FCA = 2-furancarboxylic acid, THFCA = tetrahydrofuran-2-carboxylic acid, DVL = δ-valerolactone, HVA = hydroxyvaleric acid, FDCA = 2,5-furandicarboxylic acid, THFDCA = tetrahydrofuran-2,5-dicarboxylic acid
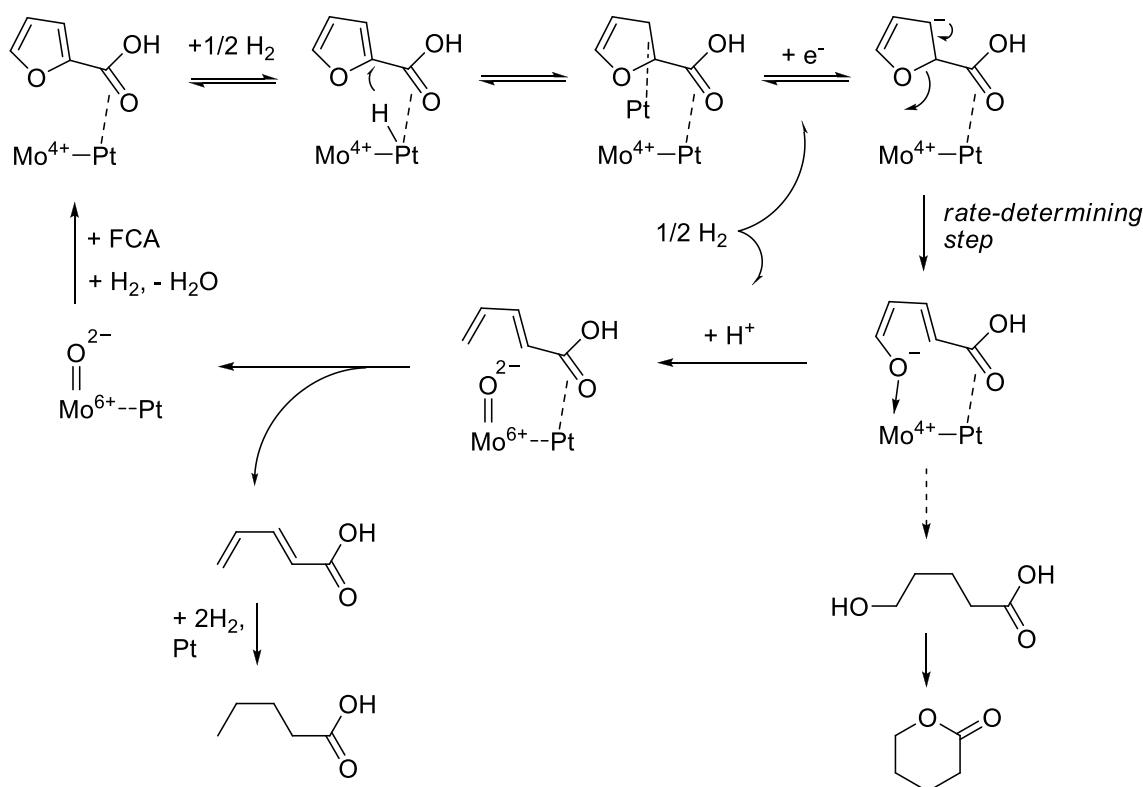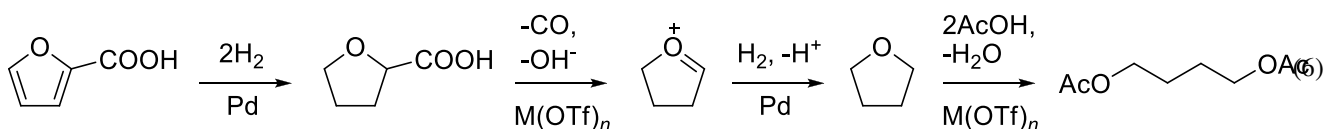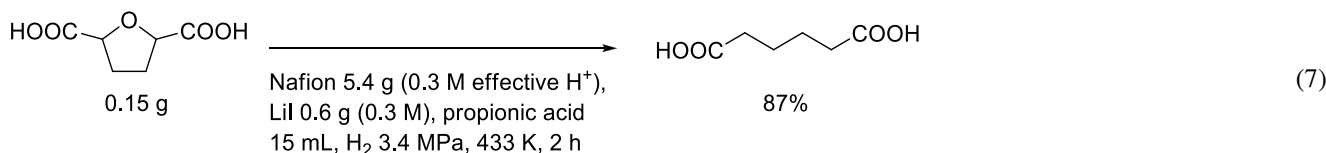
Fig. 5 Proposed reaction mechanism of FCA reduction to valeric acid over Pt-MoO$_x$/TiO$_2$ catalyst. Reprinted with permission from Ref. [52] by American Chemical Society

