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Submission date: 01-Aug-2019 12:37PM (UTC+0700)

Submission ID: 1156701369

File name: A.1.c.08_Green_Chem.,_2019,_21,_2307_2315.pdf (1.54M)

Word count: 8097

Character count: 37696



Cite this: *Green Chem.*, 2019, **21**, 2307

One-pot selective conversion of C5-furan into 1,4-pentanediol over bulk Ni–Sn alloy catalysts in an ethanol/H₂O solvent mixture†

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Inexpensive bulk Ni–Sn alloy-based catalysts demonstrated a unique catalytic property in the selective conversion of C5-furan compounds (e.g., furfuraldehyde (FFald), furfuryl alcohol (FFalc), and 2-methylfuran (2-MTF)) in an ethanol/H₂O solvent mixture and selectively produced 1,4-pentanediol (1,4-PeD) in a one-pot reaction. The synergistic actions between the bulk Ni–Sn alloy catalyst, hydrogen gas, and the hydroxylated H₂O or ethanol/H₂O solvents are believed to play a prominent role in the catalytic reactions. Bulk Ni–Sn alloy catalysts that consisted of Ni₃Sn or Ni₃Sn₂ alloy phases allowed an outstanding yield of 1,4-PeD up to 92% (from FFald), 67% (from FFalc), and 48% (from 2-MTF) in ethanol/H₂O (1.5 : 2.0 volume ratio) at 433 K, 3.0 MPa H₂ and 12 h. As the reaction temperature increased to 453 K, the yield of 1,4-PeD slightly decreased to 87% (from FFald), whereas it slightly increased to 71% (from FFalc). The bulk Ni–Sn alloy catalysts were reusable without any significant loss of selectivity.

Received 16th December 2018,
Accepted 12th March 2019

DOI: 10.1039/c8gc03938k

rsc.li/greenchem

Introduction

The catalytic conversion of biomass-derived feedstock into high-value chemicals and fuels using bimetallic heterogeneous catalysts has received increasing attention in recent decades.¹ Furfuraldehyde (FFald) and its common derivatives (e.g., furfuryl alcohol (FFalc), tetrahydrofurfuryl alcohol (THFalc), and 2-methylfuran (2-MTF)) are most promising biorefinery platform C5-furanic compounds, which can be used as solvents, plasticisers, monomers in the production of resins, in the agrochemicals industry, or as gasoline blends.^{1b–d} FFald and its derivatives can also be transformed into α,ω -diols such as 1,2-, 1,4- or 1,5-pentanediol (PeD), which can be used as a component of disinfectants, as an ingredient of various cosmetic products, and as monomers of polyesters and polyurethanes.²

In previously published studies, bimetallic copper chromite was the first industrial catalyst for the synthesis of α,ω -diols through the catalytic conversion of FFald or FFalc under harsh

reaction conditions (448–573 K, 10–25 MPa H₂, in ethanol). Under these harsh reaction conditions, the maximum yields of diols were 30% (1,5-PeD) and 40% (1,2-PeD), and no 1,4-PeD was obtained.³ Xu *et al.* reported the direct conversion of FFald into 1,2-PeD (16% yield) and 1,5-PeD (35% yield) in ethanol over the spinel-type Pt/CoAl₂O₄ catalyst and gave only a 6.2% yield of 1,4-PeD at 413 K, 1.0 MPa H₂ for 24 h.⁴ Tomishige and co-workers reported the hydrogenolysis of FFald in water using a Rh–Ir–ReO_x/SiO₂ catalyst and produced only a 13% yield of 1,4-PeD at 393 K after 24 h.⁵ The yield of 1,4-PeD considerably increased (ca. 30% yield) when the Pd–Ir–ReO_x/SiO₂ catalyst was employed under the same reaction conditions.⁶ Despite extensive research,^{1e,3–6} only catalytic hydrogenation of levulinic acid (LA), ethyl levulinate, or γ -prolactone (GVL) could afford a significant yield of 1,4-PeD in the presence of heterogeneous noble metal-based catalysts such as Ru or in Mo-modified supported Ru, Pt, and Rh systems. Moderate to good yields of 1,4-PeD (70–95%) were achieved over those catalysts under severe reaction conditions (e.g., >473 K and 6–15 MPa H₂).⁷ Therefore, the development of new transition metal-based heterogeneous catalyst systems for the effective synthesis of α,ω -diols, especially 1,4-PeD, from C5-furan compounds (e.g., FFald, FFalc, and 2-MTF) is of great interest and is a highly challenging work.

The synthetic protocol of 1,4-PeD production from the FFald platform was first pioneered by Leuck *et al.*⁸ They claimed that 1,4-PeD (40%) and 1,2,5-(1,4,5-)pentanetriol (~50%) were obtained from FFald in the presence of the

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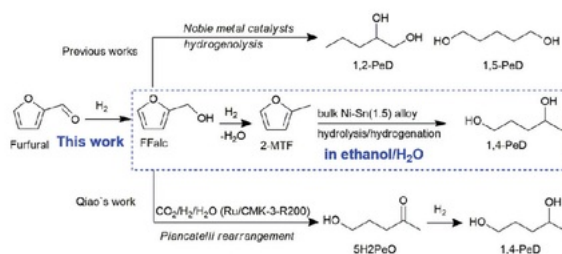
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†Electronic supplementary information (ESI) available: General procedures, characterisation of catalysts, evaluation of various bulk Ni–Sn(1.5) catalysts, ¹H-NMR and ¹³C-NMR of the mixture and the isolated products. See DOI: 10.1039/c8gc03938k

