BUKTI KORESPONDENSI
ARTIKEL JURNAL INTERNASIONAL BEREPUTASI

Judul artikel : The Promotion Effect of Cu on the Pd/C Catalyst in the Chemoselective Hydrogenation of Unsaturated Carbonyl Compound

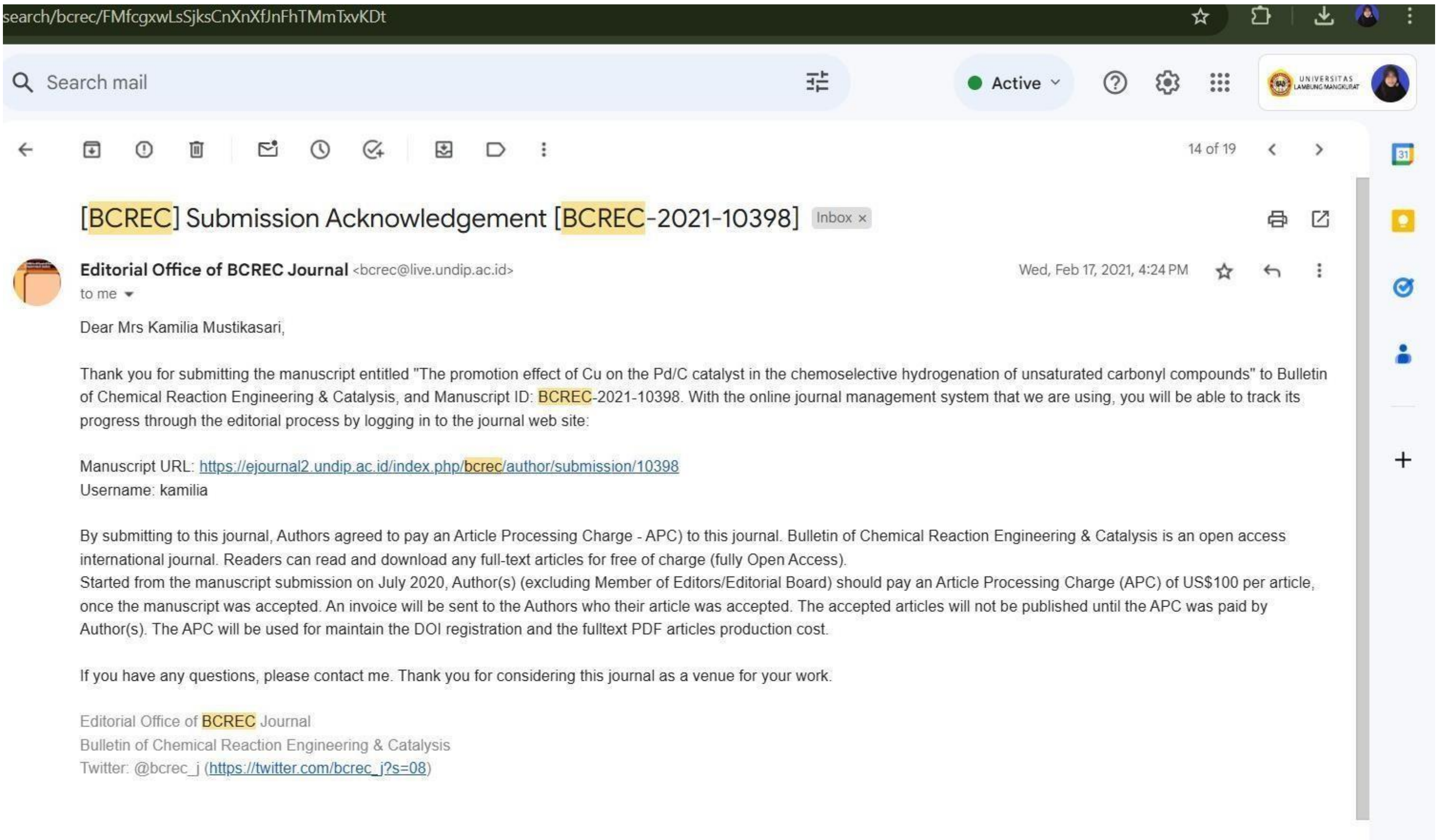
Jurnal : Bulletin of Chemical Reaction Engineering & Catalysis, 2021, volume 16 (2), 267 – 279

Penulis :

No.	Perihal	Tanggal
1.	Bukti konfirmasi submit artikel dan artikel yang disbumit	17 Februari 2021
2.	Bukti konfirmasi review dan hasil review pertama	4 Apr 2021
3.	Bukti konfirmasi submit revisi pertama, respon kepada reviewer, dan artikel yang diresubmit	28 Apr 2021
4.	Bukti konfirmasi artikel accepted	28 Apr 2021
5.	Bukti permintaan proofreading	4 Mei 2021
6.	Resubmit artikel yang sudah di Proofreading, dan Graphical abstrak	7 Mei 2021
7.	Bukti konfirmasi artikel published online	11 Mei 2021

1. Bukti Konfirmasi Submit Artikel dan Artikel yang Disubmit

(17 Pebruari 2021)



[BCREC] Submission Acknowledgement [BCREC-2021-10398]

Editorial Office of BCREC Journal <bcrec@live.undip.ac.id>
to me

Wed, Feb 17, 2021, 4:24 PM

Dear Mrs Kamilia Mustikasari,

Thank you for submitting the manuscript entitled "The promotion effect of Cu on the Pd/C catalyst in the chemoselective hydrogenation of unsaturated carbonyl compounds" to Bulletin of Chemical Reaction Engineering & Catalysis, and Manuscript ID: BCREC-2021-10398. With the online journal management system that we are using, you will be able to track its progress through the editorial process by logging in to the journal web site:

Manuscript URL: https://ejournal2.undip.ac.id/index.php/bcrec/author/submission/10398
Username: kamilia

By submitting to this journal, Authors agreed to pay an Article Processing Charge - APC) to this journal. Bulletin of Chemical Reaction Engineering & Catalysis is an open access international journal. Readers can read and download any full-text articles for free of charge (fully Open Access).
Started from the manuscript submission on July 2020, Author(s) (excluding Member of Editors/Editorial Board) should pay an Article Processing Charge (APC) of US$100 per article, once the manuscript was accepted. An invoice will be sent to the Authors who their article was accepted. The accepted articles will not be published until the APC was paid by Author(s). The APC will be used for maintain the DOI registration and the fulltext PDF articles production cost.

If you have any questions, please contact me. Thank you for considering this journal as a venue for your work.

Editorial Office of BCREC Journal
Bulletin of Chemical Reaction Engineering & Catalysis
Twitter: @bcrec_j (https://twitter.com/bcrec_j?s=08)

The promotion effect of Cu on the Pd/C catalyst in the chemoselective hydrogenation of unsaturated carbonyl compounds

Kamilia Mustikasari,[1,2] Rodiansono,[1,2]* Maria Dewi Astuti,[1,2] Sadang Husain,[2,3] Sutomo[4]

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Lambung Mangkurat University, Jl. A. Yani Km 36.0 Banjarbaru South Kalimantan, Indonesia 70714.

[2]Catalysis for Sustainable Energy and Environment (CATSuRe), Lambung Mangkurat University.

[3]Department of Physics, Faculty of Mathematics and Natural Sciences, Lambung Mangkurat University, Jl. A. Yani Km 36 Banjarbaru, Indonesia 70714.

[4]Department of Pharmacy, Faculty of Mathematics and Natural Sciences, Lambung Mangkurat University, Jl. A. Yani Km 36 Banjarbaru, Indonesia 70714.

**Corresponding author: rodiansono@ulm.ac.id (R. Rodiansono).*

Telp. /Fax.: +62 511 477 3112

Abstract

Highly efficient and selective hydrogenation of α,β–unsaturated carbonyl compounds to unsaturated alcohol using bimetallic palladium-copper supported on carbon (denoted as Pd–Cu(3.0)/C; 3.0 is Pd/Cu molar ratio) catalyst is demonstrated. Pd–Cu(3.0)/C catalyst was prepared via a simple hydrothermal route under air atmosphere at 150°C for 24 h followed by reduction with hydrogen at 400°C for 1.5 h. The chemoselective hydrogenation of typical α,β–unsaturated carbonyl ketone (2-cyclohexene-1-one) and aldehyde (*trans*-2-hexenaldehyde), and chemoselective hydrogenation of FFald and (E)-non-3-en-2-one mixture demonstrated high productivity, leading to high selectivity of unsaturated alcohols. The presence of bimetallic Pd–Cu alloy phase with relatively high H_2 uptakes was observed, enabling to preferentially hydrogenate C=O rather than to C=C bonds under mild reaction conditions. Pd–Cu(3.0)/C catalyst was found to stable and reusable for at least four reaction runs and the activity and selectivity of the catalyst can be restored to the original after rejuvenation with H_2 at 400^{o}C for 1.5 h.

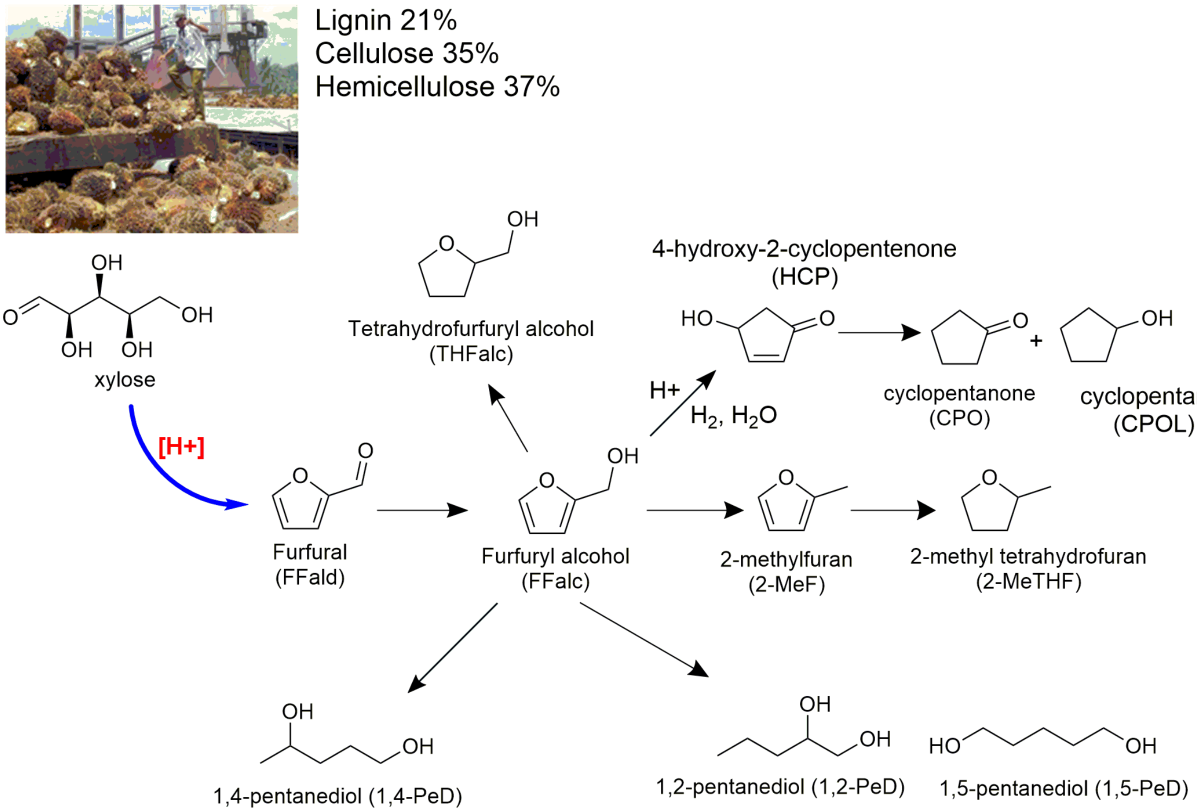
Keywords: bimetallic palladium-copper; chemoselective hydrogenation; furfural; furfuryl alcohol; unsaturated alcohol

1. Introduction

The chemoselective hydrogenation of the C=O bond in α,β−unsaturated ketones/aldehydes has been extensively studied because the unsaturated alcohols that it forms are important in the production of a variety of fine chemicals, such as pharmaceuticals, perfumes, and flavorings [1,2]. Typically, the chemoselective reduction of the carbonyl group is achieved using reducing agents [3], Meerwin-Ponndorf-Verly [4], or using organometallic catalysts [5]. These processes often use costly chemicals and solvents which require separations. In this context, heterogeneous catalysis is viewed as an alternative, more sustainable route for the production of these high-value chemicals at an industrial scale [6–8]. Simple preparation and recovery of heterogeneous catalysts are desirable features for the chemical industry.

Recent works indicate that bimetallic catalysts have the potential to enhance the selectivity in the hydrogenation of many different classes of chemicals [9], such as alkynes, alkenes[10], and carbonyl compounds [11,12] as well as biomass-derived molecules [13–15]. It is well known that the group 9 and 10 metals, such as Rh, Ir, Ni, Pd, and Pt, generally hydrogenate the C=C bond more easily than the C=O bond of α,β−unsaturated aldehydes [16]. To improve the chemoselective hydrogenation of the C=O group, the modification of the above mentioned metals is necessary, i.e., the addition of more electropositive metals [17] or the use of oxide supports that strongly interact with the active metals [18]. In these contexts, we have described previously that the chemoselective behaviors of Ni-based catalysts can be controlled by doping the second metals, such as tin (Sn) or indium (In) to form bimetallic Ni−Sn or Ni-In alloy. Both bulk and supported Ni−Sn and Ni−In alloy catalyst have obviously demonstrated high chemoselectivity in the hydrogenation of α,β-unsaturated ketones/aldehydes toward unsaturated alcohols[19–23].

It is well-known that furfural (FFald), a versatile and biogenic biomass-derived compound, which can be obtained from acidic dehydration of arabinose or xylose of hemicellulosic biomasses [24]. Further catalytic conversion of FFald via chemoselective hydrogenation, hydrogenolysis, hydrogenation-arrangement using both monometallic and bimetallic transition metal catalysts produced a variety of high value chemicals such as furfuryl alcohol (FFalc), tetrahydrofurfuryl alcohol (THFalc), methyl-furan (MeF), methyl tetrahydrofuran (MeTHF), pentanediol (PeD), and cyclopentanone (CPO) or cyclopentanol (CPOL) as shown in Scheme 1[25–27].



Scheme 1 Conceivable reaction networks for the catalytic transformation of FFald that involve hydrogenation, hydrogenolysis, decarbonylation, ring opening hydrogenation, and hydrogenation-rearrangement pathways.

Platinum-group metal (PGM) constitute the most studied catalyst components for hydrogenation of FFald and demonstrated high activity and selectivity towards FFalc, which were included Sn modified Pt-based [28] and Ni-based catalysts [20,21] due to their intrinsic high catalytic ability under mild conditions, high selectivity towards a specific product, high stability under various reaction conditions, and tolerance to poisons [29,30]. Although platinum is the most widely used element in catalysis, palladium is receiving increasing attention owing to its similar catalytic properties to platinum and wider availability. However, the catalytic behavior of Pd-based catalyst on the hydrogenation of unsaturated aldehydes/ketones or oxygenated biomass-derived compounds that consisted of C=O and C=C bonds preferentially promoted decarbonylation or decarboxylation reactions. For example, when Pd/C is used as catalyst for hydrogenation of FFald in the presence of H_2 gas, a wide range of competing reactions, such as unselective hydrogenation of furan-ring or aldehyde groups and incomplete hydrodeoxygenation have been reported [31,32]. Therefore, introduction of a secondary metal species or deposition of Pd nanoparticles on the support that strongly interact with the actives metal are frequently adopted as an effective approach to acquire target products in satisfactory yields [30].

In the present report, we have extended our study on the preparation of bimetallic palladium copper catalyst supported on active carbon (denoted as Pd–Cu(3.0)/C; 3.0 is molar ratio of Pd/Cu). Bimetallic Pd–Cu(3.0)/C catalyst was prepared via the hydrothermal treatment of a solution that contained Pd and Cu species at 150°C for 24 h followed by H_2 treatment at 400°C for 1.5 h. The effect of the Pd/Cu molar ratio, solvent use and reaction parameters (initial H_2 pressure, reaction temperature) on the activity and selectivity in the hydrogenation of FFald are also studied.

2. Materials and Methods

2.1 Materials

Palladium (II) chloride ($PdCl_2$; Tokyo Chemical Industries Co. (TCI)), copper (II) nitrate ($Cu(NO_3)_2{\cdot}3H_2O$; Merck) were purchased and used as received. Microporous carbon (C, $S_{BET} = 815\ m^2g^{-1}$) was purchased from WAKO Pure Chemical Industries, Ltd. Ltd. unless otherwise stated. Furfural, furfuryl alcohol, tetrahydrofurfuryl alcohol, *iso*-propanol, ethanol, and authentic organic reactants and products were purchased from Tokyo Chemical Industries Co. (TCI). All organic chemical compounds were purified using standard procedures prior to use.

2.2 Catalyst characterisation

All catalysts were characterized by powder X-ray diffraction (XRD) Miniflex 600 Rigaku with Cu as monochromatic source K a radiation (λ = 0.15444 nm). XRD operated at 40 kV and 15 mA with solar slit 1.25°, scan step 5° min^{-1} and using a Ni Kβ filter. The crystallite size of palladium was estimated by using the Scherrer`s equation. ICP-AES (inductive-coupled plasma-atomic emission spectroscopy) measurements were performed on an SPS 1800H plasma spectrometer of Seiko Instruments Inc. (Ni: 221.7162 nm). The Brunauer-Emmet-Teller (BET) surface area (S_{BET}) and pore volume (Vp) were measured using N_2 physisorption at -196°C on a Belsorp Max (BEL Japan). The samples were degassed at 200°C 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 [33]. The active surface areas were determined by H_2 chemisorption. After the catalyst was heated at 120°C under vacuum for 30 min, it was heated at 400°C under H_2 for 30 min and under vacuum for 30 min, followed by evacuation to room temperature for 30 min. The adsorption of H_2 was conducted at 0°C. The active surface area was calculated from the volume of

H_2 desorbed by assuming an H/Pd stoichiometry of one, respectively and the number of Pd atom for the (111) plane is 1.5 x 10^{15} per cm^2 Pd based on an equal distribution of the three lowest index planes of Pd [34].

2.3 Preparation of catalysts

A typical procedure of the synthesis of bimetallic palladium-copper supported on carbon (denoted as Pd–Cu(3.0)/C (3.0 molar ratio of Pd/Cu)) catalyst is described as follows: $PdCl_2$ (0.472 mmol) was dissolved in deionized water (denoted as solution A), and $Cu(NO_3)_2 \cdot 3H_2O$ (0.156 mmol) was dissolved in ethanol/2-methoxy ethanol (2:1) (denoted as solution B) at room temperature. Solutions A and B 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 dropwised 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 reduced with hydrogen at 400°C for 1.5 min.

2.4 Catalytic reactions

2.4.1 Hydrogenation of FFald

Catalyst (0.05 g), FFald (1.1 mmol), *trans*-decahydronaphthalene (decalin) (0.2 mmol), and *iso*-PrOH (3 mL) as solvent were placed into a glass reaction tube, which fitted inside a stainless-steel reactor. After H_2 was introduced into the reactor with an initial H_2 pressure of 3.0 MPa at room temperature, the temperature of the reactor was increased to 130°C. After 1.5 h (90 min), the conversion of FFald and the yield of FFalc were determined by GC analysis using an internal standard technique. The Pd–Cu(3.0)/C catalyst was easily separated using either simple centrifugation or filtration. The solvent was removed in vacuo, and the residue was purified via silica-gel column chromatography.

