



Research Article

One-pot Selective Conversion of Biomass-derived Furfural into Cyclopentanone/Cyclopentanol over TiO₂ Supported Bimetallic Ni-M (M = Co, Fe) Catalysts

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Abstract

One-pot selective conversion of biomass-derived furfural (FFald) into cyclopentanone (CPO) or cyclopentanol (CPL) using bimetallic nickel-based supported on TiO₂ (denoted as Ni-M(3.0)/TiO₂; M = Co and Fe; 3.0 is Ni/M molar ratio) have been investigated. Catalysts were synthesized via a hydrothermal method at 150 °C for 24 h, followed by H₂ reduction at 450 °C for 1.5 h. X-ray Diffraction (XRD) analysis showed that the formation of Ni-Co alloy phase at $2\theta = 44.2^\circ$ for Ni-Co(3.0)/TiO₂ and Ni-Fe alloy at $2\theta = 44.1^\circ$ for Ni-Fe(3.0)/TiO₂. The amount of acid sites was measured by using ammonia-temperature programmed desorption (NH₃-TPD). Ni-Co(3.0)/TiO₂ has three NH₃ desorption peaks at 180 °C, 353 °C, and 569 °C with acid site amounts of 1.30 $\mu\text{mol.g}^{-1}$, 1.0 $\mu\text{mol.g}^{-1}$, and 2.0 $\mu\text{mol.g}^{-1}$, respectively. On the other hand, Ni-Fe(3.0)/TiO₂ consisted of NH₃ desorption peaks at 214 °C and 626 °C with acid site amounts of 3.3 $\mu\text{mol.g}^{-1}$ and 2.0 $\mu\text{mol.g}^{-1}$, respectively. Both Ni-Co(3.0)/TiO₂ and Ni-Fe(3.0)/TiO₂ catalysts were found to be active for the selective hydrogenation of FFald to furfuryl alcohol (FFalc) at low temperature of 110 °C, H₂ 3.0 MPa, 3 h with FFalc selectivity of 81.1% and 82.9%, respectively. High yields of CPO (27.2%) and CPL (41.0%) were achieved upon Ni-Fe(3.0)/TiO₂ when the reaction temperature was increased to 170 °C, 3.0 MPa of H₂, and a reaction time of 6 h. The yield of CPO+CPL on the reused catalyst decreased slightly after the second reaction run, but the activity was maintained for at least three consecutive runs. Copyright © 2020 BCREC Group. All rights reserved

Keywords: Bimetallic Ni-M (M=Co and Fe); Furfural; Furfuryl alcohol; Cyclopentanone; Cyclopentanol

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1. Introduction

The production of variety of chemicals and fuels via catalytic conversion of biomass-derived has received increasing attention in recent dec-

ades. For example, furfural (FFald) has scalable produced from hemicellulosic biomass using both homogeneous and heterogeneous acid catalyst systems [1-3]. Further catalytic hydrogenation/hydrogenolysis of FFald over bimetallic catalysts provided various derivatives molecules such as furfuryl alcohol (FFalc), tetrahydrofurfuryl alcohol (THFalc), 2-methylfuran(2-

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MeTF), cyclopentanone (CPO), cyclopentanol (CPL), and α,ω -diols such as 1,2-, 1,4-, or 1,5-pentanediol (PeD) [4-6].

Recently, cyclopentanone (CPO) and cyclopentanol (CPL), versatile chemical intermediates that containing five-membered alicyclic rings, can be obtained via combined-step of hydrogenation and rearrangement of biomass-derived furfural in aqueous media using carbon supported platinum or palladium-based catalysts [7-9]. CPO and CPL can be utilized as precursor of medicines, rubber, fuel energy, and materials CPO is also used in the fragrance and perfume industry as there are the major ingredients of jasmine family [10-12]. Traditionally, the synthesis of CPO involves catalytic vapor-phase cyclization of 1,6-hexandiols or ester of adipic acid with yields of 53% and 22%, respectively [13-14].

Several previous works on the synthesis of CPO from FFald have been extensively investigated, the highest yield of CPO and CPL together (81%) was achieved over 5% Pt/C under very high pressure of H₂ (8 MPa) and temperature of 160 °C [7]. By using similar Pt/NC-BS catalyst, Liu *et al.* reported that maximum yield of CPO (76%) was obtained from FFald at 150 °C and 3.0 MPa H₂ [15]. Date *et al.* reported that efficient reductive rearrangement of furfural using Pd/SiO₂ catalyst resulted cyclopentanone with 87% yield (at 98% conversion of FFald) at 165 °C and 5 MPa H₂ [16]. However, precious metals, such as Au, Ru, Pd, and Pt were utilized in these catalyst systems. Therefore, alternative economical and eco-friendly heterogeneous catalysts that would ensure the preferred hydrogenation and rearrangement of furanic ring into CPO/CPL are highly desired.

