Selective Conversion of 2-Methylfuran to 1,4-Pentanediol Catalyzed by Bimetallic Ni-Sn Alloy

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Abstract

The selective conversion of 2-methylfuran (2-MeF) to 1,4-pentanediol (1,4-PeD) over bimetallic nickel-tin alloy catalysts in the ethanol/H2O solvent mixture was studied. By using bulk Ni-Sn(x); x = 3.0 and 1.5 catalysts, a maximum yield of 1,4-PeD (49%) was obtained at 94% conversion of 2-MeF. The dispersion of Ni-Sn(x) on the aluminium hydroxide (AlOH) or γ-Al2O3 supports allowed to an outstanding yield of 1,4-PeD (up to 64%) at 433 K, 3.0 MPa of H2 within 12 h. Ni-Sn(3.0)/AlOH catalyst was found to be reusable and the treatment of the recovered Ni-Sn(3.0)/AlOH catalyst with H2 at 673 K for 1 h restored the catalyst’s original activity and selectivity. Copyright © 2019 BCREC Group. All rights reserved

Keywords: Ni-Sn alloy catalysts; selective conversion; 2-methylfuran; 1,4-pentanediol; 2-methyltetrahydrofuran

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1. Introduction

The catalytic transformation of biomass-derived furans and their derivatives into a variety of specialty chemicals, fuel additives, and solvents have received considerable attention in the past decade as green alternatives to the petrochemicals processes [1]. Among of biomass-derived furans, 2-methylfuran (2-MeF) has highly promising physical and chemical properties for application as alternative fuels or as precursor of various valuable chemical intermediates [2]. Industrial scale production of 2-MeF had obtained via direct conversion of furfural which is in turn available on an industrial scale by the hydrolysis-dehydration of hemicellulose part of agriculture wastes and forest residues [3] by using copper-, nickel-, or palladium-based catalysts [4].

Further catalytic conversion of 2-MeF over Pt-metal groups through furan ring hydrogenation produced the 2-methyltetrahydrofuran(2-MeTHF) as the main product [5]. Aliaga et al. reported the 2-MeF hydrogenation on Pt nanocatalyst and the product selectivity was depended on the reaction temperatures, whereas the selectivities of 1-pentanol (98%) and 2-pentanol were obtained at 313 K and 363 K, respectively. They proposed that the Pt-surface catalyst and 2-MeF interaction through heterocyclic π-cloud
binding in nearly flat configuration; this allows ring opening, leading to the formation of pentanol isomer under mild conditions [6]. Guliants et al. also reported the deuterium-labelling study during the hydrogenation of 2-MeF over carbon-supported Pd or Pt catalysts and indicated that C=C furan ring hydrogenation occurred at low reaction temperature while C-O bond hydrogenolysis favoured at elevated temperatures [7].

2-MeF also can be transformed into 1,4-pentanediol (1,4-PeD), one of important α,ω-diols through the hydrogenolysis reactions using monometallic or bimetallic heterogeneous catalysts [8] which can be used as a component of disinfectants, an ingredient of various cosmetic products, monomers of polyesters and polyurethanes [9]. The synthesis of 1,4-PeD from 2-MeF was proposed firstly by Schniepp et al. in the presence of reduced Ni on Celite catalyst at 423 K, 10.3 MPa of H2, a reaction time of 1.5 h and afforded a mixture of 2-MeTHF (30% yield), 5-hydroxy-2-pentanone (5H2PeO) (31% yield), and 1,4-PeD (4% yield). By changing the reaction period to 8 h under the similar reaction conditions, 36% yield of 2-MeTHF and 62% yield 1,4-PeD were obtained. They proposed that 1,4-PeD was formed through hydrosilylation-hydrogenation of furan ring in the form of either an open-chain (5-hydroxy-2-pentanone, 5H2PeO) or cyclic structure (2-methyl-2-hydroxy tetrahydromethylfuran, 2H2MeTHF) intermediates [10,11]. However, the addition of homogeneous acidic materials (e.g. formic acid or acetic glacial) are substantially required to obtain such of 1,4-PeD or 5H2PeO, whereas the presence of acid may cause the dissolution of the active nickel metal catalyst into the reaction solution [12]. Similarly, Soos [13], Zolotarev et al. [13] and Perchenok et al. [14] have also reported the catalytic transformation of 2-MeF into 5H2PeO using alloyed nickel-chromium or nickel-aluminium catalysts and afforded 5H2PeO 30% in yields which is subsequently hydrogenated to the final product of 1,4-PeD.

In this paper, we describe for the first the catalytic behaviour of bimetallic nickel-tin alloy both bulk and supported catalysts [15-18] in the selective conversion of 2-MeF to 2-methyl tetrahydrofuran (2-MeTHF) and 1,4-pentanediol (1,4-PeD). The catalytic reactions were performed in an autoclave reactor system of Taiatsu Techno (a Pyrex tube was fitted inside of a sus316 jacket to protect the vessel from corrosion in acidic media) in an ethanol/H2O solvent mixture under mild reaction conditions (393-453 K, ~3.0 MPa, and 12 h).