RANEY®Ni catalyst, hydrogen gas (H₂), hydroxylated solvents such as H₂O, alcohols (methyl, ethyl, or butyl alcohols) or alcohol/H₂O mixtures, and trace amounts of glacial acetic acid. Schniepp *et al.* reported the catalytic conversion of 2-MTF in the presence of the reduced nickel on Celite (Ni/Celite) in a 1,4-dioxane–H₂O solvent mixture with trace amounts of formic acid at 8.3 MPa and 423 K for 8 h, affording a mixture of 2-MTHF and 1,4-PeD with yields of 36% and 62%, respectively. The authors proposed that 1,4-PeD was formed through hydrolysis–hydrogenation of the furan ring in the form of either open-chain (5-hydroxy-2-pentanone, 5H2PeO) or cyclic structure (2-methyl-2-hydroxy tetrahydrofuran, 2H2MTHF) intermediates.⁹ Most recently, Qiao and co-workers reported the catalytic conversion of FFald to 1,4-PeD over bifunctional Ru/CMK-3 catalysts under CO₂/H₂ pressure in H₂O at 353 K. They proposed that a multi-step catalytic reaction of FFald *via* an acid-catalysed Piancatelli rearrangement of the furan ring generated 4-hydroxy-2-cyclopentanone (4-HCP) which subsequently converted to an acetopropyl alcohol (AP or 5H2PeO) and 1,4-PeD. Although the reaction time was extended to 30 h, the highest yield of 1,4-PeD was 90%.¹⁰ However, explanations regarding the reaction mechanism of the formation of 5H2PeO or 1,4-PeD during the catalytic reactions, selectivity of the catalyst system, and relatively high yields of undesired by-products are still unclear; moreover, the use of noble metal Ru-based catalysts is expensive in view of industrial applications.

In our previously published studies of bimetallic Ni–Sn alloys consisting of the Ni₃Sn₂₈ or Ni₃Sn₂ alloy, both bulk and supported catalysts showed high activity and selectivity during the hydrogenation of FFald to FFalc^{11,12} and in the hydrogenation of biomass-derived levulinic acid to γ -valerolactone (GVL) in water (99% yield) without the formation of 1,4-PeD.^{13a,b} Additionally, TiO₂- and γ -Al₂O₃-supported Ni₃Sn₂ alloy catalysts exhibited high activity in the selective hydrogenation of dodecanoic acid to dodecane-1-ol with a high yield (*ca.* 93%) at 433 K and 3.0 MPa H₂ after 12 h.^{13c}

In this paper, we report our extended studies on the catalytic hydrogenation of FFald in H₂O or alcohol/H₂O instead of alcohol solvents. The hydrogenation reaction of FFald in alcohol solvents selectively yielded 90–95% FFalc. Surprisingly, the catalytic hydrogenation reaction of FFald in H₂O or ethanol/H₂O selectively gave 1,4-PeD, and a remarkable yield of this product was obtained (up to 92%). We propose that the formation of 1,4-PeD involved (1) C=O hydrogenation of FFald to rapidly produce FFalc, followed by (2) dehydration–hydrogenation of FFalc on the surface of the Ni–Sn alloy to form 2-MTF or 2-MTHF and (3) hydrolysis–hydrogenation of the unsaturated furan ring (C=C) to give 1,4-PeD selectively (Scheme 1). Our innovative strategy offers the upgrading of renewable biomass-derived C5-furanic compounds into a high added-value product of 1,4-PeD and utilises an inexpensive bulk Ni–Sn alloy catalyst in the environmentally friendly solvent of H₂O or ethanol/H₂O *via* hydrolysis/hydrogenation of FFald, FFalc, or 2-MTF; this reaction is substantially distinct from the established mechanism in the formation of 1,2-PeD and 1,5-PeD as previously reported.^{3–6,14,15}



Scheme 1 Possible routes of the catalytic transformation of FFald into α,ω -diols.

Results and discussion

Catalyst characterisation

Six classes of bulk nickel–tin alloy catalysts (denoted Ni–Sn(*x*), *x* = Ni/Sn feeding ratio) were easily synthesised *via* hydrothermal treatment of solutions that contained Ni and Sn species⁴ with various Ni/Sn ratios (*ca.* 4.0; 3.0; 2.0; 1.5; 1.0; and 0.75) at 423 K for 24 h, followed by H₂ treatment at 673 K for 1.5 h, as described in previous reports.¹¹ The physicochemical properties of the bulk Ni–Sn alloys are summarised in Table S1 in ESI.† Methods for catalyst preparation, the physicochemical properties²⁶ *e.g.*, XRD, ICP-AES, N₂ adsorption (BET method), H₂- and CO-chemisorption, and NH₃-TPD, catalytic activity tests and product analyses are described in the ESI.†

Based on the ICP-AES analyses, the compositions of the bulk Ni–Sn alloys were approximately equivalent to the feeding ratios of each precursor and were reflected in the composition of each Ni–Sn alloy phase (Table S1,† entries 1–3).^{11a} The major alloy components of Ni–Sn(4.0) and Ni–Sn(3.0) were Ni₃Sn, whereas those of Ni–Sn(2.0), Ni–Sn(1.5), and Ni–Sn(1.0) were Ni₃Sn₂, and that of Ni–Sn(0.75) was Ni₃Sn₄ (Fig. S1 in ESI.†).^{11,16} The results of the simulated calculations using the multi-Rietveld analysis program LH-Riet in the Reitica software package¹⁷ for each of the XRD patterns of the synthesised bulk Ni–Sn alloy catalysts confirmed that the estimated proportions of the major alloy components were approximately 66% Ni₃Sn for Ni–Sn(3.0), 91% Ni₃Sn₂ for Ni–Sn(1.5), and 87% Ni₃Sn₄ for Ni–Sn(0.75) after the treatment with H₂ at 673 K.³³ *e* profiles are shown in Fig. S3–S5 in the ESI.†^{11a} The Ni K-edge X-ray absorption near-edge structure (XANES) spectra of the fresh Ni–Sn(3.0), Ni–Sn(1.5), and Ni–Sn(0.75) alloy catalysts revealed a shoulder peak at 328 V, and the identical photon energy for Ni foil indicated that the Ni atoms in the bulk Ni–Sn alloys were Ni⁰.¹⁸ The absorption peaks were also observed at approximately 8340 eV, whereas the intensity of these peaks increased with decreasing Ni/Sn ratios, that is, Ni–Sn(3.0) < Ni–Sn(1.5) < Ni–Sn(0.75). The three kinds of bulk Ni–Sn alloys each exhibited characteristic Ni K-edge XANES spectra (Fig. S2 in the ESI.†). The H₂ uptake decreased as the Sn content increased (decreasing Ni/Sn ratio), whereas the H₂ uptake of Ni₃Sn was greater than those of Ni₃Sn₂ and Ni₃Sn₄.¹⁸ The acid sites of the catalysts were probed with NH₃-TPD, and the