Catalysts based on Ni, which is also a Pt-group metal, would be good candidates because of the similarity of their catalytic behavior to that of Pt, and such catalysts have been widely used for numerous chemical reactions both in the laboratory and in industry [17]. A few reports have shown that bimetallic Ni-based exhibited a unique catalytic performance for the hydrogenation and rearrangement of furfural to cyclopentanone/cyclopentanol, such as: bimetallic Ni-Fe/SBA-15 catalyst in a methanol/water solvent [18]. Yang *et al.* reported the use of bimetallic Ni-Cu in the conversion of furfural to cyclopentanone and claimed that furfuryl alcohol, 4-hydroxy-2-cyclopentenone and 2-cyclopentenone were verified as three key intermediates and rearrangement of the furan ring was independent of hydrogenation, starting from furfuryl alcohol rather than furfural [19]. In our previous reports, the synthetic pro-

cedure for bimetallic Ni-based with second metals of Sn, In, Co, and Fe applied for chemoselective hydrogenation of biomass-derived furfural, levulinic acid, and dodecanoic acid, have developed. Most recently, the bulk bimetallic Ni-Sn alloy for hydrogenation and rearrangement of FFald in H₂O or H₂O/ethanol solvents and provided CPO and CPL as minor products was applied [20-21]. Therefore, in the present report, an extended investigation on the catalytic conversion of FFald and FFalc using bimetallic Ni-Co(3.0) and Ni-Fe(3.0) supported on TiO₂ (denoted as Ni-Co(3.0)/TiO₂ and Ni-Fe(3.0)/TiO₂ whereas 3.0 is Ni/Co or Ni/Fe molar ratio based on the feeding ratio) is described. Both Ni-Co(3.0)/TiO₂ and Ni-Fe(3.0)/TiO₂ catalysts were synthesized via hydrothermal method according to previous reports [22-23].

2. Materials and Methods

2.1 Materials

Nickel (II) chloride hexahydrate (NiCl₂.6H₂O 98%) cobalt (II) chloride hexahydrate (CoCl₂.6H₂O 99%), iron (III) chloride hexahydrate (FeCl₃.6H₂O 99%) NaOH 99%, ethylene glycol (EG, 99.5%) were purchased from Merck Millipore. NaBH₄ 95%, furfural (98% GC), furfuryl alcohol (98% GC), tetrahydrofurfuryl alcohol (98% GC), 2-methylfuran (98% GC), 1,6-hexanediol (97% GC) were purchased from Tokyo Chemical Industries Co. Ltd. (TCI) and used as received. Titanium oxide powder (TiO₂, S_{BET} = 50 m²/g; anatase structure) was purchased from WAKO Pure Chemical Industries Co. Ltd and used as received.

2.2 Synthesis of Ni/TiO₂

A typical procedure of the synthesis of TiO₂ supported Ni catalyst is described as follows [22]. NiCl₂.6H₂O (0.4392 gram) was dissolved in deionised water and TiO₂ (1 g) was added at room temperature; the temperature was subsequently raised to 50 °C 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 150 °C 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 treated under hydrogen at 450 °C for 1.5 h. A similar procedure was also applied for the syn-

thesis of supported Co/TiO₂ and Fe/TiO₂ catalysts.

2.3 Synthesis of Ni-Co(3.0)/TiO₂ and Ni-Fe(3.0)/TiO₂

A typical procedure of the synthesis of TiO₂ supported Ni-Co (3.0 is feeding ratio) alloy catalyst is described as follows [22]: NiCl₂·6H₂O (0.4408 gram) was dissolved in deionized water (denoted as solution A), and CoCl₂·6H₂O (0.1488 gram) was dissolved in deionized water (denoted as solution B) at room temperature. Solutions A, B, and TiO₂ (1 g) were mixed at room temperature; the temperature was subsequently raised to 50 °C 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 150 °C 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 treated under hydrogen at 450 °C for 1.5 h. A similar procedure was also applied for the synthesis of Ni-Fe(3.0) alloy supported on TiO₂ catalysts.

2.4 Catalyst Characterization

XRD measurements were recorded on a Mac Science M18XHF instrument using monochromatic Cu-Kα radiation ($\lambda = 0.15418$ 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 ($\alpha_1 = 0.154057$ nm, $\alpha_2 = 0.154433$ nm). ICP measurements were performed on an SPS 1800H plasma spectrometer of Seiko Instruments Inc. The BET surface area (S_{BET}) and pore volume (V_p) were measured using N₂ physisorption at 77 K on a Belsorp Max (BEL Ja-

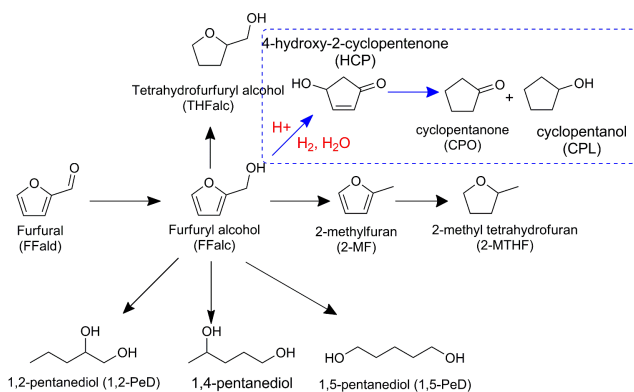
pan). The samples were degassed at 473 K for 2 h to remove physisorbed gases prior to the measurement. The amount of nitrogen adsorbed onto the samples was used to calculate the BET surface area via the BET equation. The pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of approximately 0.995 according to the Barrett–Joyner–Halenda (BJH) approach based on desorption data [24]. The ammonia-temperature programmed-desorption (NH₃-TPD) was carried out on a Belsorp Max (BEL Japan). The samples were degassed at elevated temperature of 100-200 °C for 2 h to remove physisorbed gases prior to the measurement. The temperature was then kept at 200 °C for 2 h while flushed with He gas. NH₃ gas (balanced NH₃, 80% and He, 20%) was introduced at 100 °C for 30 min, then evacuated by helium gas to remove the physisorbed also for 30 min. Finally, temperature programmed desorption was carried out at temperature of 100-800 °C and the desorbed NH₃ was monitored by TCD.