2.4.2 Product Analysis

GC analysis of the reactant (FFald) and products (FFalc and THFalc) was performed on a Shimadzu GC-8A equipped with a flame ionization detector and silicone OV-101 packing. 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 ^{13}C NMR spectra were obtained on a JNM-AL400 spectrometer at 400 MHz; the samples for NMR analysis were dissolved in chloroform-d_1 with TMS as the internal standard. The products were confirmed by a comparison of their GC retention time, mass, ^{1}H and ^{13}C NMR spectra with those of authentic samples. The conversion, yield and selectivity of the products were calculated according to the following equations:

$$Conversion = \frac{\text{introduced mol reactant (Fo) - remained mol reactant (Ft)}}{\text{introduced mol reactant (Fo)}} x100\%$$

$$Yield = \frac{\text{mol product}}{\text{consumed mol reactant } (\Delta F)} x100\%$$

$$Selectivity = \frac{\text{mol product}}{\text{total mol product}} x100\%$$

where F_0 is the introduced mol reactant (furfural, FFald), F_t is the remaining mol reactant, and ΔF 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 characterization

The physico-chemical properties (e.g., specific surface area BET (S_{BET}), pore volume, pore diameter, and H_2 uptakes) of the synthesized bimetallic Pd–Cu(3.0)/C catalysts are summarized in **Table 1**. The S_{BET} of as prepared, H_2-reduced, and recovered Pd-Cu(3.0)/C was 637, 712, and 601 $m^2.g^{-1}$, respectively, which are lower than that of the S_{BET} of the carbon support (C, $S_{BET} = 815$ m^2g^{-1}).

Figure 1 shows the XRD pattern of commercial Pd/C(5%wt), as-prepared and pre-reduced bimetallic Pd–Cu(3.0)/C catalysts. In the case of as-prepared Pd–Cu(3.0)/C catalyst, the typical diffraction peaks at $2\theta = 39.96^o$, 46.16^o, 67.6^o were clearly observed, which can be attributed to the metallic species of Pd(111), Pd(200), and Pd(020) (JCPDS#05-0681), respectively[35]. The diffraction peak of Pd(111) at $2\theta = 40.8^o$ become broadened, which can be attributed as the formation of bimetallic Pd-Cu alloy after reduction with H_2 at 400°C for 90 min[36]. By using the Scherrer`s equation, the average crystallite sizes of Pd(111) in as prepared Pd-Cu(3.0)/C were 4.2 nm, whereas in Pd–Cu(3.0)/C was unable to calculate due to the overlapping diffraction peaks of Pd(111) and Pd–Cu alloy phase (Figure 1c). A small peak at $2\theta = 29.6^o$ which can be assigned as the $Cu_2O(110)$ species (JCPDS# 78-2076) was also observed both in the as prepared and reduced Pd–Cu(3.0)/C samples (Figure 1b-c). Additionally, the broadened peak at $2\theta = 21.3^o$ can be attributed to the diffraction peaks of C(111) of carbon support[37].

Figure 2 shows the profiles of N_2-adsorption/desorption and plot of volume of adsorbed-N_2 versus pore distribution using BJH approach (with cut-off the pore size of 1.21 nm) confirmed that there are no significant change of the pore structure of catalyst support during the introducing Pd metal or thermal activation using N_2 or H_2 at 400°C. It has been reported that carbon support has high thermal and chemical stability at the range of 300-500°C under H_2 or N_2 atmosphere [38,39].

3.2 Catalytic reactions

3.2.1 Screening of second metal

In the first set experiments, the catalytic hydrogenation of biomass-derived FFald using various bimetallic Pd-based catalysts were performed and the results are summarized in Table 2. By using commercial Pd/C (5%wt Pd) catalyst, the main product was THFalc (80%) as the result of total hydrogenation of both C=C and C=O bonds in FFald with small amount yields of FFalc (2%) and 2-MeF (8%) at 100% conversion of FFald (entry 1). Using Pd–Cu(3.0)/C catalyst without pre-reduction with H_2, the conversion of FFald was only 56% and yielded 28% FFalc, 15% THFalc, and 13% others (others consist of furfural condensation according to GC and GC-MS data) (entry 2) [40]. After a small amount of Cu (0.156 mmol; Pd/Cu molar ratio ≅ 3.0) was introduced and Pd–Cu(3.0)/C catalyst was pre-reduced with H_2 at 400°C, the product selectivity remarkably shifted to FFalc (68% in yield) at 73% conversion of FFald (entry 3). An increase in the reaction temperature from 100°C to 130°C gave a notable increase in FFalc yield from 68% to 94%, respectively (entries 3 and 4). After reaction time was extended to 3 h, the yield of FFalc slightly decreased to 92% while THFalc and 2-MeF yield remained unchanged at >99% conversion of FFald (entry 5). This result suggests that further hydrogenation of C=C furan ring was significantly inhibited over bimetallic Pd–Cu(3.0)/C catalyst. Sitthisa et al have noticed that the presence of Cu in Pd–Cu/SiO_2 catalyst greatly enhanced the affinity of Pd towards η^2(C-O)-furfural interaction, facilitated the formation of hydroxyalkyl species then easily hydrogenated to FFalc. On the other hand, the further hydrogenation of C=C or decarbonylation rate is greatly reduced on bimetallic Pd–Cu system [32]. Furthermore, investigation of the effect of various second metals such as tin (Sn), cobalt (Co), nickel (Ni), and iron (Fe) on the conversion of FFald and yield of FFalc was also performed and the results are also summarized in **Table 2**. However, those bimetallic Pd–M/C (M = Sn, Co, Ni, and Fe) catalysts gave unsatsified results both conversion of FFald and yield of FFalc under the same reaction conditions (entries 6-9). Therefore, further investigation will be focused on the bimetallic Pd-Cu catalysts, including the effect of solvent used, reaction temperature, initial H_2 pressure, time profiles, and reusability test.

3.2.2 Effect of solvent

The results of solvent screening for FFald hydrogenation are summarized in **Table 3**. Alcohols, such as 2-propanol (*iso*-PrOH), 1-propanol, ethanol, and methanol, and 1,4-dioxane (typical cyclic ether) are superior to other solvents, giving quantitatively high yields of FFalc (entries 1-5). On the other hand, FFald hydrogenation did not proceed effectively in toluene, giving only a 43% FFalc yield at the same conditions (entry 6). These results are very good agreement with the catalytic reaction results over bimetallic Ni-Sn alloy catalysts as reported previously [19,21]. The formation of 1,2-, 1,5-, and 1,4-pentanediol as the hydrogenolyzed products or condensation product was firstly observed in H_2O solvent, therefore we furtherly evaluated the catalytic reaction both in H_2O solvent only and the alcohols/1,4-dioxane-H_2O mixture solvent and the results are also summarized in Table 3. In ethanol: H_2O (1.5: 2.0 v/v), 2-propanol: H_2O (1.5: 2.0 v/v), and 1,4-dioxane: H_2O (1.5: 2.0 v/v) mixture solvents, the reaction not only hydrogenation of C=O and C=C bonds of reactant but also hydrogenolysis of furan ring, giving significantly high yield of pentanediol (entries 8-10). These results are in accordance with our results in the hydrogenolysis of FFald to 1,4-pentanediol in ethanol: H_2O (1.5: 2.0 v/v) mixture solvent using bulk Ni-Sn alloy catalyst as reported previously [41]. Additionally, a notable high yield of cyclopentanone (CPO) and cyclopentanol (CPOL) was obtained when 1,4-dioxane or 1,4-dioxane-H_2O mixture solvent was used. These results are very consistent with the previous work of Dewi Astuti et al. using bimetallic Ni–Fe(3.0)/TiO_2 catalysts under the identical reaction conditions [27]. Therefore, further investigation on the hydrogenolysis of FFald using bimetallic Pd–based catalysts will be reported in our upcoming manuscript.

3.2.3 Effect of reaction temperature

The effect of temperature on the catalytic hydrogenation of FFald to FFalc was evaluated over Pd–Cu(3.0)/C catalyst, and the results are shown in **Figure 3**. Differences in the conversion of FFald and product distributions at different temperature are clearly observed. At lower temperature (90-110^{o}C), the maximum conversion of FFald was around 87% with selectivity of FFalc was nearly 100%. An increase of the reaction temperature from 100^{o}C to 130^{o}C gave a notable increase in FFalc yield from 68% to 94%, respectively followed by a slight increase of THFalc from 3% to 5%. At those of reaction temperatures, the enhancement of decarbonylation reaction rate of FFald did not occure as indicated by remained unchange of 2-MeF yield. Moreover, further increase of reaction temperature to 150-190^{o}C promoted the hydrogenation of C=C bond as well as the decarbonylation reactions, giving increase in yields of THFalc and 2-MeF, respectively. It has been reported that the decarbonylation reaction of FFald corresponding to 2-MeF using catalyst of platinum metal groups (Pd, Pt, and Ir) is favourably occurred at relatively high reaction temperature (190-220^{o}C)[42] or vapor phase hydrogenation [31]. The presence of second metals such as Cu or Fe was significantly inhibited the further reaction of FFald or FFalc such as total hydrogenation of C=C/C=O bonds or decarbonylation/decarboxylation, therefore the selectivity of desired product FFalc maintained along with the wide range reaction conditions[32].

3.2.4 Effect of initial H_2 pressure

The effect of the initial H_2 pressure on the FFald conversion and product selectivity in shown in **Figure 4.** FFald conversion and FFalc selectivity gradually increased as the initial H_2 pressure increased, whereas the THFalc increased at initial H_2 pressure of 0.5-1.0 MPa and remained unchanged at the higher initial H_2 pressure. On the other hand, yield of 2-MeF decreased to 0% at initial pressure between 2.5 MPa and 3.0 MPa.

3.3 Time profiles

The reaction profiles of FFald hydrogenation at 130°C on the bimetallic Pd–Cu(3.0)/C catalyst are shown in **Figure 5**. At the early reaction time (0.5 h), FFald conversion was 42% to produce 100% FFalc selectivity, indicating that C=O hydrogenation was took place easily using bimetallic Pd–Cu(3.0)/C catalyst. After reaction was prolonged to 1.0 h, a notable increase of FFald was obtained (87%) with yields of FFalc and THFalc were 85% and 2%, respectively. It has been reported that Pd exhibits a low rate for hydrogenation of the C=O bond compared with other metals commonly used for hydrogenation [43]. Our current results show that a great enhancement both conversion of FFald and selectivity of FFalc which can be attributed to the promotional effect of the second metal Cu as has already described in previous reports [31,32]. The maximum yield of FFalc (94%) was achieved after a reaction time of 1.5 h at full conversion of FFald. When the reaction time was extended to 3-6 h, further hydrogenation reaction of C=C bond obviously occurred as indicated by the increase of THFalc yield. On the other hand, the yield of 2-MeF was almost unchanged after a reaction time of 6 h (3%), suggesting the decarbonylation of FFald or FFalc did not occur effectively using bimetallic Pd–Cu(3.0)/C catalyst under the current operating conditions as mentioned previously.

3.4 Hydrogenation of α,β-unsaturated ketone and aldehyde

A substrate scope of the presence of Pd–Cu(3.0)/C catalyst in the hydrogenation of α,β-unsaturated ketone and aldehyde was examined and the results are summarized in **Table 4** and **Table 5**.

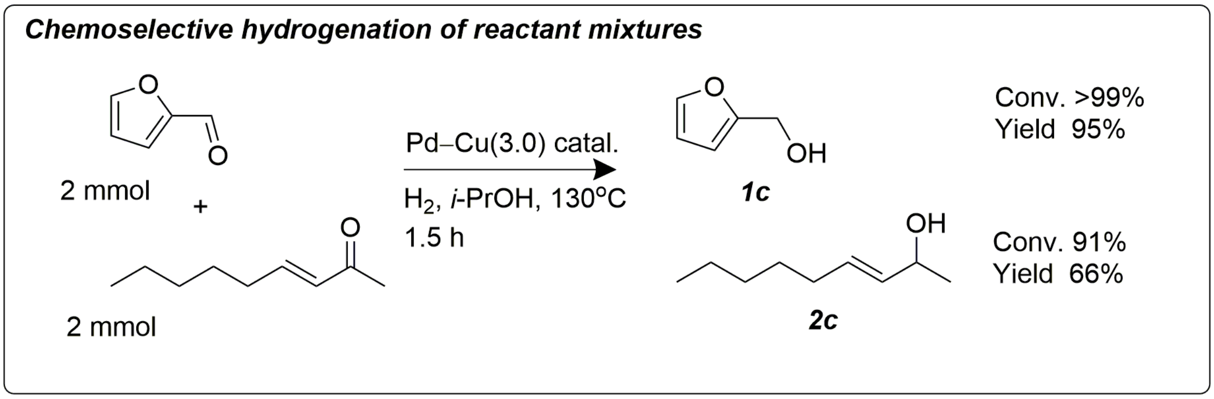
In the case of hydrogenation of ketone, 2-cyclohexene-1-one was selected as a typical α,β-unsaturated ketone substrate. Using a commercial Pd/C (5%wt Pd) catalyst, 33% conversion of 2-cyclohexene-1-one was obtained with the selectivities of product **2a** and **3a** were 24% and 76%, respectively without the formation of product **1a** (entry 1). A remarkably high selectivity of product **1a** (96%) was obtained over Pd–Cu(3.0)/C catalyst at temperature of 100°C for 1.5 h at 54% conversion (entry 2). This is a result of promoting effect of Cu on Pd/C, leading to high affinity toward C=O bond rather than C=C bond of the substrate. An increase reaction temperature from 100°C to 130°C not only enhanced the conversion to 94% but also caused further hydrogenation C=C bond, therefore the selectivity to **3a** increased significantly (entry 3). Moreover, the extent of reaction time to 3.0 h gave a completed reaction (>99% conversion) with product selectivities of **1a** and **3a** were 68% and 32%, respectively (entry 4).

Next, we examined the catalytic reaction of typical α,β-unsaturated aldehyde (*trans*-2-hexenaldehyde) using bimetallic Pd–Cu(3.0)/C catalyst and the results are summarized in **Table 5.**

Using Pd/C catalyst at 130°C and 1.5 h, 65% conversion of *trans*-2-hexenaldehyde was achieved and yielded 100% selectivity of n-hexanol (**1b**), which means both C=C and C=O bonds of reactant were simultaneously hydrogenated under the reaction conditions (entry 1). Interestingly, bimetallic Pd–Cu(3.0)/C catalyst gave a remarkable selectivity to 2-henxene-ol **(1a)** (96%) at 87% conversion at 100°C for 1.5 h (entry 2). When the reaction temperature was increased to 130°C or reaction time was extended to 3 h, the selectivity of saturated alcohol significantly increased indicating the further hydrogenation of C=C was obviously occurred (entries 3 and 4).

3.5 Chemoselective hydrogenation of reactant mixtures

To complete our investigation in the selective hydrogenation of C=O bond rather than C=C bond, the catalytic reaction of a mixture of FFald (typical unsaturated aldehyde) and (E)-non-3-en-2-one (typical unsaturated ketone) (molar ratio to 1.0) was examined using bimetallic Pd–Cu(3.0)/C catalysts and the results showed in **Scheme 2**. Under the current operating conditions, at a full conversion of FFald with 95% yield of FFalc (**1c**) was obtained. On the other hand, the conversion of (E)-non-3-en-2-one was 91% with moderate yield of unsaturated alcohol (**2c**) (66%). These results suggest that the bimetallic Pd–Cu(3.0)/C catalyst can be applied for selective hydrogenation of α,β-unsaturated ketone and aldehyde to corresponding unsaturated alcohol from moderate to high yield.



Scheme 2. Chemoselective hydrogenation of aldehyde (FFald) and ketone ((E)-non-3-en-2-one) reactant mixtures. Reaction conditions: catalyst, 0.05 g; substrate, 2.0 mmol; *iso*-PrOH, 3.5 mL, 3.0 MPa H_2, 130°C, 1.5 h.

3.6 Reusability test

A reusability test was performed on the Pd–Cu(3.0)/C catalyst in the selective hydrogenation of FFald and the results are summarized in **Table 6**. The used Pd–Cu(3.0)/C catalyst was easily separated by either simple centrifugation or filtration after the reaction. The activity of the catalyst decreased while the selectivity was maintained for at least four consecutive reaction runs. The catalytic activity and selectivity of the used Pd–Cu(3.0)/C catalyst can be restored to the original by simple reduction with H_2 at 400°C for 1.5 h.

4. Conclusions

We have described the promotional effect of second metal Cu on Pd/C catalyst in the chemoselective hydrogenation of biobased furfuraldehyde (FFald) and typical α,β-unsaturated ketones/aldehydes. The presence of Cu (0.012 mmol) in Pd/C to form bimetallic Pd-Cu alloy phases obviously enhanced the selectivity of Pd towards C=O rather than C=C bonds in furfural or typical α,β-unsaturated ketones/aldehydes, leading to high yield of unsaturated alcohols. The formation of bimetallic Pd–Cu alloy phase in Pd–Cu(3.0)/C catalyst was clearly observed after reduction with H_2 at 400°C for 1.5 h, which plays a pivotal role during the chemoselective hydrogenations. Pd–Cu(3.0)/C catalyst was found to stable and reusable for at least four reaction runs and the activity and selectivity of the catalyst can be restored to the original after rejuvenation with H_2 at 400°C for 1.5 h.

5. Acknowledgments

The authors acknowledge the RISET DASAR (contract number DIPA-042.06-1.401516/2020) from Ministry of Education and Culture, Indonesian Government, which all financially supported this work. We would also like thank to Professor Shogo Shimazu for kind help in XRD, H_2-chemisorption, and N_2-adsorption/desorption-BET measurements.

6. References

[1] H.E. Hoydonckx, W.M. Van Rhijn, M. Van Rhijn, D.E. De Vos, P.A. Jacobs, Furfural and Derivatives, in: Ullmann's Encycl. Ind. Chem., 2012: pp. 285–309. doi:10.1002/14356007.a12_119.pub2.

[2] H. Kimura, Progress in one-step amination of long-chain fatty alcohols with dimethylamine development of key technologies for industrial applications, innovations, and future outlook, Catal. Rev. - Sci. Eng. 53 (2011) 1–90. doi:10.1080/01614940.2011.556913.

[3] L. Pasumansky, C.T. Goralski, B. Singaram, Lithium aminoborohydrides: Powerful, selective, air-stable reducing agents, Org. Process Res. Dev. 10 (2006) 959–970. doi:10.1021/op0600759.

[4] J.S. Cha, Recent developments in Meerwein-Ponndorf-Verley and related reactions for the reduction of organic functional groups using aluminum, boron, and other metal reagents: A review, Org. Process Res. Dev. 10 (2006) 1032–1053. doi:10.1021/op068002c.

[5] T. Ohkuma, N. Kurono, N. Arai, Development of asymmetric reactions catalyzed by ruthenium complexes with two kinds of ligands, Bull. Chem. Soc. Jpn. 92 (2019) 475–504. doi:10.1246/bcsj.20180328.

[6] P. GALLEZOT, D. RICHARD, Selective Hydrogenation of a, b-Unsaturated Aldehydes, Catal. Rev. 40 (1998) 81–126. doi:10.1080/01614949808007106.

[7] P. Mäki-Arvela, T. Salmi, B. Holmbom, S. Willför, D.Y. Murzin, Synthesis of sugars by hydrolysis of hemicelluloses- A review, Chem. Rev. 111 (2011) 5638–5666. doi:10.1021/cr2000042.

[8] P. Claus, Selective hydrogenation of alpha,beta-unsaturated aldehydes and other C = O and C = C bonds containing compounds, Top. Catal. 5 (1998) 51–62. doi:10.1023/a:1019177330810.

[9] M. Luneau, J.S. Lim, D.A. Patel, E.C.H. Sykes, C.M. Friend, P. Sautet, Guidelines to Achieving High Selectivity for the Hydrogenation of α,β-Unsaturated Aldehydes with Bimetallic and Dilute Alloy Catalysts: A Review, Chem. Rev. (2020). doi:10.1021/acs.chemrev.0c00582.

[10] F.R. Lucci, J. Liu, M.D. Marcinkowski, M. Yang, L.F. Allard, M. Flytzani-Stephanopoulos, E.C.H. Sykes, Selective hydrogenation of 1,3-butadiene on platinum-copper alloys at the single-atom limit, Nat. Commun. 6 (2015) 1–8. doi:10.1038/ncomms9550.