results are shown in Fig. S6 and Table S2 in the ESI.† The acid density decreased as the Sn loading amount increased, as indicated by the molar ratio of Ni/Sn. Ni-Sn(3.0) had the maximum acid density ($473 \mu\text{mol g}^{-1}$), followed by Ni-Sn(1.5) ($276 \mu\text{mol g}^{-1}$) and Ni-Sn(0.75) ($173 \mu\text{mol g}^{-1}$). The acidity of R-Ni/AlOH was $474 \mu\text{mol g}^{-1}$, and those of the unmodified RANEY® Ni¹⁹ and blank $\gamma\text{-Al}_2\text{O}_3$ ²⁰ was $195 \mu\text{mol g}^{-1}$ and $180 \mu\text{mol g}^{-1}$, respectively (entries 5 and 6, Table S2, ESI†). The acidity emerges mainly from Ni species and depends on the atomic arrangement formed in the bimetallic Ni-Sn alloy crystals.^{18,21}

Catalytic reactions

Effect of solvent. In the first 9 experiments, we studied the effect of solvents used in the catalytic conversion of FFald in the presence of the bulk Ni-Sn(1.5) alloy, and the results are summarised in Table 1.

As expected, in alcoholic solvents such as methanol, ethanol, 1-propanol, and 2-propanol, or in 1,4-dioxane (classified as a cyclic ether), the yields of FFald were 90–95% with a small amount of THFalc and 1,5-PeD when the reaction was complete (entries 1–5). In alcohols or 1,4-dioxane, the hydrogenation reactions of C=O selectively dominated to produce FFald (yield up to 95%). Only a very small amount of FFald was over-hydrogenated to THFalc, dehydrated to 2-MTF, subsequently hydrogenated to 2-MTHF, or hydrogenolysed to 1,5-PeD. The further hydrogenation/hydrogenolysis of FFald is inhibited in organic solvents. However, a remarkable difference was observed in H₂O, where the products were distributed as 1,4-PeD (60% yield), 1,2-PeD (10% yield), and 2H2MTHF (30% yield) (entry 6), indicating that water can enhance the ring opening of FFald or FFald, which is in accordance with

the work reported by Zhang *et al.*^{22a} In ethanol/H₂O (2.5 : 1.0 volume ratio), the yield of 1,4-PeD increased significantly to 71%, while the yield of 2H2MTHF was only 14%, which drastically diminished by approximately three times (entry 7). An outstanding high 1,4-PeD yield (92%) with a very low remaining yield of 1,5-PeD and 2H2MTHF (2% and 6%, respectively) was achieved in ethanol/H₂O (1.5 : 2.0 volume ratio) (entry 8) (the ¹H and ¹³C NMR spectra of the crude yield and the isolated product of 1,4-PeD are shown in Fig. S7, S8, and S9, respectively, in the ESI†). The high yield of 1,4-PeD may be the result of the effective actions of the ethanol and H₂O solvent system, generating a significant interaction between the substrate (FFald), solvents, and the active surface of the catalyst, leading to the high yield of 1,4-PeD and inhibiting the C=C hydrogenation of the furan ring to THFalc.²² Moreover, the yield of 2H2MTHF drastically dropped to only 6% (entry 8). On the other hand, in ethanol/H₂O (1.0 : 2.5 volume ratio), the product distributions were very similar to the results of the H₂O solvent (entry 9). We also examined the catalytic reactions in 2-propanol/H₂O (1.5 : 2.0 volume ratio), methanol/H₂O (1.5 : 2.0 volume ratio), 1-propanol/H₂O (1.5 : 2.0 volume ratio) and 1,4-dioxane/H₂O (1.5 : 2.0 volume ratio) as solvents, and the main product was FFald (50–72% yield), followed by a low yield of 1,4-PeD (22–32%), 2H2MTHF (5–13%), and 1,5-PeD (3–8%) (entries 10–13). Only in the 1,4-dioxane/H₂O system did THFalc form (11% yield, entry 13), confirming that the solvent significantly inhibited C=C hydrogenation, as previously reported.^{11,12} Therefore, we conclude that the optimised solvent system for the catalytic conversion of FFald to 1,4-PeD using a bulk Ni-Sn alloy was ethanol/H₂O (1.5 : 2.0 volume ratio).

Table 1 Results of solvent screening for catalytic conversion of FFald to 1,4-PeD using the bulk Ni-Sn(1.5) alloy

Entry	Solvent ^a	Conversion ^b /%	Yield ^c /%						
			1,4-PeD	1,2-PeD	1,5-PeD	FFald	THFalc	2H2MTHF	2-MTHF
1	Methanol	100	0	0	0	90	7	0	3
2	Ethanol	100	0	0	2	92	3	0	3
3	2-Propanol	100	0	0	9	91	0	0	0
4	1-Propanol	100	0	0	0	90	5	0	5
5	1,4-Dioxane	100	0	0	2	95	1	0	2
6	H ₂ O	100	60	10	0	0	0	30	0
7	Ethanol/H ₂ O (2.5 : 1.0)	100	71	0	8	6	0	14	1
8	Ethanol/H ₂ O (1.5 : 2.0)	100	92	0	2	0	0	6	0
9	Ethanol/H ₂ O (1.0 : 2.5)	100	57	4	3	0	0	29	7
10	2-Propanol/H ₂ O (1.5 : 2.0)	100	25	0	3	72	0	0	0
11	Methanol/H ₂ O (1.5 : 2.0)	100	24	0	6	65	0	5	0
12	1-Propanol/H ₂ O (1.5 : 2.0)	100	32	0	5	60	0	3	0
13	1,4-Dioxane/H ₂ O (1.5 : 2.0)	100	22	0	8	46	11	13	0