2.5 Catalytic Reaction

The catalyst (50 mg), furfural (1.1 mmol), and ethanol/H₂O (1.5 mL/2.0 mL) as the solvent were placed into a glass reaction tube, which fit inside a stainless steel reactor. After H₂ was introduced into the reactor at an initial H₂ pressure of 3.0 MPa at room temperature, the temperature of the reactor was increased to 110-170 °C. After 3 h, the conversion of furfural (FFald) and the yields of furfuryl alcohol (FFalc) and tetrahydrofurfuryl alcohol (THFalc) were determined using GC analysis. The used Ni-Co(3.0)/TiO₂ catalyst was easily separated using either simple centrifugation (4000 rpm for 10 min) or filtration, then finally dried overnight under vacuum at room temperature prior to re-usability testing.

2.6 Product Analysis

GC analysis of the reactant (FFald) and products (FFalc, THFalc, 2-MeTF, cyclopentanone, and cyclopentanol) was performed on a Shimadzu GC-8A with a flame ionization detector equipped with a silicone OV-101 packed column (length (m) = 3.0; inner diameter (mm) = 2.0; methyl-silicone from Sigma-Aldrich Co. Ltd.). Gas chromatography-mass spectrometry (GC-MS) was performed on a Shimadzu GC-17B equipped with a thermal conductivity detector and an RT-βDEXsm 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-



Scheme 1. Possible reaction pathways for the hydrogenation/hydrogenolysis of furfural.

d1 with TMS as the internal standard. The products were confirmed by a comparison of their GC retention time, mass, ¹H and ¹³C NMR spectra with those of authentic samples.

The conversion of reactant, yield, and selectivity of the products were calculated according to the following equations:

$$\text{Conversion} = \frac{F_0 - F_t}{F_0} \times 100\% \quad (1)$$

$$\text{Yield} = \frac{P_i}{F_0 - F_t} \times 100\% \quad (2)$$

$$\text{Selectivity} = \frac{P_i}{P_{\text{total}}} \times 100\% \quad (3)$$

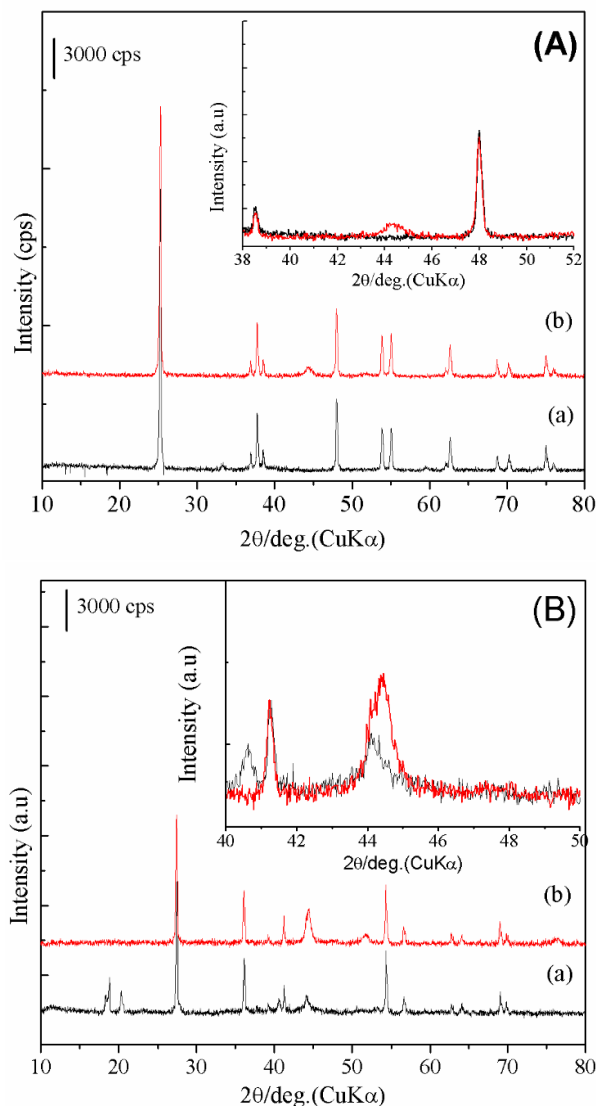


Figure 1. XRD patterns of (A) bimetallic Ni-Co(3.0) supported on TiO₂ and (B) Ni-Fe(3.0) supported on TiO₂ (a) before and (b) after reduction with H₂ at 450 °C for 1.5 h.

where F_0 is the introduced mol reactant (furfural, FFald) (mol), F_t is the remaining mol reactant (mol), P_i is mol product (mol), and P_{total} is total mol products (mol), which are all obtained from GC analysis using an internal standard technique.

3. Results and Discussion

3.1 Catalyst Characterization

The XRD patterns of both as-prepared and after reduction with H₂ at 450 °C for bimetallic Ni-Co(3.0)/TiO₂ and Ni-Fe(3.0)/TiO₂ catalysts are shown in Figures 1 (A and B). The diffraction peaks were compared with the JCPDS-ICDD of standard data of Ni metal (JCPDS 04-0850), Co metal (JCPDS 15-0806), NiO (JCPDS 14-0117), and TiO₂ anatase structure (JCPDS No. 21-1272).

Figure 1(A) shows the XRD patterns of bimetallic Ni-Co(3.0)/TiO₂ before and after reduction with H₂ at 450 °C for 1.5 h. A small diffraction peak at $2\theta = 33.43^\circ$ was observed for as-prepared Ni-Co(3.0)/TiO₂ which is attributed as NiO(100). The formation of bimetallic Ni-Co alloy also was observed at $2\theta = 44.49^\circ$ which overlapping with Ni(111) and Co(111) after reduction with H₂ at 450 °C in the form of face-centered cubic (fcc) [25-27].