[11] Z. Guo, C. Xiao, R. V. Maligal-Ganesh, L. Zhou, T.W. Goh, X. Li, D. Tesfagaber, A. Thiel, W. Huang, Pt Nanoclusters Confined within Metal–Organic Framework Cavities for Chemoselective Cinnamaldehyde Hydrogenation, ACS Catal. 4 (2014) 1340–1348. doi:10.1021/cs400982n.

[12] A.M. Silva, O.A.A. Santos, M.J. Mendes, E. Jordão, M.A. Fraga, Hydrogenation of citral over ruthenium-tin catalysts, Appl. Catal. A Gen. 241 (2003) 155–165. doi:10.1016/S0926-860X(02)00463-5.

[13] K. Gupta, R.K. Rai, A.D. Dwivedi, S.K. Singh, Catalytic Aerial Oxidation of Biomass-Derived Furans to Furan Carboxylic Acids in Water over Bimetallic Nickel–Palladium Alloy Nanoparticles, ChemCatChem. 9 (2017) 2760–2767. doi:10.1002/cctc.201600942.

[14] M. Sankar, N. Dimitratos, P.J. Miedziak, P.P. Wells, C.J. Kiely, G.J. Hutchings, Designing bimetallic catalysts for a green and sustainable future, Chem. Soc. Rev. 41 (2012) 8099–8139. doi:10.1039/c2cs35296f.

[15] D.M. Alonso, S.G. Wettstein, J.A. Dumesic, Bimetallic catalysts for upgrading of biomass to fuels and chemicals, Chem. Soc. Rev. 41 (2012) 8075–8098. doi:10.1039/c2cs35188a.

[16] P. Mäki-Arvela, J. Hájek, T. Salmi, D.Y. Murzin, Chemoselective hydrogenation of carbonyl compounds over heterogeneous catalysts, Appl. Catal. A Gen. 292 (2005) 1–49. doi:10.1016/j.apcata.2005.05.045.

[17] L. Altmann, X. Wang, H. Borchert, J. Kolny-Olesiak, V. Zielasek, J. Parisi, S. Kunz, M. Bäumer, Influence of Sn content on the hydrogenation of crotonaldehyde catalysed by colloidally prepared PtSn nanoparticles, Phys. Chem. Chem. Phys. 17 (2015) 28186–28192. doi:10.1039/c5cp00280j.

[18] S. Liang, C. Hao, Y. Shi, The Power of Single-Atom Catalysis, ChemCatChem. 7 (2015) 2559–2567. doi:10.1002/cctc.201500363.

[19] R. Rodiansono, T. Hara, N. Ichikuni, S. Shimazu, A novel preparation method of nisn alloy catalysts supported on aluminium hydroxide: Application to chemoselective hydrogenation of unsaturated carbonyl compounds, Chem. Lett. 41 (2012) 769–771. doi:10.1246/cl.2012.769.

[20] R. Rodiansono, S. Khairi, T. Hara, N. Ichikuni, S. Shimazu, Highly efficient and selective hydrogenation of unsaturated carbonyl compounds using Ni-Sn alloy catalysts, Catal. Sci. Technol. 2 (2012) 2139–2145. doi:10.1039/c2cy20216f.

[21] R. Rodiansono, T. Hara, N. Ichikuni, S. Shimazu, Development of Nanoporous Ni-Sn Alloy and Application for Chemoselective Hydrogenation of Furfural to Furfuryl Alcohol, Bull. Chem. React. Eng. Catal. 9 (2014) 53–59. doi:10.9767/bcrec.9.1.5529.53-59.

[22] R. Rodiansono, M.D. Astuti, S. Khairi, S. Shimazu, Selective Hydrogenation of Biomass-derived Furfural over Supported Ni3Sn2 Alloy: Role of Supports, Bull. Chem. React. Eng. Catal. 11 (2016) 1–9. doi:10.9767/bcrec.11.1.393.1-9.

[23] R. Rodiansono, M.D. Astuti, D.R. Mujiyanti, U.T. Santoso, S. Shimazu, Novel preparation method of bimetallic Ni-In alloy catalysts supported on amorphous alumina for the highly selective hydrogenation of furfural, Mol. Catal. 445 (2018) 52–60. doi:10.1016/j.mcat.2017.11.004.

[24] S. Dutta, S. De, B. Saha, M.I. Alam, Advances in conversion of hemicellulosic biomass to furfural and upgrading to biofuels, Catal. Sci. Technol. 2 (2012) 2025–2036. doi:10.1039/C2CY20235B.

[25] J.-P. Lange, E. van der Heide, J. van Buijtenen, R. Price, Furfural—A Promising Platform for Lignocellulosic Biofuels, ChemSusChem. 5 (2012) 150–166. doi:10.1002/cssc.201100648.

[26] S. Chen, R. Wojcieszak, F. Dumeignil, E. Marceau, S. Royer, How Catalysts and Experimental Conditions Determine the Selective Hydroconversion of Furfural and 5-Hydroxymethylfurfural, Chem. Rev. 118 (2018) 11023–11117. doi:10.1021/acs.chemrev.8b00134.

[27] M.D. Astuti, D. Kristina, R. Rodiansono, D.R. Mujiyanti, One-pot Selective Conversion of Biomass-derived Furfural into Cyclopentanone/Cyclopentanol over TiO2 Supported Bimetallic Ni-M (M = Co, Fe) Catalysts, Bull. Chem. React. Eng. Catal. 15 (2020) 231–241. doi:10.9767/bcrec.15.1.6307.231-241.

[28] Á. O'Driscoll, T. Curtin, W.Y. Hernández, P. Van Der Voort, J.J. Leahy, Hydrogenation of Furfural with a Pt-Sn Catalyst: The Suitability to Sustainable Industrial Application, Org. Process Res. Dev. 20 (2016) 1917–1929. doi:10.1021/acs.oprd.6b00228.

[29] F. Liao, T.W.B. Lo, S.C.E. Tsang, Recent Developments in Palladium-Based Bimetallic Catalysts, ChemCatChem. 7 (2015) 1998–2014. doi:10.1002/cctc.201500245.

[30] K. V. Kovtunov, D.A. Barskiy, O.G. Salnikov, A.K. Khudorozhkov, A. V. Bukhtiyarov, I.P. Prosvirin, E.Y. Gerasimov, V.I. Bukhtiyarov, I. V. Koptyug, Strong Metal-Support Interactions for Pd Supported on TiO2 Catalysts in Heterogeneous Hydrogenation with Parahydrogen, ChemCatChem. 630090 (2015) 2581–2584. doi:10.1002/cctc.201500618.

[31] N. Pino, S. Sitthisa, Q. Tan, T. Souza, D. López, D.E. Resasco, D.E.R. c Natalia Pino a, Surapas Sitthisa c, Qiaohua Tan c, Talita Souza b, Diana López a, Structure, activity, and selectivity of bimetallic Pd-Fe/SiO2 and Pd-Fe/c- Al2O3 catalysts for the conversion of furfural, J. Catal. 350 (2017) 30–40. doi:10.1016/j.jcat.2017.03.016.

[32] S. Sitthisa, T.P. Prasomsri, T. Sooknoi, R.G. Mallinson, D.E. Resasco, Conversion of furfural and 2-methylpentanal on Pd/SiO2 and Pd–Cu/SiO2 catalysts Surapas, J. Catal. (2011) 17–27.

[33] S. Lowell, J.E. Shields, M.A. Thomas, M. Thommes, Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density, Kluwer Academic Publishers: Dordrecht, The Netherlands., 2004.

[34] P.C. Aben, Palladium areas in supported catalysts. Determination of palladium surface areas in supported catalysts by means of hydrogen chemisorption, J. Catal. 10 (1968) 224–229. doi:10.1016/S0021-9517(68)80002-8.

[35] M. Snåre, I. Kubičková, P. Mäki-Arvela, K. Eränen, J. Wärnå, D.Y. Murzin, Production of diesel fuel from renewable feeds: Kinetics of ethyl stearate decarboxylation, Chem. Eng. J. 134 (2007) 29–34. doi:10.1016/j.cej.2007.03.064.

[36] Y. Yang, L. Chen, Y. Chen, W. Liu, H. Feng, B. Wang, X. Zhang, M. Wei, Selective hydrogenation of furfural on intermetallic compounds with outstanding catalytic performance, Green Chem. (2019) 1–11. doi:10.1039/c9gc01119f.

[37] Z. Wei, J. Lou, C. Su, D. Guo, Y. Liu, S. Deng, An Efficient and Reusable Embedded Ru Catalyst for the Hydrogenolysis of Levulinic Acid to Γ-Valerolactone, ChemSusChem. 10 (2017) 1720–1732. doi:10.1002/cssc.201601769.

[38] Q. Xu, K.C. Kharas, B.J. Croley, A.K. Datye, The Sintering of Supported Pd Automotive Catalysts, ChemCatChem. 3 (2011) 1004–1014. doi:10.1002/cctc.201000392.

[39] J. Lu, B. Fu, M.C. Kung, G. Xiao, J.W. Elam, H.H. Kung, P.C. Stair, Coking- and sintering-resistant palladium catalysts achieved through atomic layer deposition, Science (80-.). 335 (2012) 1205–1208. doi:10.1126/science.1212906.

[40] A. Gandini, Furans as offspring of sugars and polysaccharides and progenitors of a family of remarkable polymers: a review of recent progress, Polym. Chem. 1 (2010) 245–251. doi:10.1039/B9PY00233B.

[41] R. Rodiansono, M.D. Astuti, T. Hara, N. Ichikuni, S. Shimazu, One-pot selective conversion of C5-furan into 1,4-pentanediol over bulk Ni-Sn alloy catalysts in an ethanol/H2O solvent mixture, Green Chem. 21 (2019) 2307–2315. doi:10.1039/c8gc03938k.

[42] N.S. Date, A.M. Hengne, K.W. Huang, R.C. Chikate, C. V. Rode, Single pot selective hydrogenation of furfural to 2-methylfuran over carbon supported iridium catalysts, Green Chem. 20 (2018) 2027–2037. doi:10.1039/c8gc00284c.

[43] T.B.L.W. Marinelli, S. Nabuurs, V. Ponec, Activity and selectivity in the reactions of substituted α,β-Unsaturated aldehydes, J. Catal. 151 (1995) 431–438.

doi:10.1006/jcat.1995.1045.

FIGURE CAPTIONS

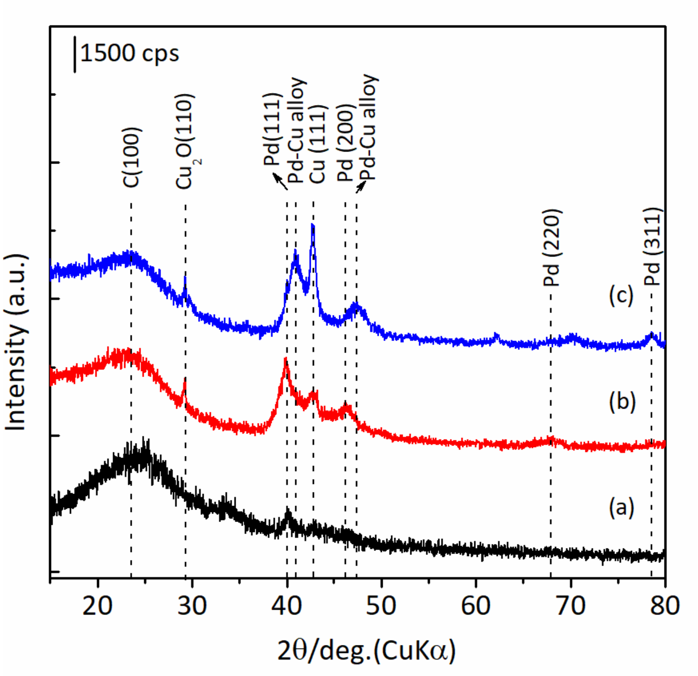


Figure 1. XRD patterns of (a) commercial Pd/C (5%wt Pd), (b) as prepared Pd–Cu(3.0)/C and (c) after reduction with H_2 treatment at 400°C for 1.5 h.

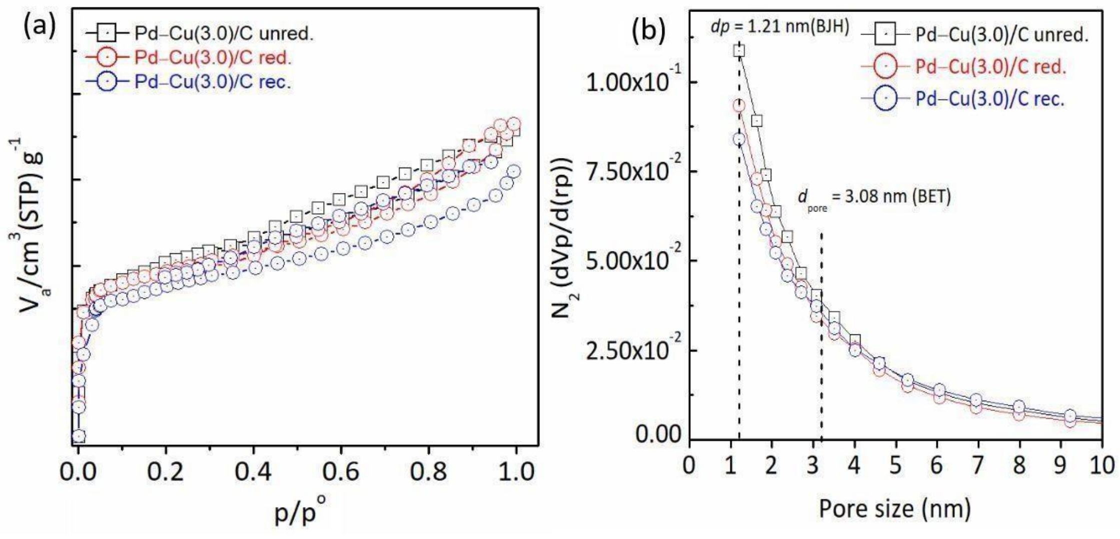


Figure 2. (a) Profiles of N_2-adosorption-desorption and (b) pore distribution (nm) versus volume of N_2-adsorbed.

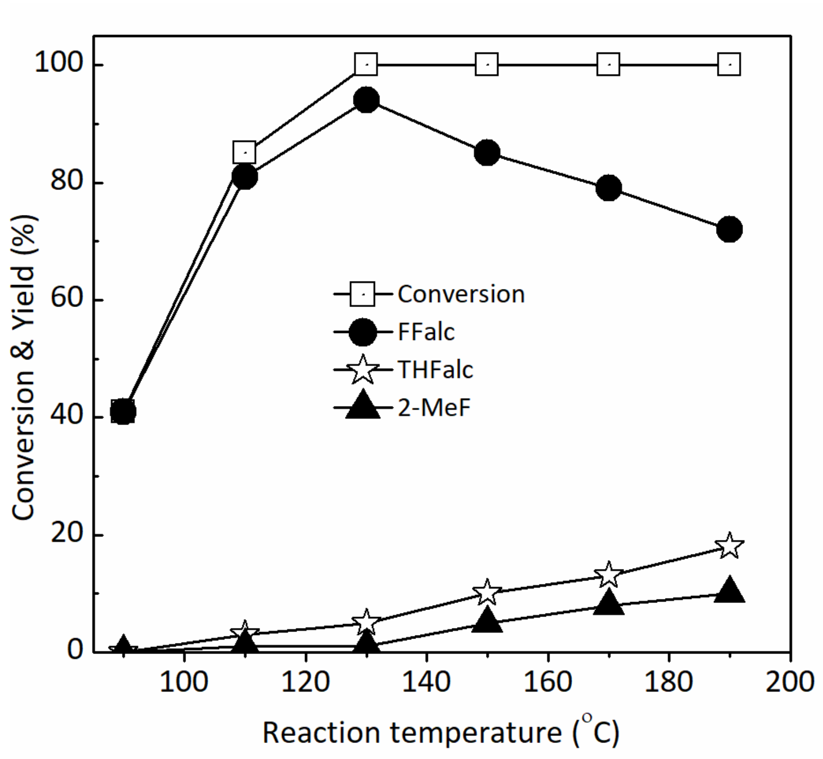


Figure 3. Effect of reaction temperature on the FFald conversion and product distribution over bimetallic Pd–Cu(3.0)/C catalyst. Reaction conditions: catalyst, 0.05 g; FFald, 1.1 mmol; *iso*-PrOH, 3 mL; H_2, 3.0 MPa, 1.5 h.

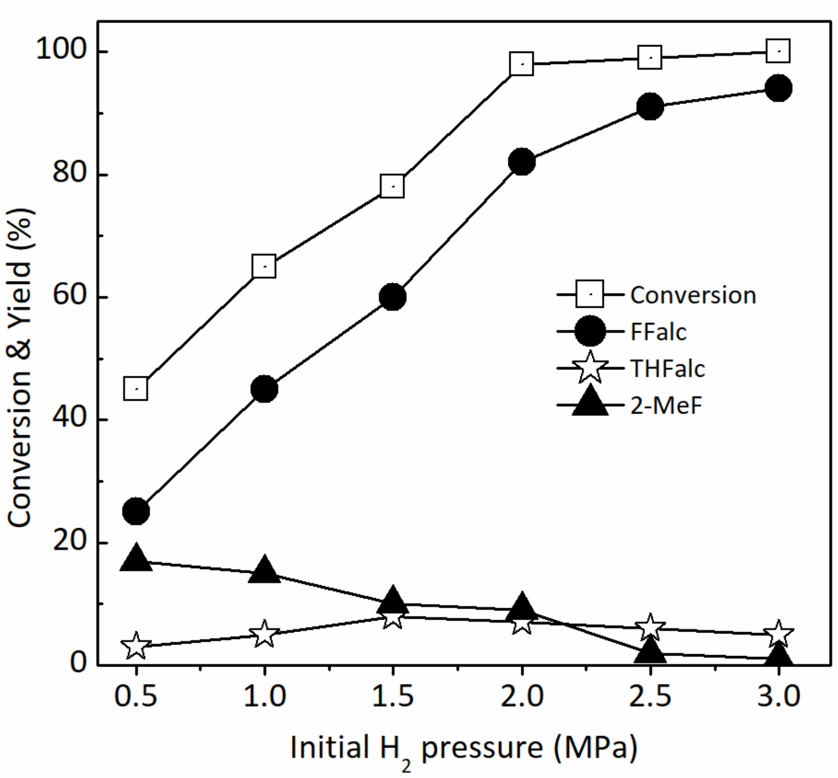


Figure 4. Effect of the initial H_2 pressure on the FFald conversion over bimetallic Pd–Cu(3.0)/C catalyst. *Reaction conditions:* catalyst, 0.05 g; FFald, 1.1 mmol; *iso*-PrOH, 3 mL; 130°C, 1.5 h.

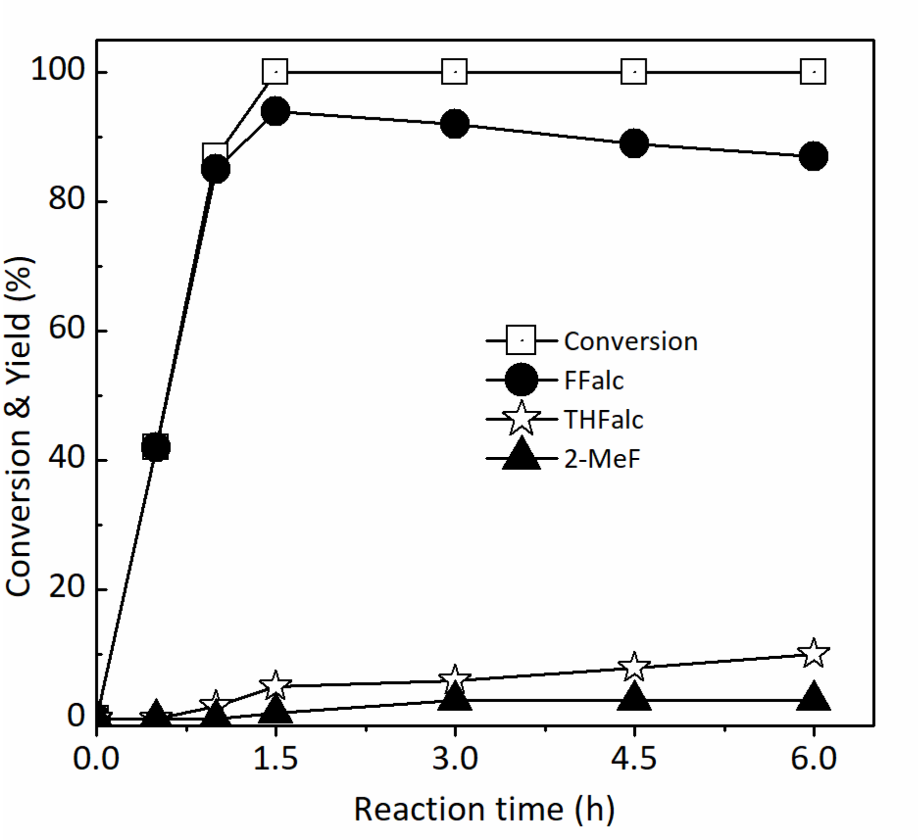


Figure 5. Time profiles of the hydrogenation of FFald over bimetallic Pd–Cu(3.0)/C catalyst. *Reaction conditions:* catalyst, 0.05 g; FFald, 1.1 mmol; *iso*-PrOH, 3 mL; 130^{o}C.