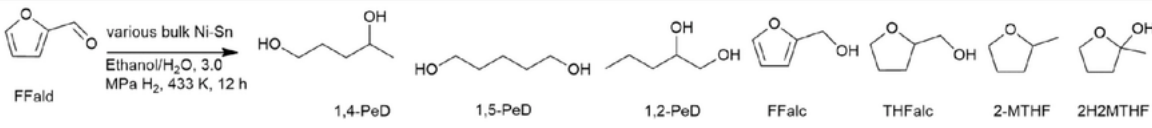
Reaction conditions: catalyst, 44 mg; substrate, 1.2 mmol; solvent, 3.5 ml; initial H₂ pressure, 3.0 MPa; 433 K; 12 h. ^a Values in parentheses are the alcohol/H₂O volume ratio. ^b Conversion of FFald was determined by GC analysis using an internal standard technique. ^c Yield of the product was determined by GC and GC-MS analyses using an internal standard technique. PeD = pentanediol. FFald = furfuryl alcohol. THFalc = tetrahydrofurfuryl alcohol. 2H2MTHF = 2-hydroxy-2-methyltetrahydrofuran. 2-MTF = 2-methylfuran. 2-MTHF = 2-methyltetrahydrofuran.

Differences in the product distribution of FFald hydrogenation in alcohols, H₂O, and alcohol/H₂O might be attributed to the presence of O-bonded water molecules to the C atom from the neighbouring -CH₂OH group and forming a new water species with one H atom of water being automatically transferred to the terminal OH group, as evidenced through the H₂¹⁸O isotopic trace experiments combined with the DFT calculations.^{22c} The oxidized tin (Sn^{IV}) slowly formed from metallic tin (Sn⁰)^{23,24} will react with H₂O to form SnO or Sn(OH). SnO or Sn(OH) in the Ni-Sn alloy catalyst might provide Brønsted acid sites similar to the Sn-OH species observed in Sn-OH/SBA15.^{25a} The autoprotolysis of alcohol/H₂O or 1,4-dioxane resulted in H₃O⁺ and ROH₂⁺ (called lyonium ions) and OH⁻ and RO⁻ (called lyate ions) *via* proton transfer from H₂O to the alcohol or 1,4-dioxane;^{25b} this process synergistically facilitated acid hydrolysis of the furan ring and subsequent hydrogenation reactions under H₂ atmosphere to produce 1,4-PeD.^{8-10,26} Hu *et al.* also suggested that the acid catalysis and hydrogenation reactions proceeded in parallel in the presence of the bulk Ni-Sn alloy.^{22b} In fact, the bulk Ni-Sn alloy possesses Brønsted acidity, as clearly indicated by the NH₃-TPD analyses (Fig. S6 and Table S2 in the ESI†).

Effect of the Ni/Sn molar ratio. To obtain insights into the Ni-Sn alloy formation, the catalytic performance of various synthesised bulk Ni-Sn alloy catalysts with different Ni/Sn molar ratios was investigated in the reaction under the same reaction conditions; the results are summarised in Table 2. A commercially available 5 wt% Pd/C,²⁷ RANEY®Ni,²⁸ RANEY®Ni supported on aluminium hydroxide (R-Ni/AlOH),²⁹ and Sn/AlOH³⁰ were also used as reference catalysts.

By using Ni-Sn(4.0) and Ni-Sn(3.0) catalysts with the major alloy phase of Ni₃Sn, 1,4-PeD yields of 64% and 70% were obtained, respectively (entries 1 and 2). 2-MTHF was also significantly obtained, indicating that the Ni₃Sn alloy is more active in the dehydration of FFalc under the reaction system (we have already studied this aspect, and it will be published in an upcoming report). Upon increasing the Sn portion in the Ni-Sn alloy as indicated by the Ni/Sn molar ratios in Ni-Sn(2.0), Ni-Sn(1.5), and Ni-Sn(1.0) catalysts with Ni₃Sn₂ as the major alloy phase, the 1,4-PeD yields were 77%, 92%, and 61%, respectively, and no THFalc formation was observed (entries 3-5). In contrast, only a 3% yield of 1,4-PeD was obtained over Ni-Sn(0.75) with a Ni₃Sn₄ alloy phase catalyst (entry 6). These results are in very good agreement with the results of FFald hydrogenation over both bulk and supported Ni-Sn(1.5) alloy catalysts that consisted of the Ni₃Sn₂ phase in iso-propanol, as reported previously.^{11,12} The formation of the Ni-Sn alloy phases in Ni-Sn(2.0) and Ni-Sn(1.5) might play an important role in the effective Ni-Sn species, which can be rationally related to be Ni₃Sn₂, as was readily detected by XRD.^{11,17,21} On the other hand, RANEY® Ni (in a slurry prior to addition to prevent oxidation or pyrophoric reaction in air) afforded a 98% yield of THFalc and 2% yield of 1,5-PeD (entry 7). A similar result was also obtained upon a commercial Pd/C (5 wt% Pd) catalyst with a 90% yield of THFalc, 6% yield of 1,5-PeD, and 4% yield of 2-MTHF (entry 8). By using the R-Ni/AlOH catalyst, mixtures of 1,4-PeD (25%), 1,5-PeD (5%), THFalc (59%), and 2H2MTHF (11%) were obtained and may be dimerisation products of furfuryl alcohol (14%) according to GC and GC-MS data³¹ (entry 9). In addition, Sn/AlOH was

Table 2 Results of catalytic conversion of FFald to 1,4-PeD using various bulk Ni-Sn alloys