The effects of solvent use, various bimetallic Ni-Sn alloy catalysts with different Ni/Sn molar ratios, and reaction parameters (temperatures, initial H2 pressure, time profiles, and reusability test) were investigated and discussed systematically.

2. Materials and Methods

2.1 Materials

Sodium hydroxide (NaOH) (97%), nickel (II) chloride hexahydrate (NiCl2·6H2O, 99.9%), tin (II) chloride dihydrate (SnCl2·2H2O, 99.9%), aluminium hydroxide (AlOH) were purchased and used as received from WAKO Pure Chemical Industries, Ltd. unless otherwise stated. γ-Al2O3 (SuF = 100 m²g⁻¹) were purchased from Japan Aerosil Co. 2-methyltetrahydrofuran (98% GC), 2-pentanol (98% GC) were purchased from Tokyo Chemical Industries, Ltd. All organic chemical compounds were purified using standard procedures prior to use.

2.2 Catalyst preparation

A typical procedure of the synthesis of aluminium hydroxide supported nickel-tin (Ni-Sn(3.0)/AlOH, 3.0 is feeding ratio) alloy catalyst is described as follows [14,17]: NiCl2·6H2O (18.0 mmol) was dissolved in deionised water (denoted as solution A), and SnCl2·2H2O (6.0 mmol) was dissolved in ethanol/2-methoxy ethanol (2:1) (denoted as solution B) at room temperature. An one gram AlOH (aluminium hydroxide, typically bayerite type), solutions A, and B were mixed at room temperature; the temperature was subsequently raised to 323 K and the mixture was stirred for 12 h. The pH of the mixture was adjusted to 12 through the dropwise addition of an aqueous solution of NaOH (3.1 M). The mixture was then placed into a sealed-Teflon autoclave for the hydrothermal reaction at 423 K for 24 h. The resulting black precipitate was filtered, washed with distilled water, and then dried under vacuum overnight. Prior to the catalytic reaction, the obtained black powder was reduced with H2 at 673 K for 1.5 h.

2.3 Catalyst characterization

XRD measurements were recorded on a Mac Science M18XHF instrument using monochromatic Cu-Kα radiation (λ = 0.15418 nm). The XRD was operated at 40 kV and 200 mA with a step width of 0.02° and a scan speed.
of 4 °.min⁻¹ (α1 = 0.154057 nm, α2 = 0.154433 nm). ICP measurements were performed on an SPS 1800H plasma spectrometer of Seiko Instruments Inc. (Ni: 221.7162 nm and Sn:189.898 nm). The BET surface area (S_BET) and pore volume (V_p) were measured using N₂ physisorption at 77 K on a Belsorp Max (BEL Japan). The samples were degassed at 473 K for 2 h to remove physisorbed gases prior to the measurement. The amount of nitrogen adsorbed onto the samples was used to calculate the Brunauer–Emmett–Teller (BET) surface area via the BET equation. The pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of approximately 0.995 according to the Barrett–Joyner–Halenda (BJH) approach based on desorption data [19]. SEM images of the synthesized catalysts were taken on a JEOL JSM-610 SEM microscope after the samples were coated using a JEOL JTC-1600 autofine coater. TEM image analyses were taken on Hitachi High-Tech H-7650 microscope with an emissive gun, operated at 150 kV.

The H₂ uptake was determined through irreversible H₂ chemisorption. After the catalyst was heated at 393 K under vacuum for 30 min, it was treated at 673 K under H₂ for 30 min. The catalysts were subsequently cooled to room temperature under vacuum for 30 min. The H₂ measurement was conducted at 273 K, and H₂ uptake was calculated according to the method described in the literature [20].

The NH₃-TPD was carried out on a Belsorp Max (BEL Japan). The samples were degassed at elevated temperature of 373-473 K for 2 h to remove physisorbed gases prior to the measurement. The temperature was then kept at 473 K for 2 h, while flushed with He gas. NH₃ gas (balanced NH₃, 80% and He, 20%) was introduced at 373 K for 30 min, then evacuated by helium gas to remove the physisorbed gas for 30 min. Finally, temperature programmed desorption was carried out at temperature of 373-1073 K and the desorbed NH₃ was monitored by TCD.

2.4 Catalytic reactions

A typical reaction procedure of 2-methylfuran (2-MeF) hydrogenation as follows. A 1.2 mmol of 2-methylfuran was dissolved in 3.5 mL ethanol/H₂O mixture (1.5: 2.0 volume ratio) and 50 mg of Ni-Sn(3.0)/Al₂O₃ catalyst were placed into an autoclave reactor system of Taiatsu Techno (a Pyrex tube was fitted inside of a SUS316 jacket to protect the vessel from corrosion in acidic media). After H₂ was introduced into the reactor (initial H₂ pressure of 3.0 MPa) at room temperature, the temperature of the reactor was raised to 433 K and the reaction time was 12 h. In the reaction, 1,4-PeD and 2-MeTHF were mainly produced, while 2H₂MeTHF and 2-PeOH were also detected. The used Ni-Sn(3.0)/Al₂O₃ catalyst was easily separated using either simple centrifugation (4000 rpm for 10 min) or filtration, dried overnight under vacuum at room temperature, then finally reduced with H₂ at 673 K for 1.5 h prior to re-usability testing.