TABLE CAPTIONS

Table 1 Physico-chemical properties of bimetallic Pd–Cu(3.0)/C catalyst

Entry	Catalyst[a]	S_{BET} (m^2.g^{-1})	Pore Vol.[b] (m^3.g^{-1})	Pore Diameter[b] (nm)	H_2 uptakes[c] (μmol.g^{-1})
1[d]	Pd–Cu(3.0)/C unred.	637	0.494	3.10	38.4
2	Pd–Cu(3.0)/C	712	0.548	3.08	39.6
3[e]	Pd–Cu(3.0)/C recovered	601	0.428	2.85	27.8

[a]The value in the parenthesis is Pd/Cu molar ratio. [b] S_{BET} was determined by N_2 adsorption at -196°C (77 K), pore volume and pore diameter were calculated according to BJH approach. [c]Based upon total the H_2 uptake at 0°C (after corrections for physical and chemical adsorption). [d]The as prepared Pd–Cu(3.0)/C without pre reduced with H_2. [e]The recovered Pd–Cu(3.0)/C after the third reaction run.

Table 2. Results of selective hydrogenation of FFald using various bimetallic Pd-based catalysts

Entry	Catalyst[a]	Composition (mmol. g^{-1})		Temp. (°C)	Conv.[b] (%)	Yield[b] (%)			
		Pd	M			FFalc	THFalc	2-MeF	Others[c]
1	Pd/C[d]	0.50	-	100	100	2	90	8	0
2	Pd–Cu(3.0)/C *unred.*	0.472	0.156	100	56	28	15	0	13
3	Pd–Cu(3.0)/C	0.472	0.156	100	73	68	3	2	0
4	Pd–Cu(3.0)/C	0.472	0.156	130	>99	94	5	1	0
5[e]	Pd–Cu(3.0)/C	0.472	0.156	130	>99	92	6	3	0
6	Pd–Sn(3.0)/C	0.461	0.152	130	53	16	5	2	20
7	Pd–Co(3.0)/C	0.464	0.151	130	43	12	15	6	10
8	Pd–Ni(3.0)/C	0.481	0.161	130	13	6	6	1	0
9	Pd–Fe(3.0)/C	0.560	0.187	130	78	43	25	5	15

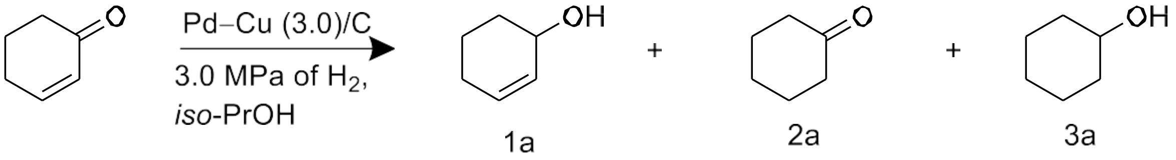
[a]The value in the parenthesis is Pd/M molar ratio (M = Cu, Sn, Co, Ni, and Fe); the bulk composition was determined by ICP-OES. Reaction conditions: catalyst (5 mg); FFald (2 mmol); solvent (2-propanol, 5 mL); temperature (130°C); initial H_2 pressure (3.0 MPa); reaction time (1.5 h). [b]Conversion and yields of FFalc THFalc, and 2-MeF were determined by GC using an internal standard technique. [c]Others consist of condensation product of FFald or FFalc according to GC/GC-MS data. [c]Commercially available Pd/C (5%wt Pd). [e]The reaction time was 3 h.

Table 3. Results of solvent screening for FFald hydrogenation over Pd–Cu(3.0)/C catalyst

Entry	Solvent	Conv.[a] (%)	Yield[a] (%)			
			FFalc	THFalc	2-MeF	Others[b]
1	1-Propanol	>99	90	8	2	0
2	2-Propanol	>99	94	5	1	0
3	Ethanol	96	94	2	0	0
4	Methanol	90	80	7	3	0
5	1,4-Dioxane	67	94	3	0	27[c]
6	Toluene	56	43	13	0	0
7	H_2O	67	27	13	7	20
8	Ethanol: H_2O (1.5: 2.0 v/v)	98	53	18	5	32[c]
9	2-Propanol/H_2O (1.5: 2.0 v/v)	99	57	15	5	22
10	1,4-Dioxane/H_2O (1.5: 2.0 v/v)	99	38	15	2	44[c]

Reaction conditions: catalyst (5 mg); FFald (2 mmol); solvent (3.5 mL); temperature (130°C); initial H_2 pressure (3.0 MPa); reaction time (1.5 h). [a]Conversion and yields of FFalc THFalc, and 2-MeF were determined by GC using an internal standard technique. [b]Others consist of the hydrogenolysis products such as 1,2-pentanediol, 1,5-pentanediol, and 1,4-pentanediol. [c]The main product of others using 1,4-dioxane solvent was cyclopentanone (CPO) and cyclopentanol (CPOL).

Table 4. Results of selective hydrogenation of typical α,β-unsaturated ketone using Pd–Cu(3.0)/C catalyst

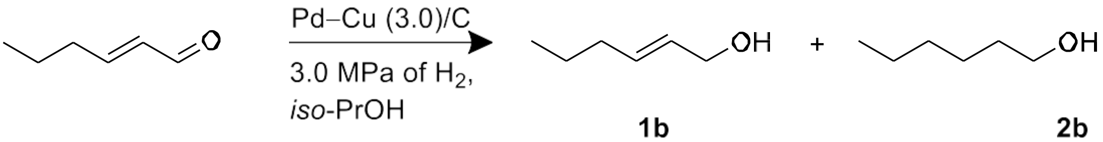


Entry	Catalyst[a]	Reaction temp. (°C)	Reaction time/h	Conv.[b] (%)	Selectivity[b] (%)		
					1a	**2a**	**3a**
1	Pd/C (5%wt)	130	1.5	33	0	24	76
2	Pd–Cu(3.0)/C	100	1.5	54	96	0	4
3	Pd–Cu(3.0)/C	130	1.5	94	90	0	10
4	Pd–Cu(3.0)/C	130	3.0	>99	68	0	32

Reaction conditions: catalyst, 0.05 g; substrate, 1.1 mmol; *iso*-PrOH, 3 mL. [a]The value in the parenthesis is Pd/Cu molar ratio, determined by ICP-OES. [b]Conversion and yield were determined by GC using an internal standard technique.

Table 5. Results of selective hydrogenation of typical α,β-unsaturated aldehyde using

Pd–Cu(3.0)/C catalyst



1b

2b

Entry	Catalyst[a]	Reaction temp. (°C)	Reaction time/h	Conv.[b] (%)	Selectivity[b] (%)	
					1b	**2b**
1	Pd/C (5%wt)	130	1.5	65	0	100
2	Pd–Cu(3.0)/C	100	1.5	87	96	4
3	Pd–Cu(3.0)/C	130	1.5	90	90	10
4	Pd–Cu(3.0)/C	130	3.0	>99	83	17

Reaction conditions: catalyst, 0.05 g; substrate, 1.1 mmol; *iso*-PrOH, 3 mL. [a]The value in the parenthesis is Pd/Cu molar ratio, determined by ICP-OES. [b]Conversion and yield were determined by GC using an internal standard technique.

Table 6. Results of the selective hydrogenation of FFald to FFalc over bimetallic Pd–Cu(3.0)/C catalyst after four consecutive reaction runs.

Entry	Reaction run-	Conversion[a] (%)	Yield[a] (%)		
			FFalc	THFalc	2-MeF
1	1st	>99	94	5	1
2	2nd	82	76	5	1
3	3rd	73	66	6	1
4[b]	4th	>99	95	4	1

Reaction conditions: catalyst (0.05 g); FFald (1.1 mmol); solvent (*iso*-PrOH, 3.5 ml); temperature (130°C); initial H_2 pressure (3.0 MPa); reaction time (1.5 h). [a]Conversion and yields of FFalc THFalc, and 2-MeF were determined by GC using an internal standard technique. [b]The used Pd–Cu(3.0)/C catalyst was reduced with H_2 at 400°C for 1.5 h before reaction.

2. Bukti konfirmasi review dan hasil review pertama (4 April 2021)

[BCREC] Revision Required of Your Manuscript [BCREC-2021-10398]

1 message

Prof. Dr. Istadi Istadi <bcrec@live.undip.ac.id> Sun, Apr 4, 2021 at 2:48 PM
Reply-To: "Prof. Dr. Istadi Istadi" <bcrec@live.undip.ac.id>
To: Mrs Kamilia Mustikasari <kmustikasari@ulm.ac.id>
Cc: Rodiansono Rodiansono <rodiansono@ulm.ac.id>, Maria Dewi Astuti <mdastuti@ulm.ac.id>, Sadang Husain <sadanghusain@ulm.ac.id>, Sutomo Sutomo <sutomo@ulm.ac.id>

Journal Name: Bulletin of Chemical Reaction Engineering & Catalysis
Article Title: The promotion effect of Cu on the Pd/C catalyst in the chemoselective hydrogenation of unsaturated carbonyl compounds
Ms-ID: BCREC-2021-10398

Dear Mrs Kamilia Mustikasari,

Reviewers have now commented on your paper (attached below this email). You will see that they are advising that you must revise your manuscript. If you are prepared to undertake the work required, I would be pleased to reconsider my decision.

For your guidance, reviewers' comments can be read in your Author online interface. If you decide to revise the work, please submit a list of changes or a rebuttal against each point which is being raised when you submit the revised manuscript.

****>>>>Please be noted that you have up to 1 (one) months from now to revise your manuscript, unless your manuscript will be considered as a new submitted manuscript. If you need additional time to complete your revision, please let us know by replying to this email and informing us of the date you expect to submit it. <<<<****

To submit a revision, please upload your revised manuscript documents to BCREC online submission interface at (https://ejournal2.undip.ac.id/index.php/bcrec) after you login as Author. Important: Please indicate the revision as blue-highlighting the revision sentences or words within your revised manuscript.

The revised document files (three files) MUST include:
- One (1) file of Revision Note file in a table form with respect to Reviewers comments including the location of the revision on the revised manuscript. Template MS Word File of this Revision Note can be downloaded here: https://bit.ly/3cvzcS8
- One (1) file of Revised Manuscript file according to Template-based format (MS Word file) (please blue-color highlighted texts in the revised sentences).
- One (1) file of Graphical Abstract file according to Guideline of Graphical Abstract (https://ejournal2.undip.ac.id/index.php/bcrec/pages/view/graphicalabstract).

GUIDELINE TO UPLOAD REVISION: To upload your revised manuscript, please login to BCREC journal submission interface (https://ejournal2.undip.ac.id/index.php/bcrec) then login using your user and password as usual. Therefore, click on "Active" and click on the title of your manuscript. Under the header of "#xxxx Summary" there are three taskbars, i.e. "Summary", "Review", "Editing" and click on "Review". In the section of Editor Decision, please upload your revised manuscript file within sub section of "Upload Author Version", please just browse the file, and click on "Upload".
For second and continuing order of revision of manuscript, please just add your latest version file(s), do not delete the previous round of file(s) of manuscript.

IMPORTANT NOTE: A GRAPHICAL ABSTRACT of each article is mandatory for this journal. Please read detail guidelines here: https://ejournal2.undip.ac.id/index.php/bcrec/pages/view/graphicalabstract/
This graphic should capture the reader’s attention and, in conjunction with the manuscript title, should give the reader a quick visual impression of the essence of the manuscript without providing specific results.
Choosing/Creating a Graphical Abstract: The graphic should be simple, but informative; The use of color is encouraged; The graphic should uphold the standards of a scholarly, professional publication; The graphic must be entirely original, unpublished artwork created by one of the coauthors; The graphic should not include a photograph, drawing, or caricature of any person, living or deceased; Do not include postage stamps or currency from any country, or trademarked items (company logos, images, and products); Avoid choosing a graphic that already appears within the text of the manuscript. Image size: please provide an image with a size of 500 × 800 pixels (height × width). Preferred file types: TIFF, JPG, PNG, PDF, or MS Office files.

The Graphical Abstracts should be submitted as a separate file during the revised manuscript submission system or otherwise, it can be submitted by email to: bcrec@live.undip.ac.id

Thank you for submitting to this journal.

Yours sincerely,

____
Prof. Dr. Istadi Istadi
Department of Chemical Engineering, Diponegoro University
bcrec@live.undip.ac.id
Twitter: @bcrec_j (https://twitter.com/bcrec_j?s=08)

{$comments}
(Editor in Chief)
Bulletin of Chemical Reaction Engineering & Catalysis
Department of Chemical Engineering, Diponegoro University, Indonesia
Website: http://bcrec.id
Email: bcrec@live.undip.ac.id

Reviewer B:

The manuscript reports interesting results, although I consider that the authors must make several clarifications and changes to be accepted for publication in the Bulletin of Chemical Reaction Engineering & Catalysis.

My observations are described below.

-Page 1. The authors shall include their first names as well as their surname.

-Page 4. Introduction.
Although it is indicated that a Pd/Cu bimetallic system was previously worked on, a brief description should be made of why copper and activated carbon are selected for the formation of the catalyst.
The authors note "…The effect of the Pd/Cu molar ratio, solvent use and reaction parameters (initial H2 pressure, reaction temperature) on the activity and selectivity in the hydrogenation of FFald are also studied…" In the manuscript they indicate that they work with catalysts with a Pd/Cu molar ratio of only 3. It is recommended to remove "The effect of the Pd / Cu molar ratio".
In the title they indicate that the reaction is for of unsaturated carbonyl compounds and they carry out the introduction only with reference to FFald. Is the objective of the work the hydrogenation of FFald or unsaturated carbonyl compounds in general?

-Page 5. Preparation of catalysts.
The authors do not indicate how activated carbon is incorporated into the bimetallic phase, nor is the mass or molar relationship between the bimetallic phase and activated carbon indicated in the manuscript. There is no bibliography in this section that indicates how the support is incorporated. It is important that these points are indicated in order to be able to interpret the results correctly.
There is an error in the hydrogenation time since 1.5 min is indicated.

-Page 5. Hydrogenation of FFald
The authors mention "…Catalyst (0.05 g), FFald (1.1 mmol), trans-decahydronaphthalene (decalin) (0.2 mmol), and iso-PrOH (3 mL) as solvent were placed into a glass reaction tube, which fitted inside a stainless -steel reactor… "
Which catalyst are you referring to?

The authors are recommended to indicate the name of the catalyst in the catalyst preparation part.

he authors begin the discussion with the results presented in Table 1. These results arise from the treatment of data obtained from the corresponding adsorption-desorption isotherm. It is recommended to start the discussion with the Nitrogen adsorption and desorption profiles and then present Table 1.

The following points should be explained:

-Table 1:
Because there is a decrease of 178 m2/g when incorporating the carbon to the bimetallic phase? They could analyze how the support is affected by applying the same catalyst synthesis process.
An increase in SBET is observed when the hydrogenation of Pd-Cu(3.0)/unred. occurs, what is this due to? Is activated carbon affected?
The results of Pd-Cu(0.3)/C recovered when the three cycles were applied, which reactive molecule does it correspond to?

-Figure 1:
How is the Pd-Cu bimetallic phase in the catalyst? The presence of Cu2O is observed, could the presence of PdO or

PdO2 occur?. What is the catalytically active phase? The reference that is included (35) does not contain information of the Pd phase.

-Figure 2:

Is the Pd-Cu (0.3)/C recovered sample the one obtained after three cycles?

The adsorption isotherm points for the Pd-Cu(3.0)/C unred. sample are not observed.

The authors indicate "… shows the profiles of N2-adsorption / desorption and plot of volume of adsorbed-N2 versus pore distribution using BJH approach (with cut-off the pore size of 1.21 nm) confirmed that there are no significant change of the pore structure of catalyst support during the introducing Pd metal or thermal activation using N2 or H2 at 400 °C…" When is activation using N2 done? It is not specified in the experimental part. When hydrogenation is carried out, the catalyst increases its specific area slightly but is still less than that of the original activated carbon. Why does this happen?

What can be observed in this figure is how the reduction of the catalyst and the catalysis process affect the textural properties.

-Page 7. Catalytic reactions. Screening of second metal.

The authors write "…Furthermore, investigation of the effect of various second metals such as tin (Sn), cobalt (Co), nickel (Ni), and iron (Fe) on the conversion of FFald and yield of FFalc was also performed and the results are also summarized in Table 2... " Under what conditions were these catalysts made? If it was with the same technique, specify it in the manuscript.

-Page 8. Effect of reaction temperature.

The authors do not explain how they conducted the experiment. What was the heating rate and the residence time of the catalyst for each temperatura?. Was the same catalyst used for the temperatures tested or was a fresh catalyst installed?

Reviewer C:

This manuscript is very well written. however, there are few inputs that might be useful for improving paper quality.

1. In section 2.3, the authors describe the hydrothermal preparation of Pd-Cu carbon. please write down the amount of Pd and Cu in the catalyst that has been produced. This is to compare the Pd content of the 5wt% Pd / C commercial catalyst.

2. In section 2.1 it is stated that carbon is a microporous material. however, in the experimental section 2.2, the author has used the BJH model to determine the pore distribution. Likewise in the discussion section, also found the discussion about mesoporous. As is well known, the BJH model is only suitable for mesoporous materials, while for microporous materials the HK model is used to explain the pore size distribution. This finding has also been shown in the results of the BJH profile which shows a peak at about 1.2 nm, where the peak is still visible upward to the left, which shows that the material is indeed a microporous material, as has been mentioned in section 2.1. Therefore, the pore size determination is not appropriate (Table 1). micropore <2 nm.

3. In addition, in the discussion of Figure 2, it is stated that "there are no significant change of the pore structure of catalyst support during the introducing Pd". The author should add pore structure of the support before adding Pd.

----

3. Bukti konfirmasi submit revisi pertama, respon kepada reviewer, dan artikel yang diresubmit (28 April 2024)

[BCREC] [BCREC-2021-10398] Revised Version Acknowledgement

4 messages

Editorial Office of BCREC Journal <bcrec@live.undip.ac.id> Wed, Apr 28, 2021 at 2:57 PM
Reply-To: Mrs Kamilia Mustikasari <kmustikasari@ulm.ac.id>
To: Mrs Kamilia Mustikasari <kmustikasari@ulm.ac.id>

Journal Name: Bulletin of Chemical Reaction Engineering & Catalysis
Article Title: The promotion effect of Cu on the Pd/C catalyst in the chemoselective hydrogenation of unsaturated carbonyl compounds
Ms-ID: BCREC-2021-10398

Dear Mrs Kamilia Mustikasari,

Thank you for submitting the revision of manuscript, entitled: "The promotion effect of Cu on the Pd/C catalyst in the chemoselective hydrogenation of unsaturated carbonyl compounds" to Bulletin of Chemical Reaction Engineering & Catalysis. With the online journal management system that we are using, you will be able to track its progress through the editorial process by logging in to the journal web site:

Manuscript URL: https://ejournal2.undip.ac.id/index.php/bcrec/author/submission/10398
Username: kamilia
Editor: Istadi Istadi

If you have any questions, please contact me. Thank you for considering this journal as a venue for your work.