Figure 1(B) shows the XRD patterns of bimetallic Ni-Fe(3.0)/TiO₂ before and after reduction with H₂ at 450 °C for 1.5 h. The formation of bimetallic alloy Ni-Fe(111) at $2\theta = 44.06^\circ$ was readily observed after reduction with H₂ at

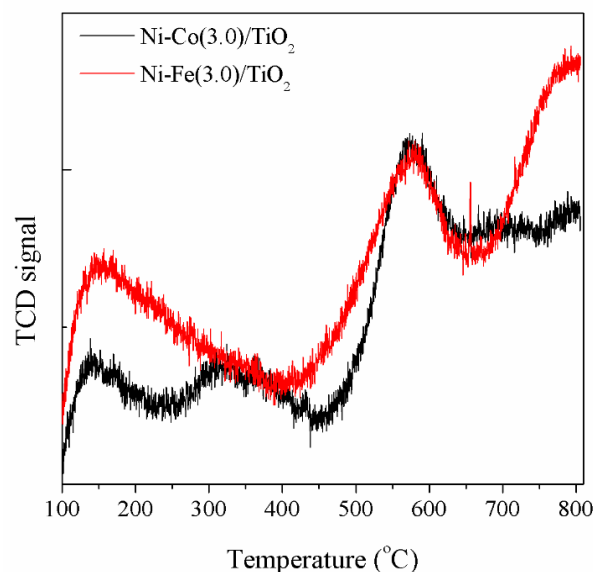


Figure 2. NH₃-TPD spectra of Ni-Co(3.0)/TiO₂ and Ni-Fe(3.0)/TiO₂ catalysts after reduction with H₂ at 450 °C for 1.5 h.

450 °C for 1.5 h as indicated in inserted figure in Figure 1(B). Small diffraction peaks were also observed at $2\theta = 51.73^\circ$ dan 75.84° which can be attributed as the characteristic peaks of Ni(200) and Ni(220) phases. Characteristic diffraction peaks at $2\theta = 36.08^\circ$; 41.24° ; 54.32° ; 56.64° ; 62.78° ; and 64.07° which can be attributed as α -Fe₂O₃ (110), (113), (116), (122), (214), and (300) phases, respectively (Figure 1B (a-b)).

The acidity of both Ni-Co(3.0)/TiO₂ and Ni-Fe(3.0)/TiO₂ was measured using ammonia (NH₃) as molecular probe and the results are shown in Figure 2 and Table 1. Ni-Co(3.0)/TiO₂ catalyst has three desorption peaks at temperature of 180 °C, 353 °C, and 569 °C with amount of acidity was 1.30 $\mu\text{mol.g}^{-1}$, 1.0 $\mu\text{mol.g}^{-1}$, and 2.0 $\mu\text{mol.g}^{-1}$, respectively (whereas the total number of acid sites was 4.3 $\mu\text{mol.g}^{-1}$) (Table 1, entry 1). On the other hand, Ni-Fe(3.0)/TiO₂ displays two desorption peaks at 214 °C and 626 °C with amount of acid sites was 3.3 $\mu\text{mol.g}^{-1}$ and 2.0 $\mu\text{mol.g}^{-1}$, respectively (Table 1, entry 2).

Table 1. Acidic properties of the synthesized Ni-Co(3.0)/TiO₂ and Ni-Fe(3.0)/TiO₂ catalysts.

| Entry | Catalyst ^a | $S_{\text{BET}}^{\text{b}}$ ($\text{m}^2.\text{g}^{-1}$) | NH ₃ -TPD data ^c | |
|-------|-----------------------------|---------------------------------------------------------------|----------------------------------------|----------------------------------------------------------|
| | | | Peak position (°C) | Acidic amount ^d ($\mu\text{mol.g}^{-1}$) |
| 1 | Ni-Co(3.0)/TiO ₂ | 58 | 180 | 1.3 |
| | | | 353 | 1.0 |
| | | | 569 | 2.0 |
| 2 | Ni-Fe(3.0)/TiO ₂ | 46 | 214 | 3.3 |
| | | | 626 | 2.0 |

^aThe value in the parenthesis is Ni/Sn molar ratio. ^bDetermined by N₂ physisorption at -196 °C using BET method. ^cAmmonia-temperature programmed desorption (NH₃-TPD). ^dAcidic amount ($\mu\text{mol.g}^{-1}$) was derived from the NH₃-TPD spectra.

Table 2. Results of the catalytic hydrogenation of biomass-derived furfural in the various solvent over Ni-Fe(3.0)/TiO₂ catalyst.

| Entry | Solvent | Conversion (%) ^a | Yield (%) ^a | | | | |
|-------|-----------------------------|-----------------------------|------------------------|--------|------------------|------------------|---------------------|
| | | | FFalc | THFalc | CPO ^b | CPL ^b | Others ^c |
| 1 | Ethanol | 100 | 45.7 | 51.3 | 0 | 0 | 3 |
| 2 | 2-Propanol | 100 | 36.2 | 60.6 | 0 | 3.2 | 0 |
| 3 | H ₂ O | 86.8 | 40.1 | 20.6 | 5.1 | 15.0 | 6.0 |
| 4 | Ethanol/H ₂ O | 84.9 | 41.5 | 10.4 | 4.2 | 25.8 | 3 |
| 5 | 2-Propanol/H ₂ O | 87.2 | 20.0 | 60.7 | 2.5 | 4.0 | 0 |

Reaction conditions: cat. (0.05 g), FFald (0.1 g), ethanol/H₂O (1.5 mL/2 mL), H₂ (3.0 MPa), temperature (150 °C), reaction time (3 h). ^aConversion and yield were determined using an internal standar technique. ^bCPO = cyclopentanone; CPL = cyclopentanol. ^cOthers are included 2-methyl furan (2-MeTF), tetrahydro methyl furan (MeTHF), and pentanediol (PeD).