2.5 Product analysis

Gas chromatography (GC) analysis of the reactant (2-MeF) and products (1,4-PeD, 2-PeOH, 2H₂MeTHF, and 2-MeTHF) was performed on a Shimadzu GC-8A with a flame ionization detector equipped with a Silicone OV-101 or a Thermon 3000 packed column length (m) = 3.0; inner diameter (mm) = 2.0; methylsilicone from Sigma-Aldrich Co. Ltd.). Gas chromatography-mass spectrometry (GC-MS) was performed on a Shimadzu GC-17B with a thermal conductivity detector equipped with an RT-bDEXsnp capillary column. ¹H and ¹³C NMR spectra were obtained on a JNM-AL400 spectrometer at 400 MHz; the samples for NMR analysis were dissolved in chloroform-d; with TMS as the internal standard. The products were confirmed by a comparison of their GC retention time, mass, ¹H NMR and ¹³C NMR spectra with those of authentic samples, except for 2H₂MeTHF due to the limitation of commercial availability [21].

The conversion of 2-MeTF, yield and selectivity of the products were calculated according to the Equations (1-3):

\[
\text{Conversion} = \frac{\text{introduced mol reactant}(F_0)}{\text{remained mol reactant}(F_r)} \times 100\%
\]

\[
\text{Yield} = \frac{\text{mol product}}{\text{consumed mol reactant}(\Delta F)} \times 100\%
\]

\[
\text{Selectivity} = \frac{\text{mol product}}{\text{total mol products}} \times 100\%
\]

where \( F_0 \) is the introduced mol reactant (2-methylfuran, 2-MeF), \( F_r \) is the remaining mol reactant, and \( \Delta F \) is the consumed mol reactant (introduced mol reactant- remained mol reactant), which are all obtained from GC analysis using an internal standard technique.

3. Results and Discussion

3.1 Catalyst characterizations

Based on the ICP-AES analyses, the compo-
sitions of the bulk and supported 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 1, entries 1-4) as described previously in elsewhere [15-18]. Four types of supports (AC, γ-Al₂O₃, amorphous alumina (AA), and AlOH) were employed for the preparation of the supported Ni-Sn(3.0) alloy catalysts using a procedure similar to that used for the synthesis of the bulk phases. The physicochemical properties of the supported Ni-Sn(3.0) alloy catalysts are also summarized in Table 1 (entries 5-7), and the XRD patterns are shown in Figure 1. The total loading amount of Ni-Sn was 2.3-2.4 mmol.g⁻¹ (based on the ICP-AES results) for all of the supported Ni-Sn(3.0) samples (the composition (mol%) of Ni and Sn are listed in Table 1). The H₂ uptake for supported Ni-Sn(3.0) catalysts were almost twice higher than that of the bulk alloy (entries 4-7). The XRD patterns also revealed that Ni₃Sn or mixture of Ni₃Sn and Ni₅Sn₂, as the major alloy phases, were formed on the AC, AA, γ-Al₂O₃, and AlOH supports (Figure 1a-c) [22].

TEM images of supported Ni-Sn(3.0)/AA and Ni-Sn(3.0)/AlOH alloy catalysts show spherical bimetallic Ni-Sn alloy particles which are roughly dispersed on the surface of aluminium hydroxide as shown in Figure 2. The differences in particle sizes of Ni-Sn alloy were easily observed between Ni-Sn(3.0)/AA and Ni-Sn(3.0)/AlOH system, a larger amount of Ni-Sn alloy nanoparticles with bigger sizes were also observed in Figure 2a.

Figure 3 shows the SEM images of bulk Ni-Sn(1.5), Ni-Sn(3.0), and supported Ni-Sn(3.0) catalysts. Scanning electron microscopy (SEM)

Table 1. Physico-chemical properties of the synthesized bulk and supported bimetallic Ni-Sn(3.0) alloy catalysts

| Entry | Catalysts | Chemical composition (mol%) | S_BET (m².g⁻¹) | Amount of acid sites (μmol/g) | H₂ uptake (μmolg⁻¹) |
|-------|-----------|-----------------------------|----------------|------------------------------|---------------------|
| 1     | Ni-Sn(0.75) | Ni₁₂.₇Sn₃₇.₃ (87% Ni₃Sn₂) | 57             | -                            | 4.7                 |
| 2     | Ni-Sn(1.5)  | Ni₅₉.₉Sn₄₀.₁ (91% Ni₃Sn₂) | 12             | -                            | 8.6                 |
| 3     | Ni-Sn(3.0)  | Ni₇₄.₅Sn₂₅.₁ (66% Ni₃Sn₂) | 6              | -                            | 12.0                |
| 4     | Ni-Sn(3.0)/AlOH | Ni₇₄.₅Sn₂₅.₁ | 120               | 491                          | 27.1                |
| 5     | Ni-Sn(3.0)/AC | Ni₇₄.₅Sn₂₅.₁ | 557               | 83                           | 31.2                |
| 6     | Ni-Sn(3.0)/γ-Al₂O₃ | Ni₇₄.₅Sn₂₅.₁ | 122               | 446                          | 29.8                |
| 7     | Ni-Sn(3.0)/AA | Ni₄₄.₆Sn₁₄.₃Al₁₄.₁ | 122               | 473                          | 32.7                |
| 8*    | R-Ni/AlOH   | Ni₄₇.₆Al₁₂.₄       | 151             | 474                          | 104                 |
| 9     | Raney®Ni    | Ni₈₆.₄Al₁₃.₆       | 66              | 195*                         | 121                 |
| 10    | γ-Al₂O₃     | -                | 120             | 180*                         | -                   |