Editorial Office of BCREC Journal
Bulletin of Chemical Reaction Engineering & Catalysis

Editorial Office of BCREC Journal <bcrec@live.undip.ac.id> Wed, Apr 28, 2021 at 2:58 PM
Reply-To: Mrs Kamilia Mustikasari <kmustikasari@ulm.ac.id>
To: Mrs Kamilia Mustikasari <kmustikasari@ulm.ac.id>

[Quoted text hidden]

Editorial Office of BCREC Journal <bcrec@live.undip.ac.id> Wed, Apr 28, 2021 at 2:58 PM
Reply-To: Mrs Kamilia Mustikasari <kmustikasari@ulm.ac.id>
To: Mrs Kamilia Mustikasari <kmustikasari@ulm.ac.id>

[Quoted text hidden]

Editorial Office of BCREC Journal <bcrec@live.undip.ac.id> Wed, Apr 28, 2021 at 3:00 PM
Reply-To: Mrs Kamilia Mustikasari <kmustikasari@ulm.ac.id>
To: Mrs Kamilia Mustikasari <kmustikasari@ulm.ac.id>

[Quoted text hidden]

The promotion effect of Cu on the Pd/C catalyst in the chemoselective hydrogenation of unsaturated carbonyl compounds

Kamilia Mustikasari,[1,2] R. Rodiansono,[1,2]* Maria Dewi Astuti,[1,2] Sadang Husain,[2,3] S. Sutomo[4]

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Lambung Mangkurat University, Jl. A. Yani Km 36.0 Banjarbaru South Kalimantan, Indonesia 70714.

[2]Catalysis for Sustainable Energy and Environment (CATSuRe), Lambung Mangkurat University.

[3]Department of Physics, Faculty of Mathematics and Natural Sciences, Lambung Mangkurat University, Jl. A. Yani Km 36 Banjarbaru, Indonesia 70714.

[4]Department of Pharmacy, Faculty of Mathematics and Natural Sciences, Lambung Mangkurat University, Jl. A. Yani Km 36 Banjarbaru, Indonesia 70714.

**Corresponding author: rodiansono@ulm.ac.id (R. Rodiansono).*

Telp. /Fax.: +62 511 477 3112

Abstract

Highly efficient and selective hydrogenation of α,β–unsaturated carbonyl compounds to unsaturated alcohol using bimetallic palladium-copper supported on carbon (denoted as Pd–Cu(3.0)/C; 3.0 is Pd/Cu molar ratio) catalyst is demonstrated. Pd–Cu(3.0)/C catalyst was prepared via a simple hydrothermal route under air atmosphere at 150°C for 24 h followed by reduction with hydrogen at 400°C for 1.5 h. The chemoselective hydrogenation of typical α,β–unsaturated carbonyl ketone (2-cyclohexene-1-one) and aldehyde (*trans*-2-hexenaldehyde), and chemoselective hydrogenation of FFald and (E)-non-3-en-2-one mixture demonstrated high productivity, leading to high selectivity of unsaturated alcohols. The presence of bimetallic Pd–Cu alloy phase with relatively high H_2 uptakes was observed, enabling to preferentially hydrogenate C=O rather than to C=C bonds under mild reaction conditions. Pd–Cu(3.0)/C catalyst was found to stable and reusable for at least four reaction runs and the activity and selectivity of the catalyst can be restored to the original after rejuvenation with H_2 at 400°C for 1.5 h.

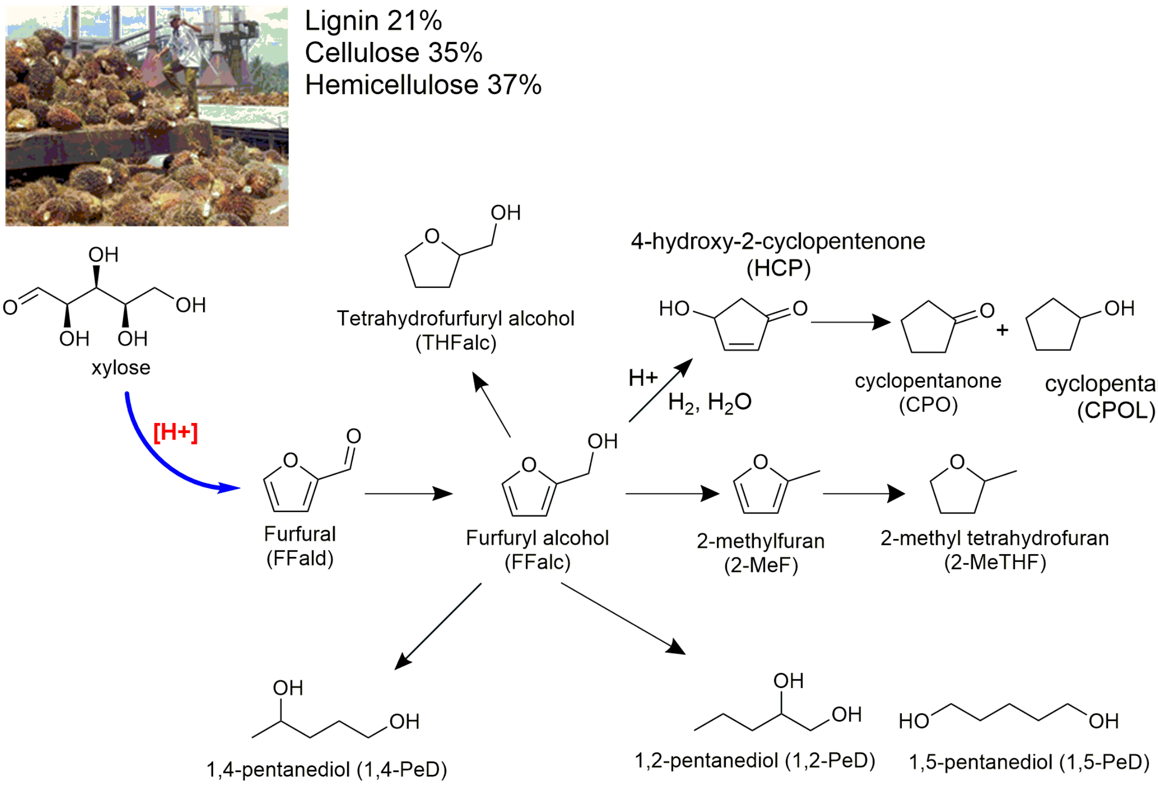
Keywords: bimetallic palladium-copper; chemoselective hydrogenation; unsaturated carbonyl compounds; unsaturated alcohol

1. Introduction

The chemoselective hydrogenation of the C=O bond in α,β−unsaturated ketones/aldehydes has been extensively studied because the unsaturated alcohols that it forms are important in the production of a variety of fine chemicals, such as pharmaceuticals, perfumes, and flavorings [1,2]. Typically, the chemoselective reduction of the carbonyl group is achieved using reducing agents [3], Meerwin-Ponndorf-Verly [4], or using organometallic catalysts [5]. These processes often use costly chemicals and solvents which require separations. In this context, heterogeneous catalysis is viewed as an alternative, more sustainable route for the production of these high-value chemicals at an industrial scale [6–8]. Simple preparation and recovery of heterogeneous catalysts are desirable features for the chemical industry.

Recent works indicate that bimetallic catalysts have the potential to enhance the selectivity in the hydrogenation of many different classes of chemicals [9], such as alkynes, alkenes[10], and carbonyl compounds [11,12] as well as biomass-derived molecules [13–15]. It is well known that the group 9 and 10 metals, such as Rh, Ir, Ni, Pd, and Pt, generally hydrogenate the C=C bond more easily than the C=O bond of α,β−unsaturated aldehydes [16]. To improve the chemoselective hydrogenation of the C=O group, the modification of the above mentioned metals is necessary, i.e., the addition of more electropositive metals [17] or the use of oxide supports that strongly interact with the active metals [18]. In these contexts, we have described previously that the chemoselective behaviors of Ni-based catalysts can be controlled by doping the second metals, such as tin (Sn) or indium (In) to form bimetallic Ni−Sn or Ni-In alloy. Both bulk and supported Ni–Sn and Ni–In alloy catalyst have obviously demonstrated high chemoselectivity in the hydrogenation of α,β-unsaturated ketones/aldehydes toward unsaturated alcohols[19–23].

It is well-known that furfural (FFald), a versatile and biogenic biomass-derived compound, which can be obtained from acidic dehydration of arabinose or xylose of hemicellulosic biomasses [24]. Further catalytic conversion of FFald via chemoselective hydrogenation, hydrogenolysis, hydrogenation-arrangement using both monometallic and bimetallic transition metal catalysts produced a variety of high value chemicals such as furfuryl alcohol (FFalc), tetrahydrofurfuryl alcohol (THFalc), methyl-furan (MeF), methyl tetrahydrofuran (MeTHF), pentanediol (PeD), and cyclopentanone (CPO) or cyclopentanol (CPOL) as shown in Scheme 1[25–27].



Scheme 1 Conceivable reaction networks for the catalytic transformation of FFald that involve hydrogenation, hydrogenolysis, decarbonylation, ring opening hydrogenation, and hydrogenation-rearrangement pathways.

Platinum-group metal (PGM) constitute the most studied catalyst components for hydrogenation of FFald and demonstrated high activity and selectivity towards FFalc, which were included Sn modified Pt-based [28] and Ni-based catalysts [20,21] due to their intrinsic high catalytic ability under mild conditions, high selectivity towards a specific product, high stability under various reaction conditions, and tolerance to poisons [29,30]. Although platinum is the most widely used element in catalysis, palladium is receiving increasing attention owing to its similar catalytic properties to platinum and wider availability. However, the catalytic behavior of Pd-based catalyst on the hydrogenation of unsaturated aldehydes/ketones or oxygenated biomass-derived compounds that consisted of C=O and C=C bonds preferentially promoted decarbonylation or decarboxylation reactions. For example, when Pd/C is used as catalyst for hydrogenation of FFald in the presence of H_2 gas, a wide range of competing reactions, such as unselective hydrogenation of furan-ring or aldehyde groups and incomplete hydrodeoxygenation have been reported [31,32]. Therefore, introduction of a secondary metal species or deposition of Pd nanoparticles on the support that strongly interact with the actives metal are frequently adopted as an effective approach to acquire target products in satisfactory yields [30].

In the present report, we have extended our study on the preparation of bimetallic palladium copper catalyst supported on active carbon (denoted as Pd–Cu(3.0)/C; 3.0 is molar ratio of Pd/Cu). Bimetallic Pd–Cu(3.0)/C catalyst was prepared via the hydrothermal treatment of a solution that contained Pd and Cu species at 150°C for 24 h followed by H_2 treatment at 400°C for 1.5 h. The promotion effect of Cu on Pd/C catalyst, solvent use and reaction parameters (initial H_2 pressure, reaction temperature) on the activity and selectivity in the hydrogenation of unsaturated carbonyl compounds are also studied.

2. Materials and Methods

2.1 Materials

Palladium (II) chloride ($PdCl_2$; Tokyo Chemical Industries Co. (TCI)), copper (II) nitrate ($Cu(NO_3)_2{\cdot}3H_2O$; Merck) were purchased and used as received. Microporous carbon (C, S_{BET} = 815 m^2g^{-1}) was purchased from WAKO Pure Chemical Industries, Ltd. Ltd. unless otherwise stated. Furfural, furfuryl alcohol, tetrahydrofurfuryl alcohol, *iso*-propanol, ethanol, and authentic organic reactants and products were purchased from Tokyo Chemical Industries Co. (TCI). All organic chemical compounds were purified using standard procedures prior to use.

2.2 Catalyst characterisation

All catalysts were characterized by powder X-ray diffraction (XRD) Miniflex 600 Rigaku with Cu as monochromatic source K a radiation (λ = 0.15444 nm). XRD operated at 40 kV and 15 mA with solar slit 1.25°, scan step 5° min^{-1} and using a Ni Kβ filter. The crystallite size of palladium was estimated by using the Scherrer`s equation.

The Brunauer-Emmet-Teller (BET) surface area (S_{BET}) and pore volume (Vp) were measured using N_2 physisorption at -196°C on a Belsorp Max (BEL Japan). The samples were degassed at 200°C 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 [33], while the micropore distribution was estimated by using Horvarth-Kawazoe (HK) approach [34].

The active surface areas were determined by H_2 chemisorption. After the catalyst was heated at 120°C under vacuum for 30 min, it was heated at 400°C under H_2 for 30 min and under vacuum for 30 min, followed by evacuation to room temperature for 30 min. The adsorption of H_2 was conducted at 0°C. The active surface area was calculated from the volume of H_2 desorbed by assuming an H/Pd stoichiometry of one, respectively and the number of Pd atom for the (111) plane is 1.5 x 10^{15} per cm^2 Pd based on an equal distribution of the three lowest index planes of Pd [35].

2.3 Preparation of Pd-Cu(3.0)/C catalysts

A typical procedure of the synthesis of bimetallic palladium-copper supported on carbon (denoted as Pd–Cu(3.0)/C (Pd = 5wt%; 3.0 molar ratio of Pd/Cu)) catalyst is described as follows [20]: $PdCl_2$ (0.472 mmol) was dissolved in deionized water (denoted as solution A), and $Cu(NO_3)_2 \cdot 3H_2O$ (0.156 mmol) was dissolved in ethanol/2-methoxy ethanol (2:1) (denoted as solution B) at room temperature. Solutions A and B were mixed at room temperature and a 1.0 g carbon (C, $S_{BET} = 815\ m^2g^{-1}$) was subsequently added; the temperature was 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 reduced with hydrogen at 400°C for 1.5 h.

2.4 Catalytic reactions

2.4.1 Hydrogenation of FFald

Pd–Cu(3.0)/C catalyst (0.05 g), FFald (1.1 mmol), *trans*-decahydronaphthalene (decalin) (0.2 mmol), and *iso*-PrOH (3 mL) as solvent were placed into a glass reaction tube, which fitted inside a stainless-steel reactor. After H_2 was introduced into the reactor with an initial H_2 pressure of 3.0 MPa at room temperature, the temperature of the reactor was increased to 130°C. After 1.5 h (90 min), the conversion of FFald and the yield of FFalc were determined by GC analysis using an internal standard technique. The Pd–Cu(3.0)/C catalyst was easily separated using either simple centrifugation or filtration. The solvent was removed in vacuo, and the residue was purified via silica-gel column chromatography.

2.4.2 Product Analysis

GC analysis of the reactant (FFald) and products (FFalc and THFalc) was performed on a Shimadzu GC-8A equipped with a flame ionization detector and silicone OV-101 packing. 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 ^{13}C NMR spectra were obtained on a JNM-AL400 spectrometer at 400 MHz; the samples for NMR analysis were dissolved in chloroform-d_1 with TMS as the internal standard. The products were confirmed by a comparison of their GC retention time, mass, ^1H and ^{13}C NMR spectra with those of authentic samples. The conversion, yield and selectivity of the products were calculated according to the following equations:

$$Conversion = \frac{\text{introduced mol reactant (Fo) - remained mol reactant (Ft)}}{\text{introduced mol reactant (Fo)}} x100\%$$

$$Yield = \frac{\text{mol product}}{\text{consumed mol reactant } (\Delta\text{F})} x100\%$$

$$Selectivity = \frac{\text{mol product}}{\text{total mol product}} x100\%$$

where F_0 is the introduced mol reactant (furfural, FFald), F_t is the remaining mol reactant, and ΔF 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 characterization

The N_2-adsorption/desorption of charcoal (C) support and the synthesized bimetallic Pd-Cu/C was performed and the profiles are shown in **Figure 1.** The hysterisies loop of adsorptio/desorption of the synthesiszed Pd-Cu/C samples show a very similar to that of former charcoal support, suggesting that there is no significant change of the pore structure of catalyst support during the introducing Pd metal or thermal activation using N_2 or H_2 at 400°C. It has been reported that carbon support has high thermal and chemical stability at the range of 300-500°C under H_2 or N_2 atmosphere [36,37].

To determine the pore size distribution of C support and the synthesized catalysts, the plot of volume of adsorbed-N_2 versus pore distribution using Horvarth-Kawazoe (HK) approach were performed as shown in Figure 2. As expected, the charcoal (C) support shows the microstructure of carbon with narrow pore size distribution of 0.59-0.66 nm (Figure 2a). After introduction of Pd-Cu, the shift of pore size distribution at ≥0.66 nm for after and before reduction and recovered samples are clearly observed. However, there is no clear evidence for the shift of pore size distribution towards small pore sizes or big pore sizes after introducing the Pd–Cu species or thermal activation using N_2 or H_2 at 400°C.

The physico-chemical properties (*e.g.*, specific surface area BET (S_{BET}), pore volume, pore diameter, and H_2 uptakes) of the synthesized bimetallic Pd–Cu(3.0)/C catalysts are summarized in **Table 1**.

The S_{BET} of as prepared, H_2-reduced, and recovered Pd–Cu(3.0)/C was 637, 712, and 601 m^2.

g^{-1}, respectively, which are lower than that of the S_{BET} of the carbon support (C, S_{BET} = 815 m^2. g^{-1}). The incorporation of metal species into pore structure of carbon will significantly reduce the specific surface area (S_{BET}) due the pore blocking or collapsed the structure by chemical or thermal treatment during the catalyst preparation[38]. The decrease in S_{BET} is consistent with the shift of pore size distribution as has been mentioned above.

Figure 3 shows the XRD pattern of commercial Pd/C(5%wt), as-prepared and pre-reduced bimetallic Pd–Cu(3.0)/C catalysts. In the case of as-prepared Pd–Cu(3.0)/C catalyst, the typical diffraction peaks at 2θ = 39.96°, 46.16°, 67.6° were clearly observed, which can be attributed to the metallic species of Pd(111), Pd(200), and Pd(020) (JCPDS#05-0681), respectively[39]. The diffraction peak of Pd(111) at 2θ = 40.8° become broadened, which can be attributed as the formation of bimetallic Pd–Cu alloy after reduction with H_2 at 400°C for 90 min[40]. By using the Scherrer`s equation, the average crystallite sizes of Pd(111) in as prepared Pd–Cu(3.0)/C were 4.2 nm, whereas in Pd–Cu(3.0)/C was unable to calculate due to the overlapping diffraction peaks of Pd(111) and Pd–Cu alloy phase (Figure 1c). A small peak at 2θ = 29.6° which can be assigned as the Cu_2O(110) species (JCPDS# 78-2076) was also observed both in the as prepared and reduced Pd–Cu(3.0)/C samples (Figure 1b-c). Additionally, the broadened peak at 2θ = 21.3° can be attributed to the diffraction peaks of C(111) of carbon support[41].

3.2 Catalytic reactions

3.2.1 Screening of second metal

In the first set experiments, the catalytic hydrogenation of biomass-derived FFald using various bimetallic Pd-based catalysts were performed and the results are summarized in **Table 2**.