3.2 Catalytic Reaction

3.2.1 Screening of solvent

The effect of solvent media for hydrogenation/hydrogenolysis of biomass-derived furfural over bimetallic Ni-Fe(3.0)/TiO₂ were investigated and the results are summarized in Table 2. Typical protic solvents (e.g., ethanol, 2-propanol, H₂O, 1,4-dioxane, ethanol/H₂O, 2-propanol/H₂O, and 1,4-dioxane/H₂O mixtures) were used as solvent.

In the alcoholic solvents, (e.g. ethanol and 2-propanol), FFald was converted completely to FFalc and THFalc (entries 1, 2). The main products were FFalc and THFalc, only a small amount of CPL was obtained (3.2%) in 2-propanol (entry 2). In alcohols, the hydrogenation of C=O and C=C occurred simultaneously to produce FFalc and THFalc, respectively. Only a small amount of hydrogenolyzed product was obtained. Interestingly, a remarkable difference was observed in H₂O, whereas the conversion of FFald was 86.8% and the products were distributed into FFalc, THFalc, CPO, and CPL with yields of 40.1%, 20.6%, 5.1%, and 15.0%, respectively (entry 3). Using ethanol/H₂O mixture solvent, a high yield of CPL (25.8%) was obtained with 84.9% FFald conversion under the same reaction conditions (entry 4). Meanwhile, in 2-propanol/H₂O solvent resulted 4.0% CPL at 87.2% conversion of FFald (entry 5). These results confirmed that the solvent significantly inhibited the C=C hydrogenation as reported previously [19,21,28]. Therefore, it can be concluded that ethanol/H₂O is suitable solvent for the catalytic conversion of FFald to CPL or CPO in presence of bimetallic catalysts.

3.2.2 Screening of catalyst

The selective hydrogenation and rearrangement of FFald to FFalc, CPO, and CPL by us-

ing various supported catalysts were evaluated and the results are summarized in Table 3. Over conventional Raney nickel (Raney®Ni) catalyst, 100% conversion of FFald and yields of FFalc (48.7%) and THFalc (51.3%) were obtained at reaction temperature of 120 °C (entry 1). Similar result was obtained over Raney nickel supported on aluminum hydroxide (R-Ni/AlOH), whereas the conversion of FFald and yield of FFalc were 100% and 96.8%, respectively. The formation of CPL was also observed with a small amount of 3.2% in yield (entry 2). By using Ni/TiO₂ catalyst, the conversion of FFald was 86.8% with selectivities of FFalc and THFalc were 59.1% and 20.6%, respectively and a small amount of CPL product (5.0%) was also obtained (entry 3). Interestingly, Co/TiO₂ afforded 56.6% of FFalc, 1.1% of THFalc, 3.2% of CPO, 27% of CPL, and 10.4% of hydrogenolyzed products at 98.3% of FFald conversion (entry 4). It can be observed that over monometallic Ni/TiO₂ and Co/TiO₂ catalysts, the products were mainly distributed to FFalc with minor product of CPO and CPL and pentanediol at high conversion of FFald. A relatively high conversion and selectivity may be a result of the strong interactions between the active metals and TiO₂ generating significant interactions between C=O groups and Ni-TiO_x sites and leading to high selectivity to unsaturated alcohols. Kijenski *et al.* have reported that Pt catalysts supported on TiO₂ gave higher selectivity to FFalc in the hydrogenation of FFald than that of Pt supported on SiO₂, ZrO₂, or MgO [29]. Rodiansono *et al.* reported that bimetallic alloy

Ni₃Sn₂ catalysts supported on TiO₂ and ZnO demonstrated high conversion of FFald and high selectivity towards FFalc almost exclusively. Eventhough the reaction temperature was increased up to 180 °C, the selectivity towards FFalc remained unchanged [23]. On the other hand, Fe/TiO₂ was not active for the hydrogenation of FFald as indicated by no hydrogenated products of FFalc and THFalc were observed (entry 5).

The synthesized bimetallic Ni-Co(3.0)/AlOH catalyst exhibited high conversion of FFald (100%) and yielded 30.8% of FFalc, 49.2% of THFalc, and 15% of CPL as the results of over hydrogenation of CPO (entry 6). Ni-Co(3.0)/TiO₂ demonstrated high yield of FFalc (62.5%) while THFalc yield was only 23.7% at FFald conversion of 87.2% (entry 7). When the reaction time was prolonged to 6 h, 100% of FFald was converted and yield of FFalc decreased to almost half (49.7%), while selectivity of THFalc increased almost two times (48.5%) suggesting the prolonged reaction time promoted the further hydrogenation of C=C furan ring to THFalc (entry 8). Interestingly, when the reaction temperature was increased to 170 °C at a reaction time of 6 h, the selectivity of FFalc dramatically decreased to only 9.4% which it may convert to CPO and CPL (36.1%) and others (13.7%) since the selectivity of THFalc remained unchanged (entry 9). A similar case was also observed upon bimetallic Ni-Fe(3.0)/TiO₂ catalyst system. Firstly, Ni-Fe(3.0)/TiO₂ catalyst afforded only 44.5% of FFalc, 10.4% of THFalc and 30% of CPO +

Table 3. Results of the catalytic hydrogenation of biomass-derived furfural over the various catalysts.