*The value in the parenthesis is Ni/Sn ratio. *Determined by ICP-AES. *BET specific surface areas, determined by N₂ physisorption at 77 K. *Amount of acidic sites (μmol g⁻¹) was derived from NH₃-TPD spectra. *H₂ uptake at 273 K (noted after corrected for physical and chemical adsorption). Based on the crystallographic databases and mol% of alloy component was calculated by Multi-Rietveld Analysis Program LH-Riet 7.00 method on the Rietica software [22,23] as described previously in elsewhere [15]. *The catalyst was synthesized from Raney nickel supported on aluminium hydroxide (R-Ni/AlOH) and tin (II) dihydrate via hydrothermal at 425 K for 2 h, dried at room temperature, then followed by H₂ reduction at 673 K for 1.5 h according to reference [16,17]. *Reference [26]. *Reference [27].
Figure 2. TEM images of (a) Ni-Sn(3.0)/AA and (b) Ni-Sn(3.0)/AlOH after reduction with H₂ at 673 K for 1.5 h.

Figure 3. SEM images of (a) bulk Ni-Sn(1.5), (b) bulk Ni-Sn(3.0), (c) Ni-Sn(3.0)/AA and (d) Ni-Sn(3.0)/AlOH after reduction with H₂ at 673 K for 1.5 h.
images for the bulk Ni-Sn(1.5), Ni-Sn(3.0), Ni-Sn(3.0)/AA, and Ni-Sn(3.0)/AlOH revealed that the morphological differences between the bulk Ni-Sn(1.5), Ni-Sn(3.0) and supported Ni-Sn(3.0) samples are readily visible. Note that the morphologies of bulk Ni-Sn (1.5) and Ni-Sn(3.0) are similar. Figure 3a shows that the bulk Ni-Sn(1.5) catalyst has a relatively flat surface. Figure 3b shows that unlike the smooth surface of Ni-Sn(1.5), the surface bulk Ni-Sn(3.0) is relatively high fragmentized. On the other hand, the spongy morphology of Ni, the Al-rich region contains hexagonal prismatic rods which are characteristic morphologies of gibbsite and bayerite, respectively, are clearly observed over Ni-Sn(3.0)/AA, and Ni-Sn(3.0)/AlOH samples as shown in Figures 3c-d [24,25].

The acid density of each synthesized supported Ni-Sn(3.0) alloy catalyst was measured by using ammonia (NH₃) as molecular probe as shown in Figure 5 and the results are also summarized in Table 1.

The acidities of the supported Ni-Sn(3.0) alloy catalysts were measured by NH₃-TPD and the profiles are shown in Figure 4. Generally, the NH₃-TPD profiles of aluminium hydoxide (AlOH), gamma-alumina (γ-Al₂O₃), and amorphous alumina (AA) supported Ni-Sn(3.0) has a good similarity and are likely due to great contribution of aluminium oxide or aluminium hydroxide of support (Figures 4b-e). The total acidity of each catalyst is estimated from the desorbed amount of NH₃ without

![Figure 4](image_url)

**Figure 4.** NH₃-TPD profiles of (a) Ni-Sn(3.0)/AC, (b) Ni-Sn(3.0)/γ-Al₂O₃, (c) Ni-Sn(3.0)/AA, (d) Ni-Sn(3.0)/AlOH catalysts after H₂ reduction at 673 for 1.5 h, and (e) R-Ni/AlOH catalyst.

![Scheme 1](image_url)

**Scheme 1.** Possible reaction pathways for the production of 1,4-pentanediol from 2-methylfuran via hydrolysis-hydrogenation over bimetallic Ni-Sn alloy catalysts in an ethanol/H₂O solvent mixture.
further identification of acid types, because it is difficult to distinguish the weak, medium and strong acid sites from such broad desorption peaks. The quantification results are summarized in Table 1. Aluminium hydroxide (Al(OH)) supported Ni-Sn(3.0) has highest acid density among the synthesized catalysts (491 µmol·g⁻¹, entry 5), 446 µmol·g⁻¹ for Ni-Sn(3.0)/γ-Al₂O₃, and 473 µmol·g⁻¹ for Ni-Sn(3.0)/AA, whereas the lowest acid density was active carbon (AC) supported Ni-Sn(3.0) (83 µmol·g⁻¹, entry 6). The acidity of R-Ni/Al(OH) was similar to the Ni-Sn(3.0)/AA (474 µmol·g⁻¹, entry 9) and that of the unmodified Raney®Ni[26] and blank γ-Al₂O₃[27] was 195 mmol·g⁻¹ and 180 µmol·g⁻¹, respectively. The acidity emerges mainly from γ-Al₂O₃ or Al(OH) supportss, which depend on the atomic arrangement formed in the bimetallic Ni-Sn alloy crystals [28, 29].