then converted to 2-hydroxyadipic acid by C–O hydrogenolysis over metal (Pt) and acid (niobium oxide). 2-Hydroxyadipic acid produced directly or indirectly from FDCA is further converted to adipic acid also by C–O hydrogenolysis. These reactions proceed in one pot. However, there is large loss of carbon balance, and the maximum obtained yield of adipic acid is 38%. Fu et al. [58] have very recently reported the reduction of FCA with the combination catalysts of Pd/C and rare earth triflates as Lewis acids in acetic acid solvent. The authors had expected that THFCA first formed by hydrogenation of FCA over Pd would suffer ring opening by addition of acetic acid and then lose an oxygen atom by C–O hydrogenolysis to 5-acetoxyvaleric acid. However, the main product actually observed was the diester of 1,4-butanediol (maximum 83% yield). The reaction time dependence shows that THFCA produced first is converted to THF via decarbonylation (stoichiometric amount of CO is detected) and hydrogenation, and then the ring opening of THF occurs (Eq. 6).

Vlachos et al. [59–61] have intensively investigated the hydrogenolysis of THFDCA to adipic acid with the help of iodide ion. The reaction was first reported by Boussie et al. [31] in a patent using the combination of Pd and HI catalysts. The iodide ion dissociates the C–O bond by S_N2 mechanism, and then the C–I bond is reduced to produce the C–H bond and to regenerate iodide. Vlachos et al. [59] clarified that Pd catalyst is not necessary in the C–O hydrogenolysis steps and that the combination of solid acid and alkali iodide can be used instead of HI, which is a toxic and very corrosive reagent [60, 61]. The adipic acid yield reached 87%, which is obtained with the combination of Nafion and LiI (Eq. 7) [60].

(6)

$$\text{HOOC}\underset{\text{0.15 g}}{\overset{\text{O}}{\diagdown}}\text{COOH} \xrightarrow[\substack{\text{Lil 0.6 g (0.3 M), propionic acid} \\ \text{15 mL, H}_2\text{ 3.4 MPa, 433 K, 2 h}}]{\text{Nafion 5.4 g (0.3 M effective H}^+\text{),}} \text{HOOC}\diagup\diagdown\diagup\text{COOH} \quad 87\% \tag{7}$$

C–O hydrogenolysis of saturated compounds is known to be catalyzed by bimetallic catalysts composed of noble metal and groups 6–7 metal oxide such as Rh–MoO$_x$, Rh–ReO$_x$, Ir–ReO$_x$ and Pt–WO$_x$ [62–68]. In these catalysts, partially reduced metal oxide directly interacts with noble metal
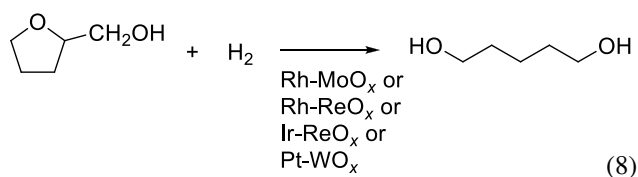
[70–75]. However, the ratio is still lower than 1 even at low conversion level over Rh-WO$_x$/SiO$_2$ catalyst. At higher conversion level, the ratio is further decreased probably because of the successive hydrogenation of the carboxyl/lactone group in DVL and 5-HVA. The reported run with the highest yield of DVL + 5-HVA over Rh-WO$_x$/SiO$_2$ is shown as Eq. (9).