By using commercial Pd/C (5%wt Pd) catalyst, the main product was THFalc (80%) as the result of total hydrogenation of both C=C and C=O bonds in FFald with small amount yields of FFalc (2%) and 2-MeF (8%) at 100% conversion of FFald (entry 1). Using Pd–Cu(3.0)/C catalyst without pre-reduction with H_2, the conversion of FFald was only 56% and yielded 28% FFalc, 15% THFalc, and 13% others (others consist of furfural condensation according to GC and GC-MS data) (entry 2) [42]. After a small amount of Cu (0.156 mmol; Pd/Cu molar ratio ≅ 3.0) was introduced and Pd–Cu(3.0)/C catalyst was pre-reduced with H_2 at 400°C, the product selectivity remarkably shifted to FFalc (68% in yield) at 73% conversion of FFald (entry 3). An increase in the reaction temperature from 100°C to 130°C gave a remarkable increase in FFalc yield from 68% to 94%, respectively (entries 3 and 4). After reaction time was extended to 3 h, the yield of FFalc slightly decreased to 92% while THFalc and 2-MeF yield remained unchanged at >99% conversion of FFald (entry 5). This result suggests that further hydrogenation of C=C furan ring was significantly inhibited over bimetallic Pd–Cu(3.0)/C catalyst. Sitthisa et al have noticed that the presence of Cu in Pd–Cu/SiO_2 catalyst to form Pd–Cu alloy phase greatly enhanced the affinity of Pd towards η^2(C-O)-furfural interaction, facilitated the formation of hydroxyalkyl species then easily hydrogenated to FFalc. On the other hand, the further hydrogenation of C=C or decarbonylation rate is greatly reduced on bimetallic Pd–Cu system [32]. Furthermore, investigation of the effect of various second metals such as tin (Sn), cobalt (Co), nickel (Ni), and iron (Fe) on the conversion of FFald and yield of FFalc was also performed and the results are also summarized in **Table 2**. Those Pd–M/C (M = Sn, Co, Ni, and Fe) catalysts were synthesized using a similar procedure to that of Pd–Cu(3.0)/C catalyst. However, those bimetallic Pd–M/C (M = Sn, Co, Ni, and Fe) catalysts gave unsatisfied results both conversion of FFald and yield of FFalc under the same reaction conditions (entries 6-9). Therefore, the catalytic reaction of FFald in the presence of bimetallic Pd–Cu(3.0)/C catalyst will be furtherly investigated, including the effect of solvent used, reaction temperature, initial H_2 pressure, time profiles, and reusability test.

3.2.2 Effect of solvent

The solvent screening for FFald hydrogenation using Pd–Cu(3.0)/C catalyst on the conversion and yield was performed and the results are summarized in **Table 3**.

Alcohols, such as 2-propanol (*iso*-PrOH), 1-propanol, ethanol, and methanol, and 1,4-dioxane (typical cyclic ether) are superior to other solvents, giving quantitatively high yields of FFalc (entries 1-5). On the other hand, FFald hydrogenation did not proceed effectively in toluene, giving only a 43% FFalc yield at the same conditions (entry 6). These results are very good agreement with the catalytic reaction results over bimetallic Ni-Sn alloy catalysts as reported previously [19,21]. The formation of 1,2-, 1,5-, and 1,4-pentanediol as the hydrogenolyzed products or condensation product was firstly observed in H_2O solvent, therefore we furtherly evaluated the catalytic reaction both in H_2O solvent only and the alcohols/1,4-dioxane-H_2O mixture solvent and the results are also summarized in Table 3. In ethanol: H_2O (1.5: 2.0 v/v), 2-propanol: H_2O (1.5: 2.0 v/v), and 1,4-dioxane: H_2O (1.5: 2.0 v/v) mixture solvents, the reaction not only hydrogenation of C=O and C=C bonds of reactant but also hydrogenolysis of furan ring, giving significantly high yield of pentanediol (entries 8-10). These results are in accordance with our results in the hydrogenolysis of FFald to 1,4-pentanediol in ethanol: H_2O (1.5: 2.0 v/v) mixture solvent using bulk Ni-Sn alloy catalyst as reported previously [43]. Additionally, a notable high yield of cyclopentanone (CPO) and cyclopentanol (CPOL) was obtained when 1,4-dioxane or 1,4-dioxane-

H_2O mixture solvent was used. These results are very consistent with the previous work of Dewi Astuti et al. using bimetallic Ni–Fe(3.0)/TiO_2 catalysts under the identical reaction conditions [27]. Therefore, further investigation on the hydrogenolysis of FFald using bimetallic Pd–based catalysts will be reported in our upcoming manuscript.

3.2.3 Effect of reaction temperature

The effect of temperature on the catalytic hydrogenation of FFald to FFalc was evaluated over Pd–Cu(3.0)/C catalyst at range temperature of 90-190°C in batch system for 1.5 h and the results are shown in **Figure 4**.

Differences in the conversion of FFald and product distributions at different temperature are clearly observed. At lower temperature (90-110°C), the maximum conversion of FFald was around 87% with selectivity of FFalc was nearly 100%. An increase of the reaction temperature from 100°C to 130°C gave a notable increase in FFalc yield from 68% to 94%, respectively followed by a slight increase of THFalc from 3% to 5%. At those of reaction temperatures, the enhancement of decarbonylation reaction rate of FFald did not occure as indicated by remained unchange of 2-MeF yield. Moreover, further increase of reaction temperature to 150-190°C promoted the hydrogenation of C=C bond as well as the decarbonylation reactions, giving increase in yields of THFalc and 2-MeF, respectively. It has been reported that the decarbonylation reaction of FFald corresponding to 2-MeF using catalyst of platinum metal groups (Pd, Pt, and Ir) is favourably occurred at relatively high reaction temperature (190-220°C)[44] or vapor phase hydrogenation [31]. The presence of second metals such as Cu or Fe was significantly inhibited the further reaction of FFald or FFalc such as total hydrogenation of C=C/C=O bonds or decarbonylation/decarboxylation, therefore the selectivity of desired product FFalc maintained along with the wide range reaction conditions[32].

3.2.4 Effect of initial H_2 pressure

The effect of the initial H_2 pressure on the FFald conversion and product selectivity in shown in **Figure 5.**

FFald conversion and FFalc selectivity gradually increased as the initial H_2 pressure increased, whereas the THFalc increased at initial H_2 pressure of 0.5-1.0 MPa and remained unchanged at the higher initial H_2 pressure. On the other hand, yield of 2-MeF decreased to 0% at initial pressure between 2.5 MPa and 3.0 MPa.

3.3 Time profiles

The reaction profiles of FFald hydrogenation at 130^{o}C on the bimetallic Pd–Cu(3.0)/C catalyst are shown in **Figure 6**.

At the early reaction time (0.5 h), FFald conversion was 42% to produce 100% FFalc selectivity, indicating that C=O hydrogenation was took place easily using bimetallic Pd–Cu(3.0)/C catalyst. After reaction was prolonged to 1.0 h, a notable increase of FFald was obtained (87%) with yields of FFalc and THFalc were 85% and 2%, respectively. It has been reported that Pd exhibits a low rate for hydrogenation of the C=O bond compared with other metals commonly used for hydrogenation [45]. Our current results show that a great enhancement both conversion of FFald and selectivity of FFalc which can be attributed to the promotional effect of the second metal Cu as has already described in previous reports [31,32]. The maximum yield of FFalc (94%) was achieved after a reaction time of 1.5 h at full conversion of FFald. When the reaction time was extended to 3-6 h, further hydrogenation reaction of C=C bond obviously occurred as indicated by the increase of THFalc yield. On the other hand, the yield of 2-MeF was almost unchanged after a reaction time of 6 h (3%), suggesting the decarbonylation of FFald or FFalc did not occur effectively using bimetallic Pd–Cu(3.0)/C catalyst under the current operating conditions as mentioned previously.

3.4 Hydrogenation of α,β-unsaturated ketone and aldehyde

A substrate scope of the presence of Pd–Cu(3.0)/C catalyst in the hydrogenation of α,β-unsaturated ketone and aldehyde was examined and the results are summarized in **Table 4** and **Table 5**.

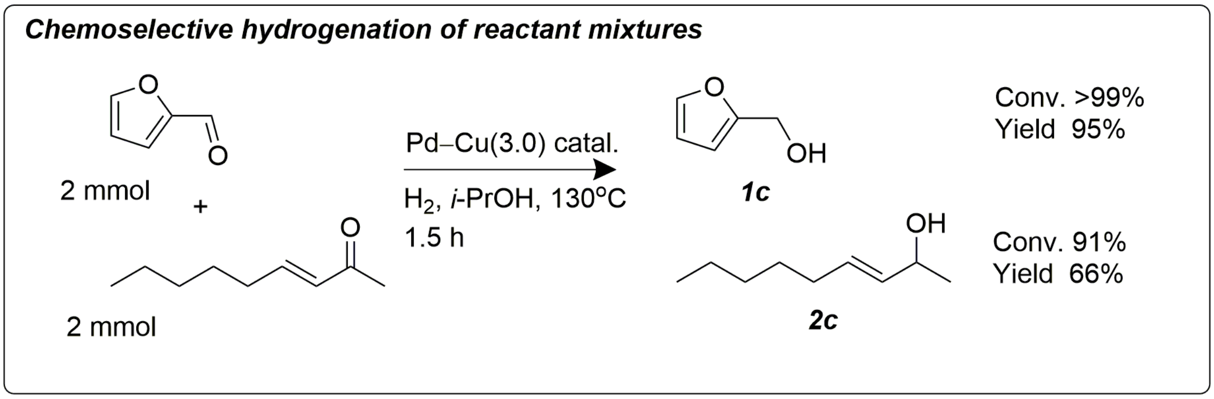
In the case of hydrogenation of ketone, 2-cyclohexene-1-one was selected as a typical α,β-unsaturated ketone substrate. Using a commercial Pd/C (5%wt Pd) catalyst, 33% conversion of 2-cyclohexene-1-one was obtained with the selectivities of product **2a** and **3a** were 24% and 76%, respectively without the formation of product **1a** (entry 1). A remarkably high selectivity of product **1a** (96%) was obtained over Pd–Cu(3.0)/C catalyst at temperature of 100^{o}C for 1.5 h at 54% conversion (entry 2). This is a result of promoting effect of Cu on Pd/C, leading to high affinity toward C=O bond rather than C=C bond of the substrate. An increase reaction temperature from 100^{o}C to 130^{o}C not only enhanced the conversion to 94% but also caused further hydrogenation C=C bond, therefore the selectivity to **3a** increased significantly (entry 3). Moreover, the extent of reaction time to 3.0 h gave a completed reaction (>99% conversion) with product selectivities of **1a** and **3a** were 68% and 32%, respectively (entry 4).

Next, we examined the catalytic reaction of typical α,β-unsaturated aldehyde (*trans*-2-hexenaldehyde) using bimetallic Pd–Cu(3.0)/C catalyst and the results are summarized in **Table 5.**

Using Pd/C catalyst at 130°C and 1.5 h, 65% conversion of *trans*-2-hexenaldehyde was achieved and yielded 100% selectivity of n-hexanol (**1b**), which means both C=C and C=O bonds of reactant were simultaneously hydrogenated under the reaction conditions (entry 1). Interestingly, bimetallic Pd–Cu(3.0)/C catalyst gave a remarkable selectivity to 2-henxene-ol **(1a)** (96%) at 87% conversion at 100°C for 1.5 h (entry 2). When the reaction temperature was increased to 130°C or reaction time was extended to 3 h, the selectivity of saturated alcohol significantly increased indicating the further hydrogenation of C=C was obviously occurred (entries 3 and 4).

3.5 Chemoselective hydrogenation of reactant mixtures

To complete our investigation in the selective hydrogenation of C=O bond rather than C=C bond, the catalytic reaction of a mixture of FFald (typical unsaturated aldehyde) and (E)-non-3-en-2-one (typical unsaturated ketone) (molar ratio to 1.0) was examined using bimetallic Pd–Cu(3.0)/C catalysts and the results showed in **Scheme 2**. Under the current operating conditions, at a full conversion of FFald with 95% yield of FFalc (**1c**) was obtained. On the other hand, the conversion of (E)-non-3-en-2-one was 91% with moderate yield of unsaturated alcohol (**2c**) (66%). These results suggest that the bimetallic Pd–Cu(3.0)/C catalyst can be applied for selective hydrogenation of α,β-unsaturated ketone and aldehyde to corresponding unsaturated alcohol from moderate to high yield.



Scheme 2. Chemoselective hydrogenation of aldehyde (FFald) and ketone ((E)-non-3-en-2-one) reactant mixtures. Reaction conditions: catalyst, 0.05 g; substrate, 2.0 mmol; *iso*-PrOH, 3.5 mL, 3.0 MPa H_2, 130°C, 1.5 h.

3.6 Reusability test

A reusability test was performed on the Pd‒Cu(3.0)/C catalyst in the selective hydrogenation of FFald and the results are summarized in **Table 6**.

The used Pd‒Cu(3.0)/C catalyst was easily separated by either simple centrifugation or filtration after the reaction. The activity of the catalyst decreased while the selectivity was maintained for at least four consecutive reaction runs. The catalytic activity and selectivity of the used Pd‒Cu(3.0)/C catalyst can be restored to the original by simple reduction with H_2 at 400^{o}C for 1.5 h.

4. Conclusions

We have described the promotional effect of second metal Cu on Pd/C catalyst in the chemoselective hydrogenation of biobased furfuraldehyde (FFald) and typical α,β-unsaturated ketones/aldehydes. The presence of Cu (0.012 mmol) in Pd/C to form bimetallic Pd-Cu alloy phases obviously enhanced the selectivity of Pd towards C=O rather than C=C bonds in furfural or typical α,β-unsaturated ketones/aldehydes, leading to high yield of unsaturated alcohols. The formation of bimetallic Pd‒Cu alloy phase in Pd‒Cu(3.0)/C catalyst was clearly observed after reduction with H_2 at 400^{o}C for 1.5 h, which plays a pivotal role during the chemoselective hydrogenations. Pd‒Cu(3.0)/C catalyst was found to stable and reusable for at least four reaction runs and the activity and selectivity of the catalyst can be restored to the original after rejuvenation with H_2 at 400^{o}C for 1.5 h.

5. Acknowledgments

The authors acknowledge the RISET DASAR (contract number DIPA-042.06-1.401516/2020) from Ministry of Education and Culture, Indonesian Government, which all financially supported this work. We would also like thank to Professor Shogo Shimazu for kind help in XRD, H_2-chemisorption, and N_2-adsorption/desorption-BET measurements.

6. References

[1] H.E. Hoydonckx, W.M. Van Rhijn, M. Van Rhijn, D.E. De Vos, P.A. Jacobs, Furfural and Derivatives, in: Ullmann’s Encycl. Ind. Chem., 2012: pp. 285–309. doi:10.1002/14356007.a12_119.pub2.

[2] H. Kimura, Progress in one-step amination of long-chain fatty alcohols with dimethylamine development of key technologies for industrial applications, innovations, and future outlook,

Catal. Rev. - Sci. Eng. 53 (2011) 1–90. doi:10.1080/01614940.2011.556913.

[3] L. Pasumansky, C.T. Goralski, B. Singaram, Lithium aminoborohydrides: Powerful, selective, air-stable reducing agents, Org. Process Res. Dev. 10 (2006) 959–970. doi:10.1021/op0600759.

[4] J.S. Cha, Recent developments in Meerwein-Ponndorf-Verley and related reactions for the reduction of organic functional groups using aluminum, boron, and other metal reagents: A review, Org. Process Res. Dev. 10 (2006) 1032–1053. doi:10.1021/op068002c.

[5] T. Ohkuma, N. Kurono, N. Arai, Development of asymmetric reactions catalyzed by ruthenium complexes with two kinds of ligands, Bull. Chem. Soc. Jpn. 92 (2019) 475–504. doi:10.1246/bcsj.20180328.

[6] P. GALLEZOT, D. RICHARD, Selective Hydrogenation of a, b-Unsaturated Aldehydes, Catal. Rev. 40 (1998) 81–126. doi:10.1080/01614949808007106.

[7] P. Mäki-Arvela, T. Salmi, B. Holmbom, S. Willför, D.Y. Murzin, Synthesis of sugars by hydrolysis of hemicelluloses- A review, Chem. Rev. 111 (2011) 5638–5666. doi:10.1021/cr2000042.

[8] P. Claus, Selective hydrogenation of alpha,beta-unsaturated aldehydes and other C = O and C = C bonds containing compounds, Top. Catal. 5 (1998) 51–62. doi:10.1023/a:1019177330810.

[9] M. Luneau, J.S. Lim, D.A. Patel, E.C.H. Sykes, C.M. Friend, P. Sautet, Guidelines to Achieving High Selectivity for the Hydrogenation of α,β-Unsaturated Aldehydes with Bimetallic and Dilute Alloy Catalysts: A Review, Chem. Rev. (2020). doi:10.1021/acs.chemrev.0c00582.

[10] F.R. Lucci, J. Liu, M.D. Marcinkowski, M. Yang, L.F. Allard, M. Flytzani-Stephanopoulos, E.C.H. Sykes, Selective hydrogenation of 1,3-butadiene on platinum-copper alloys at the single-atom limit, Nat. Commun. 6 (2015) 1–8. doi:10.1038/ncomms9550.

[11] Z. Guo, C. Xiao, R. V. Maligal-Ganesh, L. Zhou, T.W. Goh, X. Li, D. Tesfagaber, A. Thiel, W. Huang, Pt Nanoclusters Confined within Metal–Organic Framework Cavities for Chemoselective Cinnamaldehyde Hydrogenation, ACS Catal. 4 (2014) 1340–1348. doi:10.1021/cs400982n.

[12] A.M. Silva, O.A.A. Santos, M.J. Mendes, E. Jordão, M.A. Fraga, Hydrogenation of citral over ruthenium-tin catalysts, Appl. Catal. A Gen. 241 (2003) 155–165. doi:10.1016/S0926-860X(02)00463-5.

[13] K. Gupta, R.K. Rai, A.D. Dwivedi, S.K. Singh, Catalytic Aerial Oxidation of Biomass-Derived Furans to Furan Carboxylic Acids in Water over Bimetallic Nickel–Palladium

Alloy Nanoparticles, ChemCatChem. 9 (2017) 2760–2767. doi:10.1002/cctc.201600942.

[14] M. Sankar, N. Dimitratos, P.J. Miedziak, P.P. Wells, C.J. Kiely, G.J. Hutchings, Designing bimetallic catalysts for a green and sustainable future, Chem. Soc. Rev. 41 (2012) 8099–8139. doi:10.1039/c2cs35296f.

[15] D.M. Alonso, S.G. Wettstein, J.A. Dumesic, Bimetallic catalysts for upgrading of biomass to fuels and chemicals, Chem. Soc. Rev. 41 (2012) 8075–8098. doi:10.1039/c2cs35188a.

[16] P. Mäki-Arvela, J. Hájek, T. Salmi, D.Y. Murzin, Chemoselective hydrogenation of carbonyl compounds over heterogeneous catalysts, Appl. Catal. A Gen. 292 (2005) 1–49. doi:10.1016/j.apcata.2005.05.045.

[17] L. Altmann, X. Wang, H. Borchert, J. Kolny-Olesiak, V. Zielasek, J. Parisi, S. Kunz, M. Bäumer, Influence of Sn content on the hydrogenation of crotonaldehyde catalysed by colloidally prepared PtSn nanoparticles, Phys. Chem. Chem. Phys. 17 (2015) 28186–28192. doi:10.1039/c5cp00280j.

[18] S. Liang, C. Hao, Y. Shi, The Power of Single-Atom Catalysis, ChemCatChem. 7 (2015) 2559–2567. doi:10.1002/cctc.201500363.

[19] R. Rodiansono, T. Hara, N. Ichikuni, S. Shimazu, A novel preparation method of nisn alloy catalysts supported on aluminium hydroxide: Application to chemoselective hydrogenation of unsaturated carbonyl compounds, Chem. Lett. 41 (2012) 769–771. doi:10.1246/cl.2012.769.

[20] R. Rodiansono, S. Khairi, T. Hara, N. Ichikuni, S. Shimazu, Highly efficient and selective hydrogenation of unsaturated carbonyl compounds using Ni-Sn alloy catalysts, Catal. Sci. Technol. 2 (2012) 2139–2145. doi:10.1039/c2cy20216f.

[21] R. Rodiansono, T. Hara, N. Ichikuni, S. Shimazu, Development of Nanoporous Ni-Sn Alloy and Application for Chemoselective Hydrogenation of Furfural to Furfuryl Alcohol, Bull. Chem. React. Eng. Catal. 9 (2014) 53–59. doi:10.9767/bcrec.9.1.5529.53-59.

[22] R. Rodiansono, M.D. Astuti, S. Khairi, S. Shimazu, Selective Hydrogenation of Biomass-derived Furfural over Supported Ni3Sn2 Alloy: Role of Supports, Bull. Chem. React. Eng. Catal. 11 (2016) 1–9. doi:10.9767/bcrec.11.1.393.1-9.