3.2 Hydrogenation of 2-methylfuran

3.2.1 Solvent screening

First, the catalytic hydrogenation of 2-methylfuran over bulk Ni-Sn(3.0) alloy catalyst both in protic (alcohols, 1,4-dioxane, and H₂O) and aprotic (acetonitrile and hexane) solvents was carried out, and the results are summarized in Table 2 and the possible reaction pathways are shown in Scheme 1. In alcohol solvents (e.g. methanol, ethanol, and propanol), the conversions of 2-MeF were 28%, 10%, 56%, and 52%, respectively and produced 2-methyl tetrahydrofuran (2-MeTHF) with ~99% selectivity (entries 1-4). Interestingly, 100% in conversion of 2-MeF was achieved under the same reaction conditions and the reaction products were distributed to 1,4-pentanediol (1,4-PeD), 2-pentanol (2-PeOH), 2-hydroxy-2-methyltetrahydrofuran (2H₂MeTHF), and 2-methyl tetrahydrofuran (2-MeTHF) with yields of 15%, 3%, 4%, and 78%, respectively (entry 5). Since the solubility of 2-MeF in H₂O solvent is relatively low, a blending solvent of ethanol/H₂O or 2-propanol/H₂O with volume ratio of 1.5/2.0 was employed as the solvent. In ethanol/H₂O, the conversion of 2-MeF was 92% and 49% yield of 1,4-PeD was obtained (which is higher than that of in H₂O solvent (increase almost 3 times)), whereas the yield of 2H₂MeTHF remarkably reduced to only 5% (entry 6). In 2-propanol/H₂O and 1,4-dioxane solvents, however, with reducing the amount of undesired product of 2H₂MeTHF to 3% or 0%, the main product was 2-MeTHF with promisingly low yield of 1,4-PeD (entries 7 and 8).

Differences in the product distribution of 2-MeF hydrogenation in alcohols, H₂O, and alcohol/H₂O may be attributed to the presence of O-bonded water molecules to the C atom from neighbouring -CH₂OH group and forming a new water species with one H atom of water being automatically transferred to the terminal OH group as it has been evidenced through the H₂¹⁸O isotopic trace experiments combined with the DFT calculations [30,31]. Alternatively, the slow formation of oxidic tin (Sn⁰⁺) from metallic tin (Sn⁰) [32,33] that

| Entry | Solvent                  | Conversiona/% | 1,4-PeD | 2-PeOH | 2H₂MeTHF | 2-MeTHF |
|-------|--------------------------|---------------|----------|--------|----------|--------|
| 1     | Methanol                 | 28            | 0        | 2      | 0        | 26     |
| 2     | Ethanol                  | 10            | 0        | 1      | 0        | 9      |
| 3     | n-Propanol              | 56            | 0        | 1      | 0        | 55     |
| 4     | 2-Propanol              | 52            | 0        | 2      | 0        | 50     |
| 5     | H₂O                      | 100           | 15       | 3      | 4        | 78     |
| 6a    | Ethanol/H₂O             | 92            | 49       | 1      | 5        | 37     |
| 7b    | 2-Propanol/H₂O          | 70            | 11       | 3      | 3        | 53     |
| 8     | 1,4-Dioxane             | 56            | 7        | 1      | 0        | 48     |
| 9     | Acetonitrile            | 21            | 1        | 0      | 0        | 20     |
| 10    | Hexane                  | 13            | 0        | 0      | 0        | 7      |

*Reaction conditions*: catalyst, 44 mg; substrate, 1.2 mmol; solvent, 3.5 mL (1.5 : 2.0 volume ratio); initial H₂ pressure, 3.0 MPa, 433 K, 12 h. *Conversion and yields were determined by GC and GC-MS analyses using an internal standard technique. *The solvent was alcohol/H₂O or 2-propanol/H₂O mixture, 3.5 mL (1.5 : 2.0 volume ratio). 1,4-PeD = 1,4-pentanediol. 2-PeOH = 2-pentanol. 2H₂MeTHF = 2-hydroxy-2-methyl tetrahydrofuran. 2-MeTHF = 2-methyl tetrahydrofuran.
generated the acid sites of Ni-Sn alloy and the autoprotolysis of the hydroxylated solvents of H₂O or alcohol/H₂O via proton transfer from H₂O to the alcohol or 1,4-dioxane [34-36] acidulated the reaction system which synergistically acted for the acid-hydrosilation of furan ring and then subsequent hydrogenation reactions under H₂ atmosphere to produce 1,4-PeD [10-14,37]. Hu et al. also suggested that the acid-catalysis and hydrogenation proceeded in parallel in the presence of supported bimetallic Ni-Sn alloy [38]. On the other hand, in aprotic solvents (e.g. acetonitrile and hexane), the catalytic reaction of 2-MeF did not proceed effectively (entries 9 and 10). Therefore, it can be concluded that the suitable solvent for the catalytic reaction of 2-MeF over bimetallic Ni-Sn(3.0) alloy catalyst is a blending ethanol/H₂O and therefore, it will be used for further investigation with various catalysts and reaction parameters (initial H₂ pressure, reaction temperature, and time profiles).