$$\underset{\substack{\text{THFCA} \\ \text{10 mmol}}}{\overset{\text{O}}{\diagdown}\text{COOH}} \xrightarrow[\substack{\text{Rh-WO}_x\text{/SiO}_2\text{ (Rh 4 wt\%,} \\ \text{W/Rh=0.25) 0.1 g, H}_2\text{O 19 g,} \\ \text{H}_2\text{ 1.5 MPa, 393 K, 48 h}}]{\text{H}_2} \underset{\substack{\text{DVL} \\ 7.5\%}}{\overset{\text{O}}{\diagdown}\overset{\text{O}}{\diagup}} + \underset{\substack{\text{5-HVA} \\ 1.9\%}}{\text{HO}\diagup\diagdown\diagup\underset{\text{O}}{\text{OH}}}$$

$$+ \underset{\substack{\text{Tetrahydrofurfuryl alcohol} \\ 10.9\%}}{\overset{\text{O}}{\diagdown}\text{CH}_2\text{OH}} + \underset{\substack{\text{1,5-Pentanediol} \\ 8.8\%}}{\text{HO}\diagup\diagdown\diagup\text{OH}} + \underset{\substack{\text{1-Pentanol} \\ 4.2\%}}{\diagup\diagdown\diagup\text{OH}} + \underset{2.3\%}{\text{Others}} + \underset{22.6\%}{\substack{\text{Loss of} \\ \text{carbon} \\ \text{balance}}} \tag{9}$$
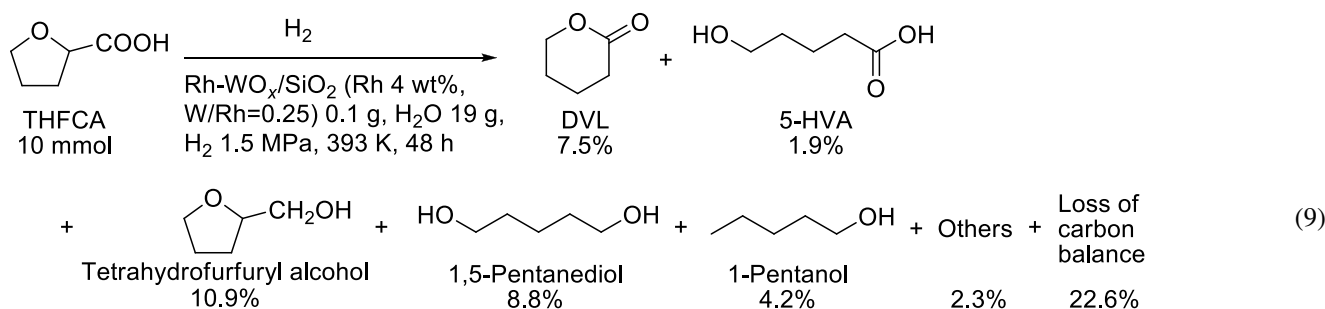
surface, and the interface site becomes catalytically active. The C–O bond neighboring to the terminal –CH$_2$OH group is selectively dissociated, as exemplified by the transformation of tetrahydrofurfuryl alcohol to 1,5-pentanediol (Eq. 8). If the same position (1,2-position of the tetrahydrofuran ring) in THFCA is dissociated, 5-HVA will be produced.