Entry	Catalyst (major phase) ^a	Conversion ^b /%	Yield ^c /%						
			1,4-PeD	1,2-PeD	1,5-PeD	FFalc	THFalc	2H2MTHF	2-MTHF
1	Ni-Sn(4.0) (Ni ₃ Sn)	100	64	0	1	0	2	25	8
2	Ni-Sn(3.0) (Ni ₃ Sn)	100	70	0	3	0	0	15	12
3	Ni-Sn(2.0) (Ni ₃ Sn ₂)	100	77	0	0	0	0	23	0
4	Ni-Sn(1.5) (Ni ₃ Sn ₂)	100	92	0	2	0	0	6	0
5 ^d	Ni-Sn(1.0) (Ni ₃ Sn ₂)	100	61	0	0	0	0	33	0
6 ^e	Ni-Sn(0.75) (Ni ₃ Sn ₄)	100	3	5	3	0	7	42	0
7	RANEY® Ni (slurry)	100	0	0	2	0	98	0	0
8	Pd/C	100	0	0	6	0	90	0	4
9	R-Ni/AlOH	100	25	0	5	0	45	11	0
10	Sn/AlOH	0	0	0	0	0	0	0	0

Reaction conditions: Catalyst, 44 mg; substrate, 1.2 mmol; solvent, ethanol/H₂O, 3.5 ml (1.5:2.0 volume ratio); initial H₂ pressure, 3.0 MPa; 433 K; 12 h. ^a Values in parentheses are the Ni/Sn molar ratio according to the ICP-AES analysis, and the identified major alloy phase was determined from crystallographic databases.¹⁶ ^b Conversion of FFald was determined by GC analysis using an internal standard technique. ^c Yield of the product was determined by GC and GC-MS analyses using an internal standard technique. ^d Unknown product may be the condensation product of FFald (approximately 5% according to GC-MS data). ^e Unknown product may be tetrahydrofurfuryl aldehyde (approximately 40%, according to GM-MS data). PeD = pentanediol. FFalc = furfuryl alcohol. THFalc = tetrahydrofurfuryl alcohol. 2H2MTHF = 2-hydroxy-2-methyltetrahydrofuran. 2-MTF = 2-methylfuran. 2-MTHF = 2-methyltetrahydrofuran.

not active in the conversion of FFald under the same reaction conditions (entry 10).

Effect of reaction temperature. The influence of reaction temperature on the product distributions in the catalytic conversion of FFald over the bulk Ni–Sn(1.5) alloy is shown in Fig. 1.

It could be expected that FFald was converted selectively to FFalc (90–87% yield) at a lower temperature (393–403 K) within the time course of the reaction (12 h), accompanied by the formation of THFalc (5–10%), 1,4-PeD (4%), 1,2-PeD (1%), and 1,5-PeD (3%). At a reaction temperature below 413 K, the reaction was predominated by C=O hydrogenation of FFald, producing a high yield of FFalc. As the temperature increased to 413 K, a remarkable yield of 1,4-PeD was obtained (61%), while the remaining FFalc formed THFalc, 1,2-PeD, and 1,5-PeD, which were also observed. In this case, the formation of 2H2MTHF was also observed for the first time. At temperatures of 423 K and 433 K, outstanding yields of 1,4-PeD (*ca.* 87% and 92%, respectively) were achieved, while the 1,5-PeD and 2H2MTHF yields remained unchanged. On the other hand, FFalc and THFalc completely disappeared, suggesting that after C=O hydrogenation of FFald to FFalc, the hydrolysis and hydrogenation of the furan ring occurred predominantly and simultaneously and produced a high yield of 1,4-PeD. At two later reaction temperatures of 443 K and 453 K, the 1,4-PeD yield slightly decreased to 75% and 69%, respectively, while the yield of 2H2MTHF significantly increased to 12% (443 K) and 21% (453 K). In addition, 2-MTHF was observed at that temperature as a result of over-hydrogenation of 2-MTF. It is well known that the formation of 2-MTF following furan ring hydrogenation to 2-MTHF proceeded efficiently during the catalytic conversions of FFald or FFalc over mono- and bi-

metallic catalysts at a relatively higher temperature (Fig. 1) or at a low pressure of H₂ (Fig. 2).

Effect of initial H₂ pressure. The effect of initial H₂ pressure on the product distributions in the catalytic conversion of FFald over the bulk Ni–Sn(1.5) alloy is shown in Fig. 2.

At the initial H₂ pressure of 0.5–1.0 MPa, the main product was THFalc, followed by small amounts of 2-MTHF and 1,2-PeD. As the initial H₂ pressure increased to 1.5 MPa, the yield of THFalc significantly decreased, while those of 2-MTHF, 1,2-PeD, and 1,5-PeD remained unchanged. In this case, 1,4-PeD was observed at the first time concomitantly with the increase in the 2H2MTHF yield. At the initial H₂ pressure of 2.0–2.5 MPa, a remarkable yield of 1,4-PeD (up to 78%) was obtained with the remaining yields of 1,5-PeD (5–9%), THFalc (11%), and 2H2MTHF (2%). A remarkable yield of 1,4-PeD (92%) was achieved at an initial H₂ pressure of 3.0 MPa, which then decreased slightly to 87% and 77% at 3.5 and 4.0 MPa, respectively. Therefore, it can be concluded that the effective catalytic conversion of FFald to 1,4-PeD can be achieved at an initial H₂ pressure of 3.0 MPa, which was used as the optimised initial H₂ pressure for the subsequent catalytic reactions.

Kinetic profiles. The reaction profiles of the catalytic conversion of FFald over bulk Ni–Sn(1.5) alloy catalysts were obtained at two different temperatures of 433 K and 453 K, and the plot is shown in Fig. 3.

At 433 K, the yield of FFalc was 81%, accompanied by 1,5-PeD, THFalc, and 2H2MTHF with yields of 2%, 7%, and 10%, respectively; no formation of 1,4-PeD was observed at 100% conversion of FFald after a reaction time of 2 h. In contrast, at 453 K and a reaction time of 2 h, representing reaction conditions that were almost identical to our previous reports,^{11,12} a 96% yield of FFalc was achieved with a small amount of

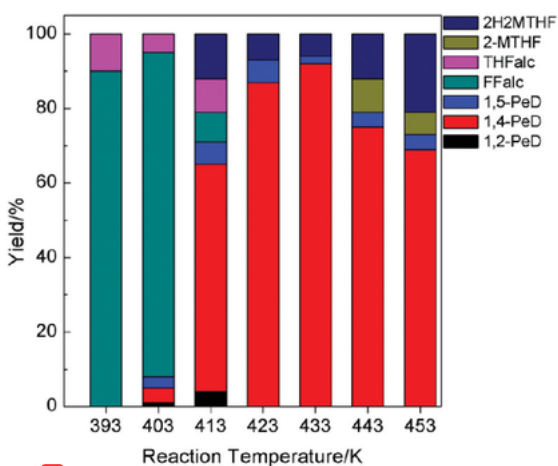


Fig. 1 Effect of reaction temperature on the product distribution (yield) in the catalytic conversion of FFald over the bulk Ni–Sn(1.5) alloy. Reaction conditions: catalyst, 44 mg; substrate, 1.2 mmol; solvent, ethanol/H₂O, 3.5 ml (1.5 : 2.0 volume ratio); initial H₂ pressure, 3.0 MPa; 12 h.