3.2.2 Catalyst screening

To obtain the insight into the role of bimetallic Ni-Sn alloy catalysts in the selective production of 1,4-PeD via hydrosilation-hydrogenation reaction of 2-MeF, various bimetallic Ni-Sn alloy both bulk and supported catalysts were evaluated, and the results are summarized in Table 3.

First, we carried out the reaction over various bulk Ni-Sn alloy catalysts with different Ni/Sn molar ratio at 433 K, initial H₂ pressure of 3.0 MPa, in blending solvent ethanol/H₂O and reaction time of 6 h or 12 h. By using Ni-Sn(0.75) alloy, the conversion of 2-MeF was only 17% and produced 9% 2-MeTHF (entry 1),

| Entry | Catalysts | Conversionb/% | Yieldb/% 1,4-PeD | 2-PeOH | 2H2MeTHF | 2-MeTHF |
|-------|-----------|---------------|-------------------|--------|----------|---------|
| 1     | Bulk Ni-Sn(0.75) | 17            | 0                 | 0      | 0        | 9       |
| 2     | Bulk Ni-Sn(1.0)  | 39            | 0                 | 0      | 0        | 21      |
| 3a    | Bulk Ni-Sn(1.5)  | 63            | 36                | 4      | 2        | 21      |
| 4     | Bulk Ni-Sn(1.5)  | 94            | 49                | 1      | 7        | 38      |
| 5     | Bulk Ni-Sn(2.0)  | 49            | 0                 | 0      | 0        | 49      |
| 6a    | Bulk Ni-Sn(3.0)  | 68            | 48                | 2      | 0        | 18      |
| 7     | Bulk Ni-Sn(3.0)  | 92            | 49                | 1      | 5        | 37      |
| 8d    | Bulk Ni-Sn(3.0)  | 100           | 33                | 5      | 1        | 61      |
| 9a    | Ni-Sn(3.0)/AA    | 88            | 31                | 3      | 3        | 51      |
| 10    | Ni-Sn(3.0)/AlOH  | 100           | 64                | 1      | 0        | 35      |
| 11    | Ni-Sn(3.0)/γ-Al₂O₃ | 100        | 51                 | 3      | 0        | 46      |
| 12    | Ni-Sn(3.0)/AC    | 100           | 43                | 6      | 4        | 47      |
| 13    | Ni-Sn(3.0)/SiO₂  | 100           | 35                | 6      | 5        | 55      |
| 14    | Ni-Sn(1.5)/AlOH  | 75            | 39                | 0      | 1        | 35      |
| 15    | Ni-Sn(1.5)/γ-Al₂O₃ | 69         | 47                | 0      | 0        | 22      |
| 16    | Ni-Sn(1.5)/AC    | 57            | 18                | 2      | 0        | 37      |
| 17    | Ni-Sn(1.5)/SiO₂  | 51            | 21                | 0      | 0        | 30      |
| 18    | R-Ni/AlOH        | 100           | 31                | 3      | 0        | 66      |
| 19    | Raney®Ni         | 100           | 0                 | 0      | 0        | >99     |
| 20    | Pd/C (5wt% Pd)   | 100           | 0                 | 0      | 0        | >99     |

*Reaction conditions:* catalyst, 50 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. *Values in the parentheses are the Ni/Sn molar ratio, determined by ICP-AES analysis.*

*aConversion and yields were determined by GC and GC-MS analyses using an internal standard technique. *Reaction time was 6 h. *Reaction time was 19 h. *The catalyst was synthesized from Raney nickel supported on aluminium hydroxide and tin (II) dihydrate via hydrothermal at 425 K for 2 h, dried at room temperature, then followed by H₂ reduction at 673 K for 1.5 h according to reference [16,17]. 1,4-PeD = 1,4-pentadienol. 2-PeOH = 2-pentanol. 2H2MeTHF = 2-hydroxy-2-methyl tetrahydrofuran. 2-MeTHF = 2-methyl tetrahydrofuran.
while over Ni-Sn(1.0) alloy was 39% conversion with 21% yield of 2-MeTHF (entry 2). Over Ni-Sn(1.5) alloy, 63% of 2-MeF was converted after a reaction time of 6 h and the main products were 1,4-PeD and 2-MeTHF with yields of 36% and 21%, respectively (entry 3). At a reaction time of 12 h, the conversion of 2-MeF increased to 94% and yields of 1,4-PeD, 2-MeF, and 2H2MeTHF also increased slightly to 49%, 38%, and 7%, respectively (entry 4). Over Ni-Sn(2.0) alloy, the conversion of 2-MeF was 49% and yielded only 2-MeTHF (49% in yield, entry 5). Interestingly, by using Ni-Sn(3.0) catalyst, 68% of 2-MeF was converted and afforded of 1,4-PeD (48% yield), 2-PEOH (2% yield), and 2-MeTHF (18% yield) after a reaction time of 6 h (entry 6). When a reaction time was prolonged to 12 h, the conversion of 2-MeF increased to 92% whereas the yield of 1,4-PeD was almost constant to 49% (entry 7). However, at 100% conversion of 2-MeF, 1,4-PeD yield decreased significantly to 33% while 2-MeTHF yield increased almost twice (61%) after a reaction time was extended to 19 h (entry 8). These results indicated that over hydrogenation of furan ring to produce 2-MeTHF occurred as it had been reported previously [10]. Therefore, it can be concluded that among the synthesized bimetallic Ni-Sn alloy catalysts, Ni-Sn alloy that consist of Ni-Sn and NiSn2 alloy species are active for the hydrolysis-hydrogenation of 2-MeF to 1,4-PeD.