$$\overset{\text{O}}{\diagdown}\text{CH}_2\text{OH} + \text{H}_2 \xrightarrow[\substack{\text{Rh-MoO}_x \text{ or} \\ \text{Rh-ReO}_x \text{ or} \\ \text{Ir-ReO}_x \text{ or} \\ \text{Pt-WO}_x}]{} \text{HO}\diagup\diagdown\diagup\text{OH} \tag{8}$$

However, these catalysts also have activity in hydrogenation of carboxylic acids. Our group [69] tested various SiO$_2$-supported bimetallic catalysts composed of noble metal (Rh, Pd, Pt, Ru and Ir) and groups 6–7 metal oxide (MoO$_x$, ReO$_x$ and WO$_x$) to C–O hydrogenolysis of THFCA. SiO$_2$ is a typical support for these bimetallic catalysts because the interaction between SiO$_2$ and the supported metal or metal oxide is weak and does not interfere with the formation of interface site between the supported species. The combination of Rh and WO$_x$ shows the highest ratio of formation amount of C–O hydrogenolysis products (DVL + 5-HVA) to that of carboxylic acid hydrogenation products (tetrahydrofurfuryl alcohol, 1,5-pentanediol and 1-pentanol). MoO$_x$ and ReO$_x$ species are known to have activity or promotion ability in carboxylic acid hydrogenation, especially when combined with Rh, and these characters lower the formation amount ratio of C–O hydrogenolysis products to carboxylic acid hydrogenation products

Comparison with Systems Using Other Biomass-Derived Substrates

Among the potential reduction products from FCA or FDCA with retention of the carboxyl groups, adipic acid is by far the most used chemical in industry. Adipic acid is currently manufactured from petroleum by hydrogenation of benzene to cyclohexane, aerobic catalytic oxidation of cyclohexane to ketone-alcohol (K-A) oil, and oxidation of K-A oil to adipic acid with nitric acid as the oxidant [76]. Adipic acid is mainly used as a monomer of polyamide, and the global production amount is in the order of 10^6 t/year. Because of the enormous use of petroleum, hydrogen and nitric acid in the current process, the production of adipic acid from biomass has been intensively investigated in these days. Other production methods of adipic acid from biomass include (i) conversion of hydrocarbons produced by BTL (biomass to liquid; combination of biomass gasification and Fischer–Tropsch synthesis) [77] in petrochemical processes, (ii) production of K-A oil by reduction of biomass pyrolysis oil (bio-oil) [78–83], (iii) direct production of adipic acid by fermentation [84], (iv) hydrodeoxygenation of sugar acids produced by oxidation of sugars [85–92], (v) extension of carbon chain of C5 biomass-derived platform chemicals such as γ-valerolactone by hydroformylation or carboxylation [93–96], and (vi) oxidative cleavage of 1,2-difunctionalized cyclohexanes produced by reduction of bio-oil [97–100]. Low yield from raw biomass (methods (i), (ii), (iii) and (vi)) and large number of steps (methods (i), (ii),

(v) and (vi)) are the main problems of these methods. The FDCA-based systems are highly competitive to these systems except (iv) in these views. The sugar-acid-based system (iv) has several similarities to the FDCA-based systems: hexoses such as glucose and cellulose are the raw biomass; the consumption amount of hydrogen in the process is the same (4 equiv.), and the whole process is composed of two or three steps from sugars. The advantages of the FDCA-based systems are that FDCA can be more easily separated and handled than sugar acids and that large-scale production of FDCA will be realized because FDCA itself can be used as a monomer of PEF resin.