| Entry | Catalysts | Conversion (%) ^a | Yield (%) ^a | | | | |
|-----------------|-----------------------------|-----------------------------|------------------------|--------|------------------|------------------|---------------------|
| | | | FFalc | THFalc | CPO ^b | CPL ^b | Others ^c |
| 1 ^d | Raney® Ni | 100 | 48.7 | 51.3 | 0 | 0 | 0 |
| 2 | R-Ni/AlOH | 100 | 0 | 96.8 | 0 | 3.2 | 0 |
| 3 | Ni/TiO ₂ | 86.8 | 59.1 | 20.6 | 0 | 5.0 | 0 |
| 4 | Co/TiO ₂ | 98.3 | 56.6 | 1.1 | 3.2 | 27.0 | 10.4 |
| 5 | Fe/TiO ₂ | 34.9 | 0 | 0 | 0 | 0 | 0 |
| 6 | Ni-Co(3.0)/AlOH | 100 | 30.8 | 49.2 | 0 | 15.0 | 2.0 |
| 7 | Ni-Co(3.0)/TiO ₂ | 87.2 | 62.5 | 23.7 | 0 | 0 | 0 |
| 8 ^e | Ni-Co(3.0)/TiO ₂ | 100 | 49.7 | 48.5 | 0 | 1.8 | 0 |
| 9 ^f | Ni-Co(3.0)/TiO ₂ | 100 | 9.4 | 40.5 | 7.1 | 29.0 | 13.7 |
| 10 | Ni-Fe(3.0)/TiO ₂ | 84.9 | 44.5 | 10.4 | 4.2 | 25.8 | 0 |
| 11 ^e | Ni-Fe(3.0)/TiO ₂ | 100 | 4.4 | 51.1 | 11.5 | 23.0 | 0 |
| 12 ^f | Ni-Fe(3.0)/TiO ₂ | 100 | 2.9 | 17.9 | 27.2 | 41.0 | 11.0 |

Reaction conditions: cat. (0.05 g), FFald (0.1 g), ethanol/H₂O (1.5 mL/2 mL), H₂ (3.0 MPa), temperature (150 °C), reaction time (3 h). ^aConversion and yield were determined using an internal standar technique. ^bCPO = cylopentanone; CPL = cyclopentanol. ^cOthers are included 2-methyl furan (2-MTF), tetrahydro methyl furan (MTHF), and pentanediol (PeD). ^dReaction temperature was 120 °C. ^eReaction time was 6 h. ^fReaction temperature and time were 170 °C and 6 h, respectively.

CPL, and there are not 1,2-PeD and 1,5-PeD products were observed at 84.9% conversion of FFald (entry 10). When reaction time was prolonged to 6 h, yield of FFald drastically decreased to only 4.4% while yields of THFalc and mixture of CPO and CPL increased slightly to 51.1% and 34.5%, respectively at 100% FFald conversion (entry 11). An outstanding high yield of CPO (27.2%) and CPL (41.0%) was obtained over Ni-Fe(3.0)/TiO₂ catalyst with remained selectivity of THFalc was 17.9% (entry 12) when reaction temperature and time of 170 °C and 6 h were applied. These results suggest that both Ni-Co and Ni-Fe catalyst systems able to activate C=C bond of C=O bonds of FFald via a selective adsorption on the Brønsted or Lewis acid sites and facilitated the hydrogenation-rearrangement of FFald or FFalc to form cyclopentanone, finally further

hydrogenation of CPO produced CPL [16,30]. In fact, the selectivity of THFalc was remained unchanged at relatively higher reaction temperature or longer reaction time.

3.2.3 Effect of reaction temperature

To understand the effect of temperature in the hydrogenation of FFald over bimetallic Ni-Co(3.0)/TiO₂ catalyst, the reactions were carried out at temperature range of 110-170 °C and the results are shown in Figure 3. In the case of Ni-Co(3.0)/TiO₂ catalyst, the increase of reaction temperature to 170 °C resulted an increase of FFald conversion up to 100%. The increase of reaction temperature enhanced the C=C bond hydrogenation of FFald or FFalc as indicated by the increase of THFalc selectivity (Figure 3a). When the reaction time was prolonged to 6 h at 170 °C, the amount of CPO and CPL mixtures remarkably increased up to 36.1% selectivity (Table 3, entry 9). It was reported that the C-O bond hydrogenolysis of furfural or furfuryl alcohol over Ni-based catalysts preferentially occurred at relatively higher reaction temperature and required longer reaction time [31].

Over Ni-Fe(3.0)/TiO₂ catalyst, FFald conversion gradually increased as the reaction temperature was increased and 100 % FFald conversion was achieved at 170 °C at a reaction time of 3 h (Figure 3b). While the selectivity of THFalc increased as the increase of reaction temperature, the amount of FFalc decreased gradually and then totally disappeared at reaction temperature of 170 °C indicating that over hydrogenation of C=C and C=O bonds occurred at higher temperature. In addition, the higher temperature not only enhanced C=C hydro-