The catalytic reaction of supported Ni-Sn(3.0) and Ni-Sn(1.5) on various supports that having a Brønsted acidity (i.e. amorphous alumina, γ-alumina, aluminium hydroxide, and active carbon) under the same reaction conditions and the results are also investigated and summarized in Table 3. In the case of supported Ni-Sn(3.0)/AA (AA = amorphous alumina) catalyst which was synthesized according to the previously published works [16,17], a moderate yield of 1,4-PeD (31%) was obtained at 88% conversion of 2-MeF under the same reaction conditions (entry 9). Interestingly, over aluminium hydroxide (AlOH) and γ-Al2O3 supported Ni-Sn(3.0) alloy catalysts, high yields of 1,4-PeD (64% and 51%, respectively) were achieved (entries 10 and 11). To the best of our knowledge, these results are the highest yield of 1,4-PeD from catalytic conversion of 2-MeF without the addition of formic acid or acetic acid glacial as it had been reported previously [10,39]. It can be also observed that aluminium hydroxide (AlOH) and γ-Al2O3 supported Ni-Sn(3.0) catalysts not only enhanced the yield of 1,4-PeD but also reduced the amount of undesired product of 2H2MeTHF. These results can be attributed to the fact that aluminium hydroxide (AlOH) and γ-Al2O3 supports have relatively high surface acidity as indicated by the NH3-TPD measurements (Figure 2 and Table 2). While over AC and SiO2 supported Ni-Sn(3.0) alloy catalysts afforded 35% and 43% 1,4-PeD in yield with remained 2H2MeTHF was 4% and 5%, respectively (entries 12 and 13). In the case of supported Ni-Sn(1.5) alloy catalysts, γ-Al2O3 supported Ni-Sn(1.5) exhibited the highest yield of 1,4-PeD (47%) among the various supports (entry 14-17). The enhancement of desired product of 1,4-PeD over AlOH or γ-Al2O3 supported Ni-Sn(3.0) and Ni-Sn(1.5) alloy catalysts can be attributed to the nature of surface acidity catalysts. NH3-TPD measurements show the differences in the surface acidity (e.g., part of strong acid, >923 K) between AlOH or γ-Al2O3 and AC supports (Figure 4 and Table 1). The strong acid site may able to interact with C=C bond of furan ring, protonated, and then hydrolysed in presence of ethanol/H2O [40-43]. Note to be important that over AlOH or γ-Al2O3 supported Ni-Sn(3.0) catalysts, no side polymerization product was observed within the reactions. In addition, Raney Ni supported on aluminium hydroxide (R-Ni/AlOH) catalyst also provided 31% in yield of 1,4-PeD (entry 18), while a commercially available Raney®Ni and 5%wt Pd/C catalyst produced >99% 2-MeTHF in yields without the formation of 1,4-PeD or 2-PEOH products (entries 19 and 20).

3.2.3 Effect of initial H2 pressure

The effect initial H2 pressure on the conversion of 2-MeF and yield of 1,4-PeD over Ni-Sn(3.0)/AlOH catalyst was evaluated at the range of 1.0-4.0 MPa and the results are shown in Figure 5. 2-MeF conversion and 2-MeTHF yield gradually increased as the initial H2 pressure increased to reach a maximum conversion (100%) at 3.0 MPa, meanwhile 1,4-PeD yield increased smoothly to maximum (64%) between 1.5 and 3.0 MPa, then slightly decreased to 60% at initial H2 pressure of 4.0 MPa.

3.2.4 Effect of reaction temperature

The influence of reaction temperature on the 2-MeTF conversion and yields of 1,4-PeD and 2-MeTHF over Ni-Sn(3.0)/AlOH alloy catalyst is shown in Figure 6. At 373 K, the conversion of 2-MeTF was 69% and yields of 2-MeTHF and 2H2MeTHF were 31% and 38%,
respectively. Since the C-O bond hydrogenolysis is enhanced at higher temperatures in comparison to the hydrogenation of the C=C bonds, lower temperatures favour the formation of 2-MeTHF and 2H2MeTHF.