5-HVA is an ω-hydroxycarboxylic acid and can be a monomer of resin [101]. The conventional production method of 5-HVA or DVL is the oxidation or dehydrogenation of 1,5-pentanediol [102]. 1,5-Pentanediol can be produced from glutaric acid [103], which is a by-product of adipic acid [104], and 1,5-pentanediol can be also produced from biomass via furfural [39–41]. Another biomass-based production method of 5-HVA or DVL is Baeyer–Villiger oxidation of cyclopentanone [105–108], which can be also produced by reduction of furfural involving Piancatelli rearrangement [4–7, 109]. Production of 1,5-pentanediol from furfural requires larger amount of hydrogen (4 equiv.) than the FCA reduction to 5-HVA or DVL (3 equiv.). Baeyer–Villiger oxidation requires a peracid or H_2O_2 as a stoichiometric oxidant. The FCA-based method has superiority to these two methods in view of the reactant cost. The product from FDCA in the same type of reaction, 2-hydroxyadipic acid, has not been regarded as the target of large-scale productions.

Valeric acid is expected to be used in the ester form as fuel additives [110–112]. The main interest in the production of valeric acid or valerates focuses on the production from levulinic acid. Levulinic acid is a very important platform chemical synthesized from sugars or lignocellulose by the treatment with hot acidic water [113, 114]. γ-Valerolactone, which is formed by hydrogenation and dehydration of levulinic acid, is an intermediate of valeric acid production. The production of γ-valerolactone from levulinic acid is relatively easy over simple metal catalysts, and the production of valeric acid from γ-valerolactone uses the combination of metal and acid catalysts. Recently, one-pot systems using the combination of metal and acid catalysts have been reported with excellent yields (> 90%) of valeric acid or valerate from levulinic acid [111, 112, 115]. The conversion requires two equiv. of hydrogen, and the production of levulinic acid from biomass does not require expensive reagent. The FCA-based route is not advantageous to levulinic acid-based method in view of the reactant cost. Strong merit is necessary to select the FCA-based route, for example, the applicability of the gas-phase flow systems.

Conclusions and Outlook

2-Furancarboxylic acid (FCA) and 2,5-furandicarboxylic acid (FDCA) are stable oxidation products of furfural and 5-hydroxymethylfurfural (HMF), which are very important and versatile platform chemicals in lignocellulose conversions, and therefore, FCA and FDCA can be also regarded as platform chemicals. In particular, because FDCA itself has been regarded as a monomer of a promising biomass-derived resin polyethylene 2,5-furandicarboxylate (PEF), large amount of inexpensive FDCA with high purity will be available when PEF is industrialized in a large scale. The important target products from FCA and FDCA are carboxylic acids because the reduction products of carboxyl groups in FCA and FDCA can be directly produced from furfural or HMF. In particular, 5-hydroxyvaleric acid (5-HVA) and adipic acid, which are the reduction products from FCA and FDCA, respectively, are promising targets in view of the importance of products and the comparison with other production methods. 5-HVA or its derivatives such as δ-valerolactone (DVL) and 5-hydroxyvalerates are produced from FCA over simple Pt catalysts. Adipic acid, which is a very important monomer in industry, is produced from FDCA via one-pot reaction or two-step method. One-pot reaction uses the combination of Pt with modifier (MoO_x) or strong acid (niobium oxide). The yield of adipic acid is low at present. Two-step method is composed of Pd-catalyzed hydrogenation to tetrahydrofuran-2,5-dicarboxylic acid (THFDCA) and hydrodeoxygenation with iodide ion. Good yield (> 85%) is obtained, although the capital cost might be higher for the two-step method. Other potentially useful reduction products from FCA and FDCA include valeric acid and 2-hydroxyadipic acid.

The studies for the reduction of FCA or FDCA with retention of the carboxyl groups have been carried out only in very recent days (published in 2010 or later) except an old report with PtO_2 (Adams catalyst) and reports for simple ring-hydrogenation systems. The number of research groups engaged in the studies of FCA or FDCA reductions is limited at present, considering that furfural and HMF reductions have been very intensively investigated by many research groups. The information of the reaction mechanisms and the structure of active centers of the catalysts is also limited, especially for the Pt-catalyzed C–O hydrogenolysis of the furan ring. We hope that more researchers will be interested in the FCA or FDCA conversions, uncovering the whole chemistry and developing more efficient systems.

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