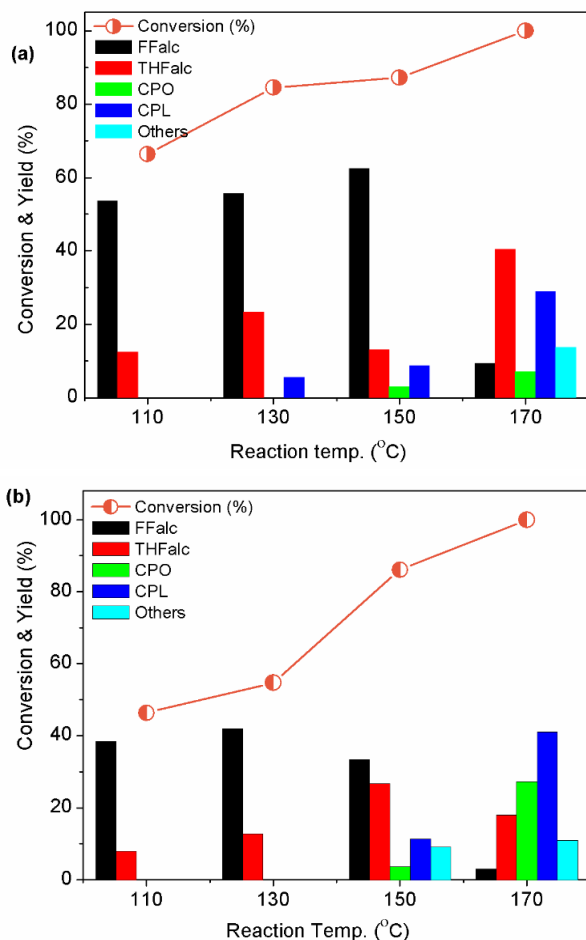


Figure 3. Effect of reaction temperature on conversion and selectivity in selective hydrogenation of FFald over (a) Ni-Co(3.0)/TiO₂ and (b) Ni-Fe(3.0)/TiO₂ catalysts. Reaction conditions: cat. (0.05 g), FFald (0.1 g), ethanol/H₂O (1.5 mL/2.0 mL), H₂ (3.0 MPa), reaction time of 6 h.

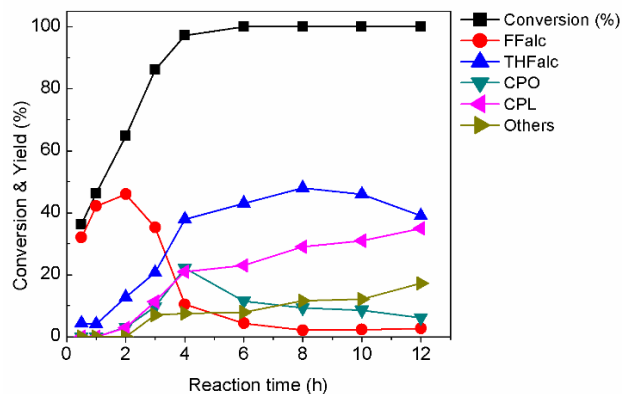


Figure 4. Kinetic profiles of catalytic conversion of FFald to CPO or CPL over supported Ni-Fe(3.0)/TiO₂ catalyst. Reaction conditions are referred to Table 1 dan 2.

genation but also facilitated the C-O hydrogenolysis resulting hydrogenolyzed products, e.g. 2-methylfuran and 2-methyltetrahydrofuran instead of 1,2-pentanediol and 1,5-pentanediol (Figure 3b) [32-33].

3.2.4 Kinetic profiles

The reaction profiles of the catalytic conversion of FFald over supported Ni-Fe(3.0)/TiO₂ catalyst were performed and the plot is shown in Figure 4. At the early reaction time (0.5-2.0 h), the conversion of FFald gradually increased from 36.4% to 64.7% and the main product was FFalc (the highest yield is 46% after reaction time of 2 h). After reaction time was prolonged to 3 h, the conversion of FFald also increased, meanwhile the yield of FFalc slightly decreased. On the other hand, yields of THFalc, CPO, and CPL increased smoothly. These re-

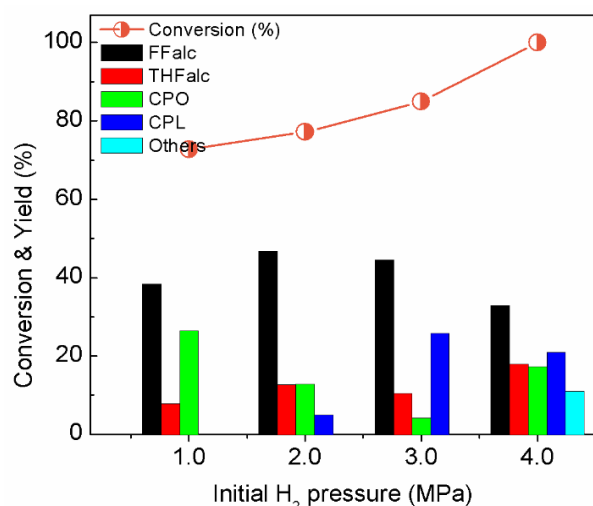


Figure 5. Effect of initial pressure of H₂ on conversion and selectivity in selective hydrogenation of FFald over Ni-Fe(3.0)/TiO₂ catalyst. Reaction conditions: cat. (0.05 g), FFald (0.1 g), ethanol/H₂O (1.5 mL/2.0 mL), and a reaction time of 6 h.

Table 4. Results of the catalytic hydrogenation of biomass-derived furfural over various supported Ni-Fe(3.0) catalysts.

| Entry | Catalysts | Conversion (%) ^a | Yield (%) ^a | | | | |
|-------|---------------------------------------------|-----------------------------|------------------------|---------------------|------------------|------------------|---------------------|
| | | | FFalc | THFalc ^c | CPO ^b | CPL ^b | Others ^c |
| 1 | Ni-Fe(3.0)/AlOH | 100 | 20.3 | 55.7 | 0 | 11.0 | 3.0 |
| 2 | Ni-Fe(3.0)/SiO ₂ | 100 | 32.7 | 28.2 | 3.2 | 9.1 | 30.0 |
| 3 | Ni-Fe(3.0)/ZnO | 100 | 53.0 | 33.3 | 3.7 | 5.0 | 5.0 |
| 4 | Ni-Fe(3.0)/C | 100 | 18.4 | 57.1 | 9.5 | 15 | 0 |
| 5 | Ni-Fe(3.0)/γ-Al ₂ O ₃ | 100 | 21.3 | 19.7 | 13.8 | 35.2 | 10 |