While higher temperatures led to a higher 1,4-PeD selectivity, they also promoted the side reactions that not depend on the catalyst and resulted in a slightly decrease in 1,4-PeD selectivity in higher temperatures. The yield of 2H2MeTHF drastically decreased as the reaction temperature increased, and then it totally disappeared over 433 K to form 1,4-PeD as the final product. However, yield of 2-MeTHF was almost constant as a result of over hydrogenation of furan ring at the temperature ranges. The highest yield of 1,4-PeD (64%) was achieved at 433 K. Therefore, we conclude that the optimised reaction temperature for the 1,4-PeD production from 2-MeTF using Ni-Sn(3.0)/AlOH was 433 K.

3.2.5 Kinetics

The kinetic profiles of catalytic reaction of 2-MeTF over supported Ni-Sn(3.0)/AlOH alloy catalyst are shown in Figure 7. It can be observed that 2-MeTF conversion increased gradually as a function of reaction time and achieved after a reaction time of 12 h. At earlier time, the products were dominated by 2H2MeTHF with maximum 21% in yield (after 2 h) then decreased gradually as the reaction time prolonged to reach almost constant after reaction time was extended up to 16 h. Meanwhile the amount of 2-MeTHF and 1,4-PeD was almost equal indicating the hydrogenation and hydrolysis of double bond of furan ring occurred in parallel as indicated in the previous reports [10,14,39-42]. As the reaction times were prolonged, yield 1,4-PeD also increased smoothly to reach maximum 64% in yield after 12 h and then gradually decreased after a reaction time of 14 h. On the other hand, yield of 2-MeTHF increased gradually after the reaction time was extended up to 16 h.

Although the remained 2H2MeTHF can be reduced or yield of 1,4-PeD can be enhanced by adding a homogeneous acid additive (e.g. formic acid or acetic glacial), the use of additives is not desirable and should be avoided if possible, as suggested by Schniepp et al.[10] and Leuck et al. [39] Especially at relatively higher temperature and initial H₂ pressure, the formation of 1,4-PeD are strongly influenced by both those parameters as shown in Figure 5 and Figure 6. Therefore, we conclude that our AlOH or γ-Al₂O₃ supported Ni-Sn(3.0) and Ni-Sn(1.5) alloy catalysts are suitable for the hydrolysis-hydrogenation reaction of 2-MeF to produce a high valuable 1,4-PeD (with yield up to 64%) product under milder reaction conditions [43].

3.2.6 Reusability test

A reusability test was performed on the Ni-Sn(3.0)/AlOH catalyst, and the results are summarized in Table 4.
The used Ni-Sn(3.0)/AlOH catalyst was easily separated by either simple centrifugation or filtration after the reaction and dried under vacuum for overnight prior to use for the next reaction. The activity of the catalyst decreased as well as the yield of 1,4-PeD both the catalytic system. In the case of Ni-Sn(3.0)/AlOH system, the amount of Ni, Sn, and Al that leached into the reaction solution was 0.58 mol%, 1.3 mol%, and 1.9 mol% after the second run, respectively. Therefore, the treatment of the recovered Ni-Sn(3.0)/AlOH catalyst (after the second runs) with H$_2$ at 673 K for 1 h is required to restore the catalyst’s original activity and selectivity.

4. Conclusion

We demonstrate that the catalytic hydrogenation of 2-methylfuran (2-MeF) in presence of bimetallic Ni-based alloy catalysts produced selectively 1,4-pentanediol (1,4-PeD) in an ethanol/H$_2$O solvent mixture. In H$_2$O, blended ethanol/H$_2$O, or 2-propanol/H$_2$O, the hydrogenation of 2-MeF was proceeded effectively. The acid density of aluminium hydroxide (AlOH) or $\gamma$-Al$_2$O$_3$ supported Ni-Sn(3.0) alloy catalysts may play a key role during the hydrolysishydrogenation of 2-methylfuran to afford 1,4-PeD with 64% in yields at 433 K, 3.0 MPa of H$_2$ within 12 h. Ni-Sn(3.0)/AlOH was found to be reusable and the treatment of the recovered Ni-Sn(3.0)/AlOH catalyst (after the second runs) with H$_2$ at 673 K for 1 h restored the catalyst’s original activity and selectivity.

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Table 4. Results of the reusability test for Ni-Sn(3.0)/AlOH in the hydrogenation of 2-MeTF

| Run | Conversion (%) | Yield (%) | Amount of leached metals (%mol) |
|-----|---------------|----------|-------------------------------|
|     | 1             | 2        | 3†                          |
|     | Ni            | Sn       | Al                           |
| Conversion (%) | 100 | 78 | 100 | 0.58 | 1.30 | 1.90 |
| Yield (%) | 64 | 57 | 67 |      |      |     |

Reaction conditions: catalyst, 50 mg; substrate, 1.2 mmol; solvent, ethanol/H$_2$O, 3.5 mL (1.5: 2.0 volume ratio); initial H$_2$ pressure, 3.0 MPa, 433 K, 12 h. †The recovered Ni-Sn(3.0)/AlOH catalyst was reduced by H$_2$ at 673 K for 1 h prior to the next reaction. ‡The amount of leached metals was determined by ICP-AES from the reaction mixture after the first reaction run. †Conversion of 2-MeF and yield of 1,4-PeD were determined by GC using an internal standard technique.

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