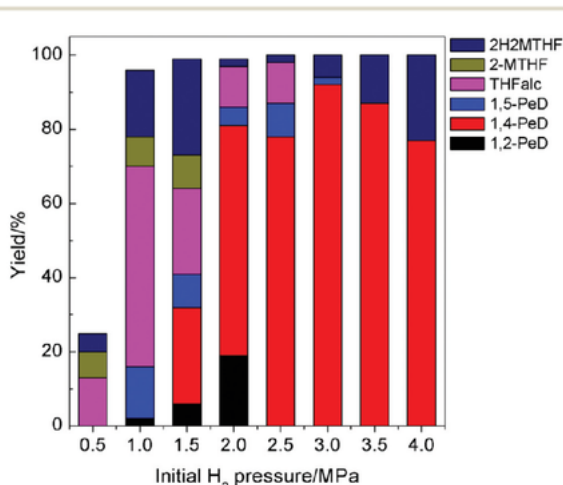


Fig. 2 Effect of initial H₂ pressure on the product distribution (yield) in the catalytic conversion of FFald over the bulk Ni–Sn(1.5) alloy. Reaction conditions: catalyst, 44 mg; substrate, 1.2 mmol; solvent, ethanol/H₂O, 3.5 ml (1.5 : 2.0 volume ratio); 12 h.

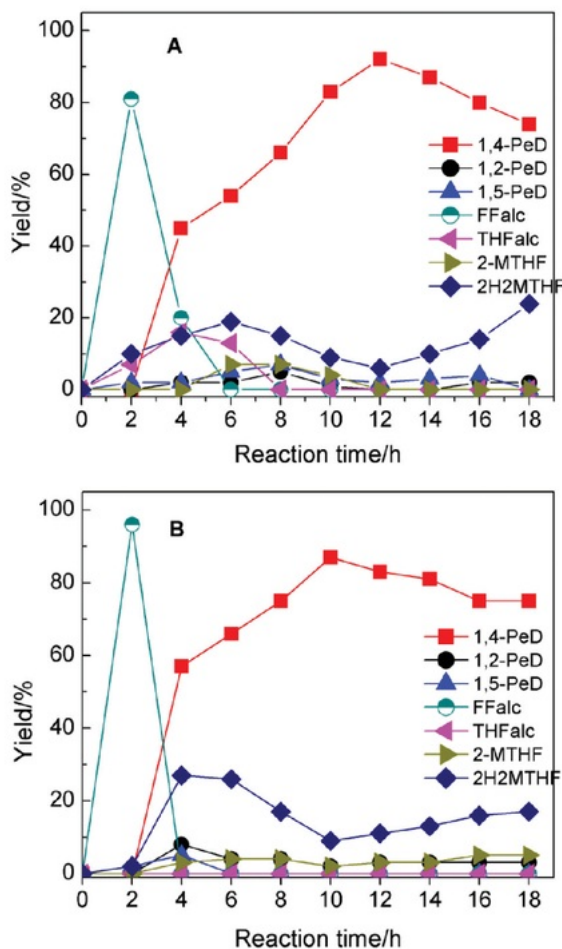


Fig. 3 Kinetic profiles of catalytic conversion of FFald into 1,4-PeD in the presence of the bulk Ni–Sn(1.5) alloy at different reaction temperatures of (A) 433 K and (B) 453 K. Reaction conditions: catalyst, 44 mg; substrate, 1.2 mmol; solvent, ethanol/H₂O, 3.5 ml (1.5 : 2.0 volume ratio); initial H₂ pressure, 3.0 MPa.

1,5-PeD (2%) and 2H₂MTHF (2%) and without the formation of 1,4-PeD. However, there are differences in the remaining yield of FFalc between 433 K and 453 K when the reaction time was prolonged. At 433 K, the FFalc yield drastically dropped to 20%, while that of THFalc nearly doubled (from 7% to 16%), as did the yield of 2H₂MTHF at a reaction time of 4 h, and FFalc was not detected after a reaction time of 6 h. In addition, the 1,2-PeD, 1,5-PeD, and 2-MTHF yields were almost constant within the time course of the reaction (Fig. 3A). At 453 K, FFalc totally disappeared with the concomitant formation of 1,4-PeD (57% yield) after 4 h, accompanied by the generation of 1,2-PeD, 2MTHF, and 2H₂MTHF as the observed reaction products (Fig. 3B). At both 433 K and 453 K, the formed FFalc was consumed rapidly as the yield of 1,4-PeD increased simultaneously to reach maximum values of 92% and 87% at different reaction times of 12 h and 10 h, respectively. Then, yields of 1,2-

PeD, 1,5-PeD, THFalc, 2-MTHF, and 2MTHF were almost constant after the prescribed reaction times. Roughly, the reaction rate of FFalc formation, as the elementary step of the reaction, was calculated at a reaction time of 120 min (2 h) at two different reaction temperatures of 433 K and 453 K. At 433 K, the reaction rate of FFalc formation was 7.83×10^{-3} mmol min⁻¹, while at 453 K, it was 8.68×10^{-3} mmol min⁻¹.