[23] R. Rodiansono, M.D. Astuti, D.R. Mujiyanti, U.T. Santoso, S. Shimazu, Novel preparation method of bimetallic Ni-In alloy catalysts supported on amorphous alumina for the highly selective hydrogenation of furfural, Mol. Catal. 445 (2018) 52–60. doi:10.1016/j.mcat.2017.11.004.

[24] S. Dutta, S. De, B. Saha, M.I. Alam, Advances in conversion of hemicellulosic biomass to furfural and upgrading to biofuels, Catal. Sci. Technol. 2 (2012) 2025–2036.

doi:10.1039/C2CY20235B.

[25] J.-P. Lange, E. van der Heide, J. van Buijtenen, R. Price, Furfural—A Promising Platform for Lignocellulosic Biofuels, ChemSusChem. 5 (2012) 150–166. doi:10.1002/cssc.201100648.

[26] S. Chen, R. Wojcieszak, F. Dumeignil, E. Marceau, S. Royer, How Catalysts and Experimental Conditions Determine the Selective Hydroconversion of Furfural and 5-Hydroxymethylfurfural, Chem. Rev. 118 (2018) 11023–11117. doi:10.1021/acs.chemrev.8b00134.

[27] M.D. Astuti, D. Kristina, R. Rodiansono, D.R. Mujiyanti, One-pot Selective Conversion of Biomass-derived Furfural into Cyclopentanone/Cyclopentanol over TiO2 Supported Bimetallic Ni-M (M = Co, Fe) Catalysts, Bull. Chem. React. Eng. Catal. 15 (2020) 231–241. doi:10.9767/bcrec.15.1.6307.231-241.

[28] Á. O'Driscoll, T. Curtin, W.Y. Hernández, P. Van Der Voort, J.J. Leahy, Hydrogenation of Furfural with a Pt-Sn Catalyst: The Suitability to Sustainable Industrial Application, Org. Process Res. Dev. 20 (2016) 1917–1929. doi:10.1021/acs.oprd.6b00228.

[29] F. Liao, T.W.B. Lo, S.C.E. Tsang, Recent Developments in Palladium-Based Bimetallic Catalysts, ChemCatChem. 7 (2015) 1998–2014. doi:10.1002/cctc.201500245.

[30] K. V. Kovtunov, D.A. Barskiy, O.G. Salnikov, A.K. Khudorozhkov, A. V. Bukhtiyarov, I.P. Prosvirin, E.Y. Gerasimov, V.I. Bukhtiyarov, I. V. Koptyug, Strong Metal-Support Interactions for Pd Supported on TiO2 Catalysts in Heterogeneous Hydrogenation with Parahydrogen, ChemCatChem. 630090 (2015) 2581–2584. doi:10.1002/cctc.201500618.

[31] N. Pino, S. Sitthisa, Q. Tan, T. Souza, D. López, D.E. Resasco, D.E.R. c Natalia Pino a, Surapas Sitthisa c, Qiaohua Tan c, Talita Souza b, Diana López a, Structure, activity, and selectivity of bimetallic Pd-Fe/SiO2 and Pd-Fe/c- Al2O3 catalysts for the conversion of furfural, J. Catal. 350 (2017) 30–40. doi:10.1016/j.jcat.2017.03.016.

[32] S. Sitthisa, T.P. Prasomsri, T. Sooknoi, R.G. Mallinson, D.E. Resasco, Conversion of furfural and 2-methylpentanal on Pd/SiO2 and Pd–Cu/SiO2 catalysts Surapas, J. Catal. (2011) 17–27.

[33] S. Lowell, J.E. Shields, M.A. Thomas, M. Thommes, Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density, Kluwer Academic Publishers: Dordrecht, The Netherlands., 2004.

[34] S. Storck, H. Bretinger, W.F. Maier, Characterization of micro- and mesoporous solids by physisorption methods and pore-size analysis, Appl. Catal. A Gen. 174 (1998) 137–146. doi:10.1016/S0926-860X(98)00164-1.

[35] P.C. Aben, Palladium areas in supported catalysts. Determination of palladium surface areas in supported catalysts by means of hydrogen chemisorption, J. Catal. 10 (1968) 224–229. doi:10.1016/S0021-9517(68)80002-8.

[36] Q. Xu, K.C. Kharas, B.J. Croley, A.K. Datye, The Sintering of Supported Pd Automotive Catalysts, ChemCatChem. 3 (2011) 1004–1014. doi:10.1002/cctc.201000392.

[37] J. Lu, B. Fu, M.C. Kung, G. Xiao, J.W. Elam, H.H. Kung, P.C. Stair, Coking- and sintering-resistant palladium catalysts achieved through atomic layer deposition, Science (80-.). 335 (2012) 1205–1208. doi:10.1126/science.1212906.

[38] S. Gong, N. Chen, S. Nakayama, E.W. Qian, Isomerization of n-alkanes derived from jatropha oil over bifunctional catalysts, J. Mol. Catal. A Chem. 370 (2013) 14–21. doi:10.1016/j.molcata.2012.11.019.

[39] JCPDS-ICDD, Powder diffraction files, JCPDS-International center for diffraction data (JCPDS-ICDD), 1991.

[40] D. Chen, P. Sun, H. Liu, J. Yang, Bimetallic Cu-Pd alloy multipods and their highly electrocatalytic performance for formic acid oxidation and oxygen reduction, J. Mater. Chem. A. 5 (2017) 4421–4429. doi:10.1039/c6ta10476b.

[41] Z. Wei, J. Lou, C. Su, D. Guo, Y. Liu, S. Deng, An Efficient and Reusable Embedded Ru Catalyst for the Hydrogenolysis of Levulinic Acid to Γ-Valerolactone, ChemSusChem. 10 (2017) 1720–1732. doi:10.1002/cssc.201601769.

[42] A. Gandini, Furans as offspring of sugars and polysaccharides and progenitors of a family of remarkable polymers: a review of recent progress, Polym. Chem. 1 (2010) 245–251. doi:10.1039/B9PY00233B.

[43] R. Rodiansono, M.D. Astuti, T. Hara, N. Ichikuni, S. Shimazu, One-pot selective conversion of C5-furan into 1,4-pentanediol over bulk Ni-Sn alloy catalysts in an ethanol/H2O solvent mixture, Green Chem. 21 (2019) 2307–2315. doi:10.1039/c8gc03938k.

[44] N.S. Date, A.M. Hengne, K.W. Huang, R.C. Chikate, C. V. Rode, Single pot selective hydrogenation of furfural to 2-methylfuran over carbon supported iridium catalysts, Green Chem. 20 (2018) 2027–2037. doi:10.1039/c8gc00284c.

[45] T.B.L.W. Marinelli, S. Nabuurs, V. Ponec, Activity and selectivity in the reactions of substituted α,β-Unsaturated aldehydes, J. Catal. 151 (1995) 431–438. doi:10.1006/jcat.1995.1045.

FIGURE CAPTIONS

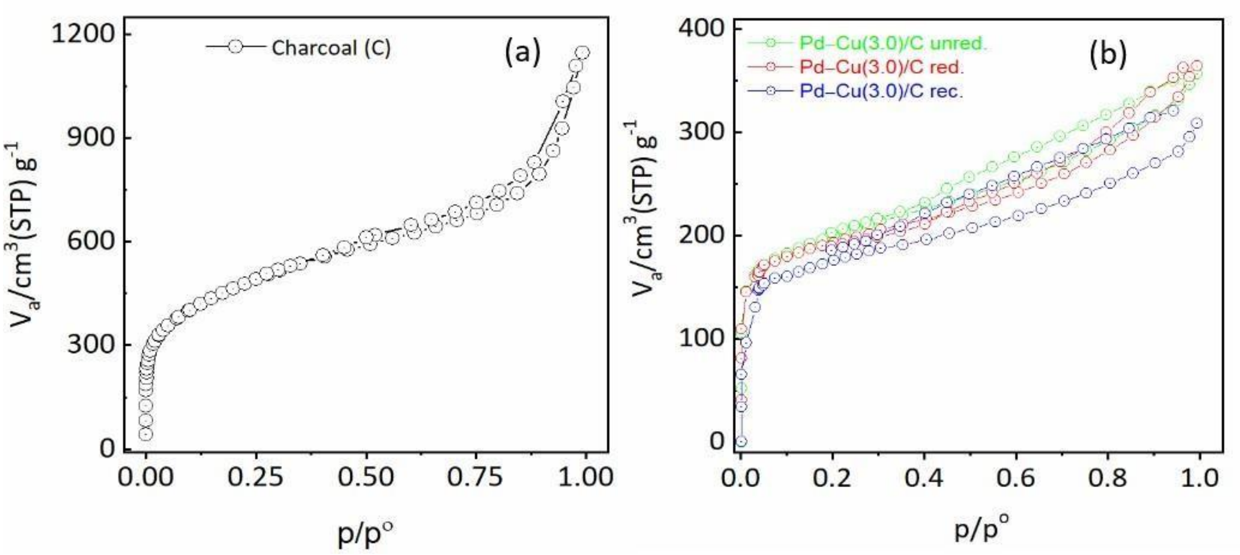


Figure 1. N_2-adsorption/desorption profiles of (a) charcoal (C) and (b) the synthesized Pd-Cu/C catalyst before and after reduction with H_2 at 400°C for 1.5 h and recovered sample.

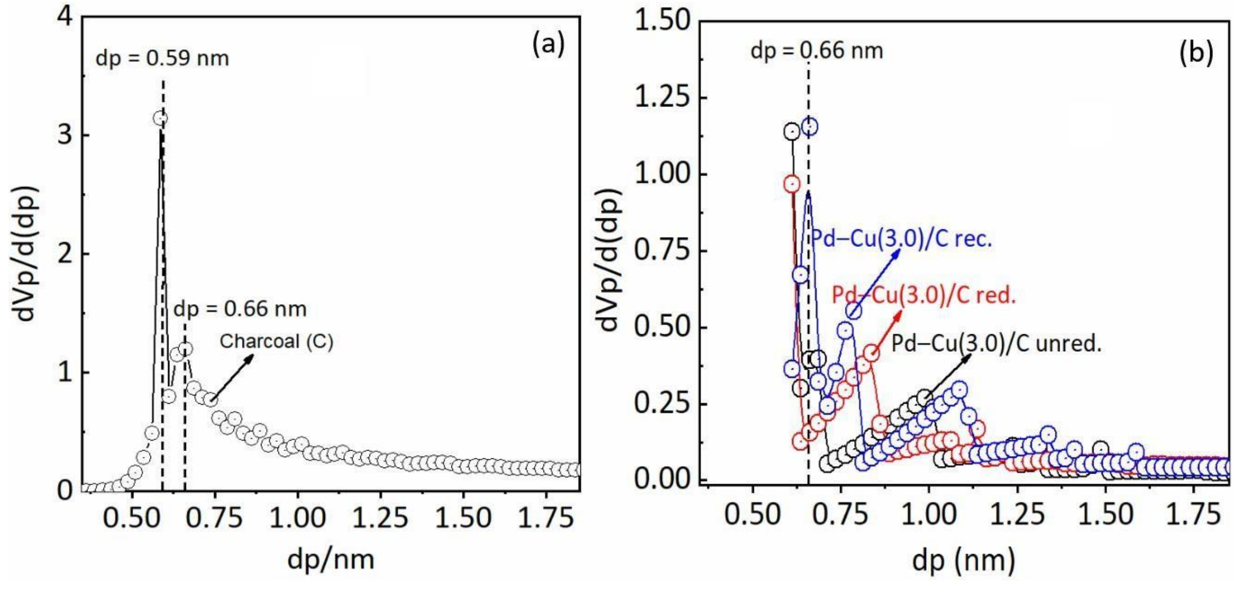


Figure 2. Pore distribution of (a) charcoal (C) and the synthesized bimetallic Pd–Cu(3.0)/C catalysts using HK approach.

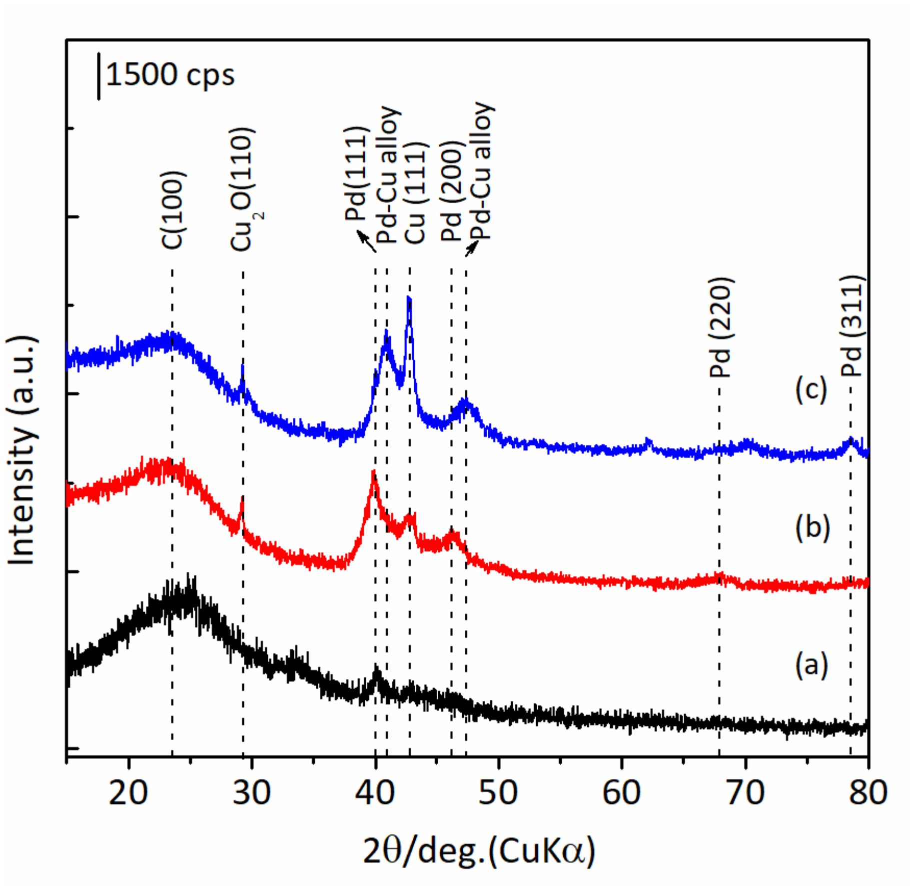


Figure 3. XRD patterns of (a) commercial Pd/C (5%wt Pd), (b) as prepared Pd–Cu(3.0)/C and (c) after reduction with H_2 at 400°C for 1.5 h.

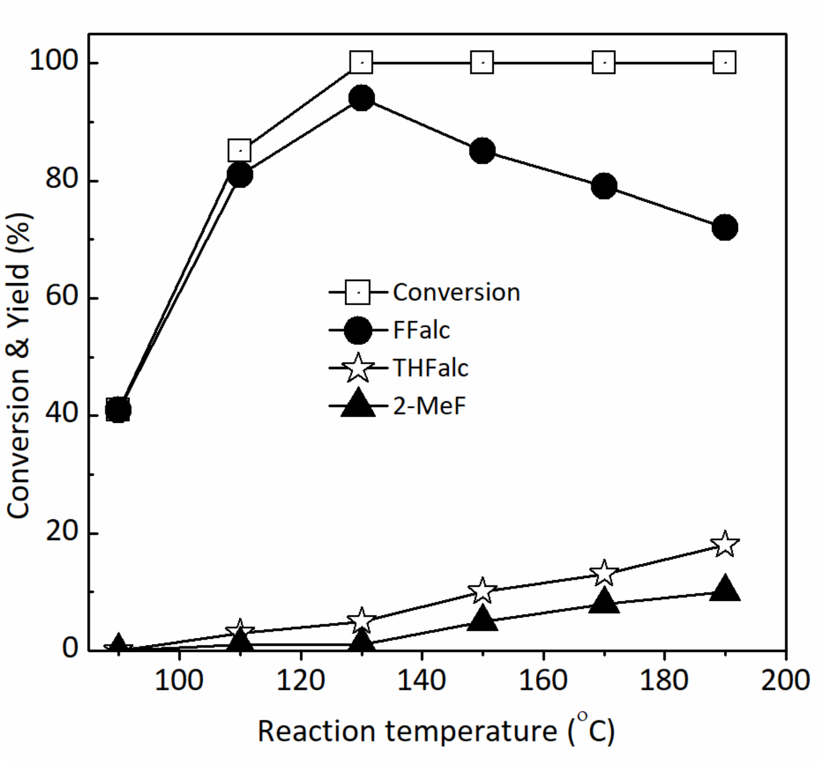


Figure 4. Effect of reaction temperature on the FFald conversion and product distribution over bimetallic Pd–Cu(3.0)/C catalyst. Reaction conditions: catalyst, 0.05 g; FFald, 1.1 mmol; *iso*-PrOH, 3 mL; H_2, 3.0 MPa, 1.5 h.

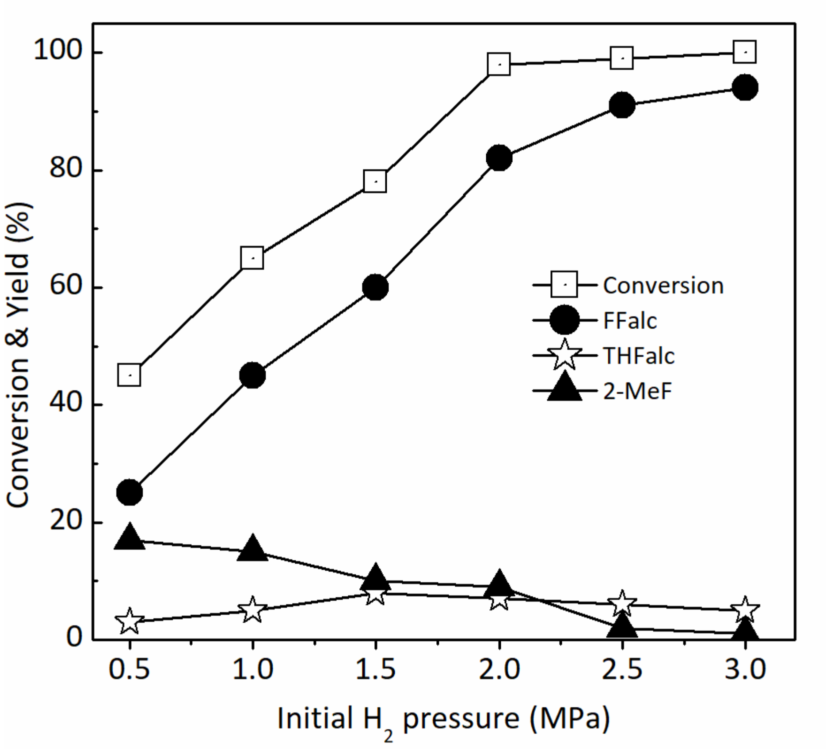


Figure 5. Effect of the initial H_2 pressure on the FFald conversion over bimetallic Pd–Cu(3.0)/C catalyst. *Reaction conditions:* catalyst, 0.05 g; FFald, 1.1 mmol; *iso*-PrOH, 3 mL; 130°C, 1.5 h.