Reaction conditions: cat. (0.05 g), FFald (0.1 g), ethanol/H₂O (1.5 mL/2 mL), H₂ (3.0 MPa), temperature (170 °C), reaction time (6 h). ^aConversion and yield were determined using an internal standard technique. ^bCPO=cyclopentanone; CPL= cyclopentanol. ^cOthers are included 2-methyl furan (2-MeTF), methyl tetrahydrofuran (MeTHF), and pentanediol (PeD).

sults indicated that, the first step reaction would be the hydrogenation of C=O bond of FFald to produce FFalc. During the reaction, FFalc is converted via Piancatelli rearrangement into CPO whereas the 4-hydroxy-2-cyclopentenone (4-HCP) is the intermediate product [10,34]. However, once the THFalc was formed, the formation of CPO or CPL will be constant as indicated in Figure 4 due to the activation and hydrogenolysis of hydrofuran ring of THFalc required a specific active site, such as strong acid site or multicenter metal catalysts [5,35].

The formation of FFalc was the first step then rearrangement of FFalc structure occurred on the acidic surface of bimetallic Ni-Sn alloy catalysts [20-21]. Therefore, similar approach would be applicable to the catalytic conversion of FFald over bimetallic Ni-Fe(3.0)/TiO₂ catalyst.

3.2.5 Effect of initial H₂ pressure

The effect of initial H₂ pressure on conversion and selectivity in hydrogenation of FFald was evaluated over Ni-Fe(3.0)/TiO₂ catalyst and the results are shown in Figure 5. The conversion of FFald gradually increased as the initial pressure of H₂ was increased to reach a maximum conversion (100%) at 4.0 MPa. At initial pressure of H₂ *c.a.* 1.0 MPa, 71% FFald

Table 5. Results of the reusability test for Ni-Fe(3.0)/TiO₂ in the hydrogenation of FFald.

| Run | 1 | 2 | 3 |
|-----------------------------------|------|------|------|
| Conversion ^a (%) | 100 | 99.8 | 99.3 |
| Yield of CPO+CPL ^b (%) | 68.2 | 59.1 | 58.2 |

Reaction conditions: cat. (0.05 g), FFald (0.1 g), ethanol/H₂O (1.5 mL/2 mL), H₂ (3.0 MPa), temperature (170 °C), reaction time (6 h). ^aConversion and yield were determined using an internal standard technique. ^bCPO = cyclopentanone; CPL = cyclopentanol.

converted to 38% FFalc, 7% THFalc, and 25% CPO in yields. Conversion of FFald slightly increased to 78% and the products were distributed to FFalc, THFalc, CPO, and CPL. The yield of CPL significantly increased to 27% as result of further hydrogenation of CPO as indicated by decreasing yield of CPO at initial H₂ pressure of 3.0 MPa. Further increasing the initial H₂ pressure to 4.0 MPa, the products distributed to 30% FFalc, 20% THFalc, 20% CPO, 21% CPL, and hydrogenolized product of pentanediol and methyl furan with yields of 11%. Therefore, the optimized initial pressure of H₂ for one-pot conversion of FFald to CPO/CPL over Ni-Fe(3.0)/TiO₂ catalyst was 3.0 MPa.

3.2.6 Effect of various supported Ni-Fe catalysts

To confirm the effect of support catalysts, Ni-Fe(3.0) was dispersed on the various supports, such as: aluminum hydroxide (AlOH), silica (SiO₂), carbon (C), ZnO, and γ -Al₂O₃, while the catalytic reaction results are summarized in Table 4. By using Ni-Fe(3.0)/AlOH catalyst, the yields of FFalc, THFalc, and CPL were 20.3%, 55.7%, and 11%, respectively (entry 1). A small amount of hydrogenolized product (<5% yield) was also obtained this catalyst. In the case of SiO₂-, ZnO-, C-, and γ -Al₂O₃-supported Ni-Fe(3.0) catalysts (entry 2-5), with a complete conversion of FFald (100%), the highest CPO + CPL yields (49%) were obtained over Ni-Fe(3.0)/ γ -Al₂O₃ catalyst (entry 5).

3.2.7 Catalyst re-usability test

A reusability test was performed on the Ni-Fe(3.0)/TiO₂ catalyst, and the results are summarized in Table 5. The used Ni-Fe(3.0)/TiO₂ was easily separated by either simple centrifugation or filtration after the reaction. The recovered catalyst was reactivated by H₂ at 450 °C for 1.5 h prior to used in the next reaction run. The yield of CPO+CPL on the reused catalyst decreased slightly after the second reaction run, but the activity was maintained for at least three consecutive runs.

4. Conclusions

The synthesis, characterization, and catalytic properties of bimetallic Ni-Co(3.0) and Ni-Fe(3.0) supported on TiO₂ catalysts was described. XRD analyses revealed that the formation bimetallic Ni-Fe(111) alloy at $2\theta = 44.06^\circ$ in Ni-Fe(3.0)/TiO₂ easily observed after reduction with H₂ at 450 °C for 1.5 h. On the other hand, Ni-Co(3.0)/TiO₂ did not provide the

formation of Ni-Co alloy phase or hardly to distinguish the overlapped peaks of Ni(111) and Co(111). Monometallic Co/TiO₂ exhibited higher selectivity towards FFalc than that of other monometallic catalysts. Bimetallic Ni-Co(3.0)/TiO₂ and Ni-Fe(3.0)/TiO₂ catalysts also demonstrated high selectivity toward FFalc at relatively lower reaction temperature. At the higher reaction temperature, the hydrogenation C=C bond and the arrangement of furan ring produced THFalc and CPO/CPL as the main products. The highest yields of CPO and CPL were 27.2% and 41.0%, respectively over Ni-Fe(3.0)/TiO₂ at 170°C for 6 h.

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