To complete the explanation of the further reaction of FFalc during the kinetic profiles, we carried out the catalytic reaction of FFalc over the bulk Ni–Sn(1.5) alloy under identical reaction conditions; the results are summarised in Table S3 in ESI† At 433 K, 100% conversion of FFalc afforded a 67% yield of 1,4-PeD, 20% yield of THFalc, 6% yield of 2H₂MTHF, and trace 1,5-PeD (entry 1, Table S3, ESI†). At a lower temperature, C=C hydrogenation is favourable, as indicated by the relatively higher yield of THFalc. On the other hand, 71% 1,4-PeD, 2% 1,5-PeD, and 26% 2H₂MTHF yields were quantitatively obtained when the reaction temperature was 453 K (entry 2, Table S3, ESI†).³³

Reusability test. A reusability test was performed on the bulk Ni–Sn(1.5) alloy catalyst, and the results are shown in Fig. 4.

The bulk Ni–Sn(1.5) alloy used was easily separated by either simple centrifugation or filtration after the reaction. The recovered catalyst was reactivated by H₂ at 673 K for 1.5 h prior to use in the next reaction run. The yield of 1,4-PeD on the reused catalyst decreased slightly after the second reaction run, but the activity was maintained for at least four consecutive runs (Fig. 4). The amounts of metal that leached into the reaction solution were analysed by ICP-AES and were found to be 1.5 mol% (Ni) and 5.0 mol% (Sn) after the fourth run. The XRD patterns of the recovered Ni–Sn(1.5) alloy before and after

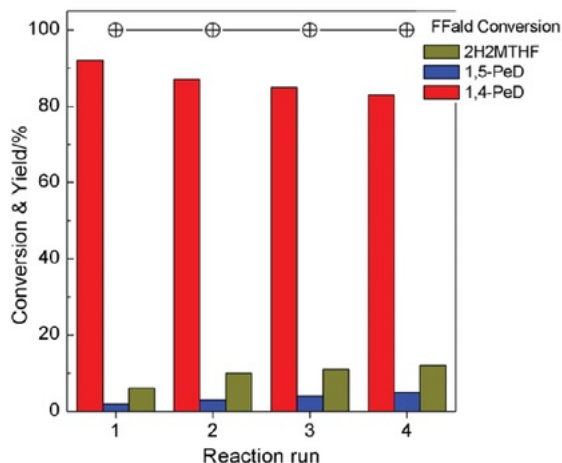


Fig. 4 Reusability test for the bulk Ni–Sn(1.5) alloy catalyst in the conversion of FFald to 1,4-PeD. Reaction conditions: catalyst, 44 mg; substrate, 1.2 mmol; solvent, ethanol/H₂O, 3.5 ml (1.5 : 2.0 volume ratio); initial H₂ pressure, 3.0 MPa; 12 h.

the H₂ treatment appeared to indicate that no change in the alloy structure occurred (Fig. S12, ESI†).

Catalytic reaction of FFald-derived molecules and plausible reaction mechanism. The catalytic conversion of 2-MTF, THFalc, 2-MTHF and 5H2PeO in the presence of the bulk of Ni-Sn(1.5) catalyst under the same reaction conditions was also carried out, and the results are summarised in Table S3 in the ESI.†³³ The catalytic reactions of 2M4,5DHF and 2H2MTHF were not performed due to the limitation of availability. Unexpectedly, 2-MTF afforded a 48% yield of 1,4-PeD, 37% yield of 2MTHF and a small amount of 2H2MTHF (7%) at 93% conversion (entry 3). The catalytic reaction of THFalc, 2-MTHF and γ -valerolactone (GVL) did not proceed in the presence of the bulk and robust structure of the Ni-Sn(1.5) alloy under the same reaction conditions, even after the reaction time was extended to 48 h (entries 4–6). In addition, hydrogenation of levulinic acid produced a >99% yield of GVL as expected and reported previously,¹³ and no 1,4-PeD product was detected (entry 7).

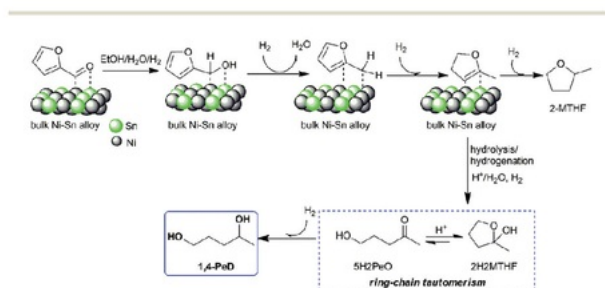
Based on the catalytic reaction results of FFald and its derivatives, we summarised the overall reactions, as shown in Scheme S1 in the ESI,† and the plausible reaction mechanism is shown in Scheme 2.

Initially, FFald was converted selectively to FFalc through C=O hydrogenation, accompanied by a small portion of THFalc owing to over-hydrogenation of C=C; this step has been verified as previously reported.^{11,12} Then, FFalc was protonated by oxidic tin (Sn²⁺)^{23,24} or autoprotolysed ethanol/H₂O solvent^{25,26} to form an unstable carbocation, whose subsequent dehydration followed by hydrogenation in the presence of H₂ gave 2-MTF. Subsequently, 2-MTF on the Ni-Sn alloy surface was rapidly hydrogenated to 2-methyl-4,5-dihydrofuran (2M4,5DHF), which was either further hydrogenated to 2MTHF under rich H₂ gas or hydrolysed to 2H2MTHF in the presence of the hydroxylated ethanol/H₂O solvent.^{8–10,34} The reaction may be too fast to monitor the formation of 2-MTF and 2M4,5DHF products at the reaction temperature >423 K, indicating that the hydrogenation of those products is extremely fast because of the participation of water, which reduces the energy barrier of the hydrolysis-hydrogenation process and significantly increases the reaction rate.²² Moreover, it is

suggested that relatively stable 2H2MTHF was formed (the ¹H NMR spectra of both crude yield and purified 1,4-PeD showed a singlet peak at $\delta = \sim 2.86$ ppm, which may be attributed to the protons of -CH₃ in 2H2MTHF (Fig. S7 and S8, ESI†)) and equilibrated through the ring-chain tautomerism to form the hydroxyketone (5H2PeO). It is well known that the reaction equilibrium between 2H2MTHF and 5H2PeO occurred *via* ring-chain tautomerism, which can proceed efficiently in acidulated reaction systems in both alcohol and H₂O.^{34,35} To prove this assumption, we carried out the reaction of 5H2PeO in the presence of dilute formic acid ($\sim 1\%$) at 323 K in an ethanol/H₂O solvent mixture for 6 h. Overall, 67% of 5H2PeO was converted into 54% of 2H2MTHF and unknown products ($\sim 13\%$) (Scheme S2a, ESI†). This result also confirmed that the excess molecular water promoted the equilibrium reaction to 2H2MTHF rather than to 5H2PeO. Since the rate of the 2M4,5DHF hydrolysis or 2H2MTHF formation is relatively faster than that of the 5H2PeO hydrogenation within the equilibrium reaction,³⁵ 2H2MTHF was quantitatively detected during the reaction. In fact, hydrogenation of 5H2PeO in the presence of the bulk Ni-Sn(1.5) alloy catalyst proceeded completely to give 1,4-PeD (>99% yield) at 433 K after 10 h. After removal of the solvent and product purification, the isolated 1,4-PeD yield was 98% (the ¹H and ¹³C NMR spectra of the isolated product of 1,4-PeD are shown in Fig. S10 and S11, respectively, in the ESI†) (Scheme S2b, ESI†).³⁶ In addition, the formation and the further reaction of FFalc or 2-MTF are the crucial steps in the formation of 1,4-PeD, which may occur in parallel with THFalc or 2-MTHF in the ethanol/H₂O solvent mixture (Scheme S2, ESI†).^{22b} Based on these overall results, inexpensive bulk Ni-Sn alloys represent promising catalyst systems for the production of high-value 1,4-PeD from C5-furans (FFald, FFalc, and 2-MTF) in an EtOH/H₂O solvent mixture without any acid additives. Moreover, our resulting yield is higher than those in the previous reports of FFald,^{8,10} and 2-MTF⁹ routes were obtained (Table S4, ESI†).

Conclusions

Inexpensive bulk Ni-Sn alloy-based catalysts demonstrate a unique catalytic property in the selective conversion of C5-furan compounds (*e.g.*, furfuraldehyde (FFald), furfuryl alcohol (FFalc), and 2-methylfuran (2-MTF)) and selectively produce 1,4-pentanediol (1,4-PeD) in a one-pot reaction. The exclusive formation of 1,4-PeD from FFald instead of 1,2- or 1,5-PeD may be the result of the synergistic actions between the selective behaviour of the Ni-Sn alloy catalyst and the use of suitable hydroxylated solvents (*e.g.*, H₂O or alcohol/H₂O). We summarised that the catalytic reaction routes may involve (a) FFald converted through C=O hydrogenation to FFalc exclusively and then (b) protonated to form the unstable carbocation whose subsequent dehydration followed by hydrogenation in the presence of H₂ gave 2-MTF under the acidulation of the reaction system by the autoprotolysis of ethanol/H₂O. (c) The formed 2-MTF on the Ni-Sn alloy surface then was partially



Scheme 2 Plausible reaction mechanism for the synthesis of 1,4-PeD from C5-furan compounds (FFald, FFalc, and 2-MTF) in the presence of the bulk Ni-Sn alloy catalyst in an ethanol/H₂O system.

hydrogenated to form 2-methyl-4,5-dihydrofuran (2M4,5DHF) that was either further hydrogenated to 2MTHF under rich H₂ gas or hydrolysed to 2H2MTHF; the latter product equilibrated through ring-chain tautomerism with hydroxyketone (5H2PeO), which was easily hydrogenated to 1,4-PeD. Bulk Ni-Sn alloy catalysts consisting of Ni₃Sn or Ni₃Sn₂ alloy phases are responsible for the enhanced yield of 1,4-PeD. The outstanding yields of 1,4-PeD up to 92% (from FFald), 67% (from FFalc), and 48% (from 2-MTF) were achieved in ethanol/H₂O (1.5 : 2.0 volume ratio) with 433 kPa H₂ and 12 h as the optimised reaction conditions. As the reaction temperature increased to 453 K, the yield of 1,4-PeD slightly decreased to 87% from FFald and slightly increased to 71% from FFalc. The bulk Ni-Sn alloy catalysts were reusable without any significant loss of the activity and selectivity after regeneration by H₂ treatment at 673 K.

Abbreviations

FFald	furaldehyde
FFalc	furfuryl alcohol
THFalc	tetrahydrofurfuryl alcohol
2-MTF	2-methylfuran
2-MTHF	2-methyltetrahydrofuran
2H2MTHF	2-hydroxy-2-methyltetrahydrofuran
2M4,5DHF	2-methyl-4,5-dihydrofuran
5H2PeO	hydroxy-2-pentanone
1,2-PeD	1,2-pentenediol
1,4-PeD	1,4-pentenediol
1,5-PeD	1,5-pentenediol
PeOH	pentanol

Conflicts of interest

This manuscript was written through contributions from all authors. All authors have given approval to the final version of the manuscript. There are no conflicts to declare.

Acknowledgements

The authors acknowledge the JSPS-DGHE through the Joint Bilateral Research Project FY 2014–2017 (grant number JSPS/BC/13145), KLN and the International Publication Project of DGHE FY 2015–2017 (grant number DIPA-042.06-0/2017), the Insentif Riset Nasional (Insinas) FY 2016–2017 (grant number of DIPA-042.01.1.427922/2016), and Hibah Penelitian Berbasis Kompetensi FY 2018 (grant number DIPA-042.06-1.4051516/2018) from the Ministry of Research, Technology, and Higher Education, which all financially supported this work.

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- 29 R-Ni/AlOH was prepared from the alkali leaching of the Ni-Al alloy using a dilute (3.1 M) NaOH aqueous solution and dried prior to the catalytic reaction. The details of the preparation procedure for this catalyst are provided in the ESI.†
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One-pot selective conversion of C5-furan into 1,4-pentanediol over bulk Ni– Sn alloy catalysts in an ethanol/H₂O solvent mixture

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