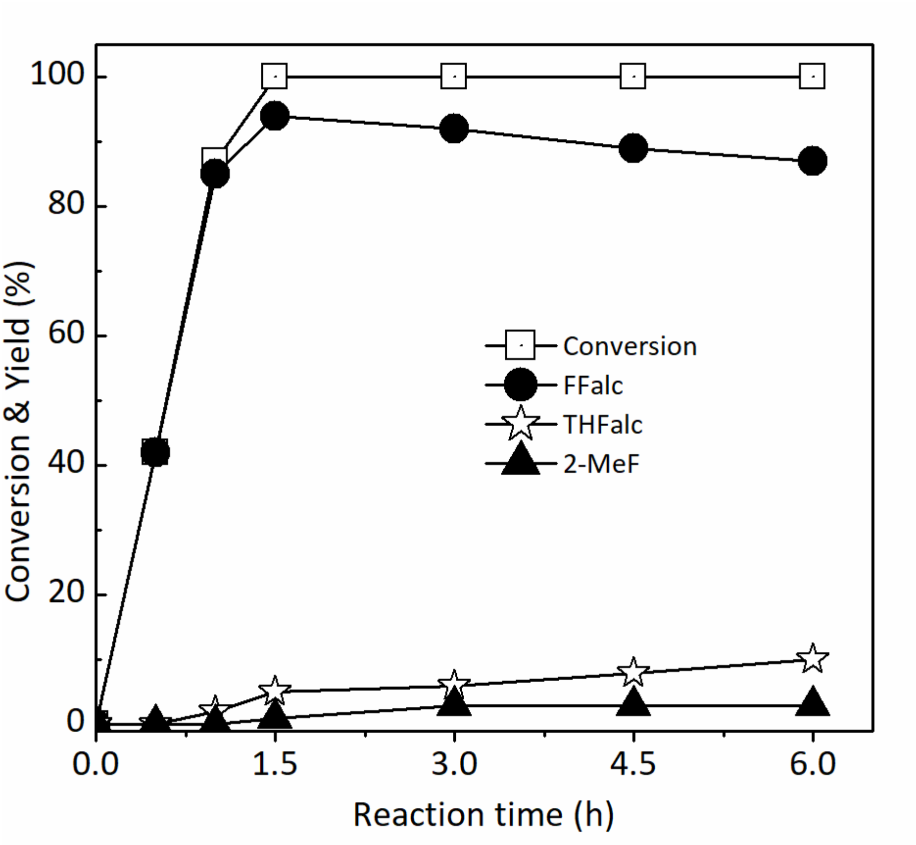


Figure 6. Time profiles of the hydrogenation of FFald over bimetallic Pd–Cu(3.0)/C catalyst. *Reaction conditions:* catalyst, 0.05 g; FFald, 1.1 mmol; *iso*-PrOH, 3 mL; 130°C.

TABLE CAPTIONS

Table 1 Physico-chemical properties of bimetallic Pd–Cu(3.0)/C catalyst

Entry	Catalyst[a]	S_{BET}[b] $(m^2.g^{-1})$	Pore Vol.[b] $(m^3.g^{-1})$	Pore Diameter[b] (nm)		H_2 uptakes[d] $(\mu mol.g^{-1})$
				BJH[b]	HK[c]	
1	Charcoal (C)	815	1.762	1.22	0.59	nd
2[e]	Pd–Cu(3.0)/C unred.	637	0.494	3.10	0.61	38.4
3	Pd–Cu(3.0)/C red.	712	0.548	3.08	0.65	39.6
4[f]	Pd–Cu(3.0)/C recovered	601	0.428	2.85	0.71	27.8

[a]The value in the parenthesis is Pd/Cu molar ratio. [b] S_{BET} was determined by N_2 adsorption at -196°C (77 K), pore volume and pore diameter were calculated according to BJH approach. [c]Pore diameter was calculated using HK method. [d]Based upon total the H_2 uptake at 0°C (after corrections for physical and chemical adsorption). [e]The as prepared Pd–Cu(3.0)/C without pre reduced with H_2. [f]The recovered Pd–Cu(3.0)/C after the third reaction run.

Table 2. Results of selective hydrogenation of FFald using various bimetallic Pd-based catalysts

Entry	Catalyst[a]	Composition (mmol. g^{-1})		Temp. (°C)	Conv.[b] (%)	Yield[b] (%)			
		Pd	M			FFalc	THFalc	2-MeF	Others[c]
1	Pd/C[d]	0.50	-	100	100	2	90	8	0
2	Pd–Cu(3.0)/C *unred.*	0.472	0.156	100	56	28	15	0	13
3	Pd–Cu(3.0)/C	0.472	0.156	100	73	68	3	2	0
4	Pd–Cu(3.0)/C	0.472	0.156	130	>99	94	5	1	0
5[e]	Pd–Cu(3.0)/C	0.472	0.156	130	>99	92	6	3	0
6	Pd–Sn(3.0)/C	0.461	0.152	130	53	16	5	2	20
7	Pd–Co(3.0)/C	0.464	0.151	130	43	12	15	6	10
8	Pd–Ni(3.0)/C	0.481	0.161	130	13	6	6	1	0
9	Pd–Fe(3.0)/C	0.560	0.187	130	78	43	25	5	15

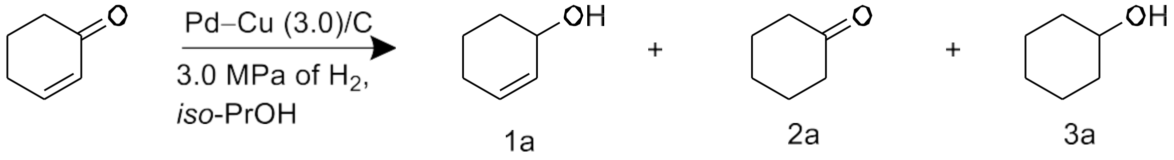
[a]The value in the parenthesis is Pd/M molar ratio (M = Cu, Sn, Co, Ni, and Fe); the bulk composition was determined by ICP-OES. Reaction conditions: catalyst (5 mg); FFald (2 mmol); solvent (2-propanol, 5 mL); temperature (130°C); initial H_2 pressure (3.0 MPa); reaction time (1.5 h). [b]Conversion and yields of FFalc THFalc, and 2-MeF were determined by GC using an internal standard technique. [c]Others consist of condensation product of FFald or FFalc according to GC/GC-MS data. [c]Commercially available Pd/C (5%wt Pd). [e]The reaction time was 3 h.

Table 3. Results of solvent screening for FFald hydrogenation over Pd–Cu(3.0)/C catalyst

Entry	Solvent	Conv.[a] (%)	Yield[a] (%)			
			FFalc	THFalc	2-MeF	Others[b]
1	1-Propanol	>99	90	8	2	0
2	2-Propanol	>99	94	5	1	0
3	Ethanol	96	94	2	0	0
4	Methanol	90	80	7	3	0
5	1,4-Dioxane	67	94	3	0	27[c]
6	Toluene	56	43	13	0	0
7	H_2O	67	27	13	7	20
8	Ethanol: H_2O (1.5: 2.0 v/v)	98	53	18	5	32[c]
9	2-Propanol/H_2O (1.5: 2.0 v/v)	99	57	15	5	22
10	1,4-Dioxane/H_2O (1.5: 2.0 v/v)	99	38	15	2	44[c]

Reaction conditions: catalyst (5 mg); FFald (2 mmol); solvent (3.5 mL); temperature (130°C); initial H_2 pressure (3.0 MPa); reaction time (1.5 h). [a]Conversion and yields of FFalc THFalc, and 2-MeF were determined by GC using an internal standard technique. [b]Others consist of the hydrogenolysis products such as 1,2-pentanediol, 1,5-pentanediol, and 1,4-pentanediol. [c]The main product of others using 1,4-dioxane solvent was cyclopentanone (CPO) and cyclopentanol (CPOL).

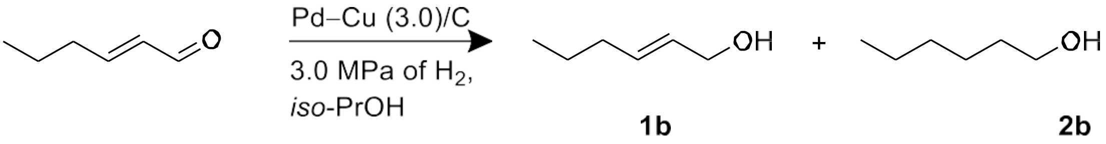
Table 4. Results of selective hydrogenation of typical α,β-unsaturated ketone using Pd–Cu(3.0)/C catalyst



Entry	Catalyst[a]	Reaction temp. (°C)	Reaction time/h	Conv.[b] (%)	Selectivity[b] (%)		
					1a	**2a**	**3a**
1	Pd/C (5%wt)	130	1.5	33	0	24	76
2	Pd–Cu(3.0)/C	100	1.5	54	96	0	4
3	Pd–Cu(3.0)/C	130	1.5	94	90	0	10
4	Pd–Cu(3.0)/C	130	3.0	>99	68	0	32

Reaction conditions: catalyst, 0.05 g; substrate, 1.1 mmol; *iso*-PrOH, 3 mL. [a]The value in the parenthesis is Pd/Cu molar ratio, determined by ICP-OES. [b]Conversion and yield were determined by GC using an internal standard technique.

Table 5. Results of selective hydrogenation of typical α,β-unsaturated aldehyde using Pd–Cu(3.0)/C catalyst



Entry	Catalyst[a]	Reaction temp. (°C)	Reaction time/h	Conv.[b] (%)	Selectivity[b] (%)	
					1b	**2b**
1	Pd/C (5%wt)	130	1.5	65	0	100
2	Pd–Cu(3.0)/C	100	1.5	87	96	4
3	Pd–Cu(3.0)/C	130	1.5	90	90	10
4	Pd–Cu(3.0)/C	130	3.0	>99	83	17

Reaction conditions: catalyst, 0.05 g; substrate, 1.1 mmol; *iso*-PrOH, 3 mL. [a]The value in the parenthesis is Pd/Cu molar ratio, determined by ICP-OES. [b]Conversion and yield were determined by GC using an internal standard technique.

Table 6. Results of the selective hydrogenation of FFald to FFalc over bimetallic Pd–Cu(3.0)/C catalyst after four consecutive reaction runs.

Entry	Reaction run-	Conversion[a] (%)	Yield[a] (%)		
			FFalc	THFalc	2-MeF
1	1st	>99	94	5	1
2	2nd	82	76	5	1
3	3rd	73	66	6	1
4[b]	4th	>99	95	4	1

Reaction conditions: catalyst (0.05 g); FFald (1.1 mmol); solvent (*iso*-PrOH, 3.5 ml); temperature (130°C); initial H_2 pressure (3.0 MPa); reaction time (1.5 h). [a]Conversion and yields of FFalc THFalc, and 2-MeF were determined by GC using an internal standard technique. [b]The used Pd–Cu(3.0)/C catalyst was reduced with H_2 at 400°C for 1.5 h before reaction.

Dear Prof. I. Istadi
Editor in Chief
Bulletin Chemical Reaction Engineering & Catalysis
Diponegoro University

We deeply appreciate you and the referees for the kind suggestions and comments on our manuscript BCREC-2021-10398. Here we would like to reply referee`s comments as follows indicated in italics. The revised manuscript has also been uploaded

Manuscript ID: BCREC-2021-10398
Title of manuscript:
The promotion effect of Cu on the Pd/C catalyst in the chemoselective hydrogenation of unsaturated carbonyl compounds
Author(s): Kamilia Mustikasari, R. Rodiansono*, Maria Dewi Astuti, Sadang Husein, S. Sutomo

Comment from Reviewer(s)	*Answer/Revision Note*	Location of Revision in Revised Manuscript
Reviewer B The authors shall include their first names as well as their surname.	*We added the first names of the authors as reviewer suggested as indicated by blue color-highlight text.*	Page 1
Although it is indicated that a Pd/Cu bimetallic system was previously worked on, a brief description should be made of why copper and activated carbon are selected for the formation of the catalyst. The authors note "…The effect of the Pd/Cu molar ratio, solvent use and reaction parameters (initial H_2 pressure, reaction temperature) on the activity and selectivity in the hydrogenation of FFald are also studied…"	*We revised the last sentence of the introduction (the fifth paragraph) as indicated by blue color-highlight text.* *The revised sentence as follows:* "……The promotion effect of Cu on Pd/C catalyst, solvent use and reaction parameters (initial H_2 pressure, reaction temperature) on the activity and selectivity in the hydrogenation of unsaturated carbonyl compounds are also studied.	Page 4. Introduction (the last paragraph)
In the manuscript they indicate that they work with catalysts with a Pd/Cu molar ratio of only 3. It is recommended to remove "The effect of the Pd / Cu molar ratio". In the title they indicate that the reaction is for of unsaturated carbonyl compounds, and they carry out the introduction only with reference to FFald. Is the objective of the work the hydrogenation of FFald or unsaturated carbonyl compounds in general?	*We omitted the term of the effect of Pd/Cu molar ratio as indicated by reviewer.* *In our present report, we investigated the selective hydrogenation of typical unsaturated carbonyl compounds, both ketone and aldehyde (see section 3.4 in Results and Discussion). To rationale and support this work, some cited references related to chemoselective hydrogenation of unsaturated carbonyl compounds were also included in Introduction (paragraphs 2 and 4).*	

The authors do not indicate how activated carbon is incorporated into the bimetallic phase, nor is the mass or molar relationship between the bimetallic phase and activated carbon indicated in the manuscript. There is no bibliography in this section that indicates how the support is incorporated. It is important that these points are indicated in order to be able to interpret the results correctly. There is an error in the hydrogenation time since 1.5 min is indicated.	*We added the additional information regarding to the loading amount of Pd (based on the initial amount of precursor) and how the carbon support was added during the preparation of catalyst as indicated by blue color-highlight text in section **2.3 (*****Preparation of Pd-Cu(3.0)/C catalysts).** *We revised the error syntax (from 1.5 min to 1.5 h) in the hydrogenation time for the activation of catalyst.*	Page 5. Preparation of catalysts.
The authors mention "…Catalyst (0.05 g), FFald (1.1 mmol), trans-decahydronaphthalene (decalin) (0.2 mmol), and iso-PrOH (3 mL) as solvent were placed into a glass reaction tube, which fitted inside a stainless -steel reactor… " Which catalyst are you referring to? The authors are recommended to indicate the name of the catalyst in the catalyst preparation part.	*We revised the sentence of catalytic reaction procedure (section 2.4.1) as suggested by reviewer.* *We added a typical name of the synthesized Pd-Cu(3.0)/C catalyst as recommended by reviewer (section 2.3).*	Page 5. Hydrogenation of FFald
The authors begin the discussion with the results presented in Table 1. These results arise from the treatment of data obtained from the corresponding adsorption-desorption isotherm. It is recommended to start the discussion with the Nitrogen adsorption and desorption profiles and then present Table 1.	*We reconstructed the explanation of catalyst characterisation (N_2 adsorption/desorption) as well as the N2 adsorption/desorption (Figure 1) and pores size distribution (Figure 2) as indicated by blue color-highlight text.* Figure 1: N_2-adsorption/desorption profiles of (a) charcoal (C) and (b) the synthesized Pd-Cu/C catalyst before and after reduction with H_2 at 400°C for 1.5 h and recovered sample. Figure 2: Pore distribution of (a) charcoal (C) and the synthesized bimetallic Pd-Cu(3.0)/C catalysts using HK approach.	Table 1
The following points should be explained: -Table 1: Because there is a decrease of 178 m2/g when incorporating the carbon to the bimetallic phase? They could analyze how the support is affected by applying the same catalyst synthesis process.	*It has been generally accepted that the control of pore structure as well as the specific surface area during the catalyst preparation is possibly due to the pore blocking or collapsed the structure by chemical or thermal treatment during the catalyst preparation or even during the recycle test.* *The study on the effect of chemical or thermal treatment during the catalyst*	Table 1

An increase in SBET is observed when the hydrogenation of Pd-Cu(3.0)/unred. occurs, what is this due to? Is activated carbon affected? The results of Pd-Cu(0.3)/C recovered when the three cycles were applied, which reactive molecule does it correspond to?	*preparation or even during the recycle test is under investigating and we will discuss furtherly it in our upcoming publication.*	
How is the Pd-Cu bimetallic phase in the catalyst? The presence of Cu2O is observed, could the presence of PdO or PdO2 occur?. What is the catalytically active phase? The reference that is included (35) does not contain information of the Pd phase.	*We compared the XRD patterns of Pd-Cu/C catalyst with JCPDS card of Pd (JCPDS#05-0681) and Cu (JCPDS# 78-2076). Unfortunately, we did not observe the formation of PdO in our samples.* *We revised the cited reference of 35 as indicated by reviewer.*	Figure 1
Is the Pd-Cu (0.3)/C recovered sample the one obtained after three cycles? The adsorption isotherm points for the Pd-Cu(3.0)/C unred. sample are not observed. The authors indicate "… shows the profiles of N2-adsorption / desorption and plot of volume of adsorbed-N2 versus pore distribution using BJH approach (with cut-off the pore size of 1.21 nm) confirmed that there are no significant change of the pore structure of catalyst support during the introducing Pd metal or thermal activation using N2 or H2 at 400 °C…" When is activation using N2 done? It is not specified in the experimental part. When hydrogenation is carried out, the catalyst increases its specific area slightly but is still less than that of the original activated carbon. Why does this happen? What can be observed in this figure is how the reduction of the catalyst and the catalysis process affect the textural properties.	*We carried out the reaction in batch reactor system and presented data of N2 adsorption of the recovered Pd-Cu(3.0)/C catalyst was obtained after the third reaction.* *We revised the pore size distribution as shown in Figure 2 using Horvarth-Kawazoe (HK) approach for microporous carbon material as reviewer was suggested as indicated by blue color-highlight texts.* *The detail procedures for catalyst characterizations including XRD analysis, N2 adsorption-desorption, and H2 chemisorption are described in **section 2.2**.* *The alteration of surface morphology or pore structure did not examine in our presence report. We will investigate it in our subsequent work.*	Figure 2
The authors write "…Furthermore, investigation of the effect of various second metals such as tin (Sn), cobalt (Co), nickel (Ni), and iron (Fe) on the conversion of FFald and yield of FFalc was also performed and the results are also summarized in Table 2... " Under what conditions were these catalysts	*We added the explanation related to those Pd-M/C catalysts as indicated by blue color-highlight texts.*	Page 7. Catalytic reactions. Screening of second metal.

made? If it was with the same technique, specify it in the manuscript.		
The authors do not explain how they conducted the experiment. What was the heating rate and the residence time of the catalyst for each temperatura?. Was the same catalyst used for the temperatures tested or was a fresh catalyst installed?	*We carried out each of the reaction at various temperature using fresh catalyst. We added the explanation of how the reaction was conducted as indicated by blue color-highlight text.* *The effect of temperature on the catalytic hydrogenation of FFald to FFalc was evaluated over Pd–Cu(3.0)/C catalyst at range temperature of 90-190°C in batch system for 1.5 h.*	Page 8. Effect of reaction temperature

Reviewer C

the authors describe the hydrothermal preparation of Pd-Cu carbon. please write down the amount of Pd and Cu in the catalyst that has been produced. This is to compare the Pd content of the 5wt% Pd / C commercial catalyst.	*We added the additional information related to the Pd and Cu amounts in Pd-Cu(3.0)/C catalysts in the Section 2.3 as suggested by the reviewer as indicated by blue color-highlight text.*	In section 2.3
it is stated that carbon is a microporous material. however, in the experimental section 2.2, the author has used the BJH model to determine the pore distribution. Likewise in the discussion section, also found the discussion about mesoporous. As is well known, the BJH model is only suitable for mesoporous materials, while for microporous materials the HK model is used to explain the pore size distribution. This finding has also been shown in the results of the BJH profile which shows a peak at about 1.2 nm, where the peak is still visible upward to the left, which shows that the material is indeed a microporous material, as has been mentioned in section 2.1. Therefore, the pore size determination is not appropriate (Table 1). micropore <2 nm.	*We revised the pore size distribution calculation as shown in Figure 2 using Horvarth-Kawazoe (HK) approach for microporous carbon material as reviewer was suggested. The additional explanations are indicated by blue color-highlight texts in Section 2.2 and Section 3.1.*	In section 3.1
In addition, in the discussion of Figure 2, it is stated that "there are no significant change of the pore structure of catalyst support during the	*We added the pore structure of the Charcoal (C) support in Table 1, Figure 1, and Figure 2 as suggested by reviewer.*	Discussion of Figure 2

introducing Pd". The author should add pore structure of the support before adding Pd.	*The additional explanations are indicated by blue color-highlight texts.*	

4. Bukti konfirmasi artikel accepted (28 April 2021)

[BCREC] Final Decision of Your Manuscript [Ms ID: BCREC-2021-10398]

1 message

Prof. Dr. Istadi Istadi <bcrec@live.undip.ac.id> Thu, Apr 29, 2021 at 7:40 AM
Reply-To: "Prof. Dr. Istadi Istadi" <bcrec@live.undip.ac.id>
To: Mrs Kamilia Mustikasari <kmustikasari@ulm.ac.id>
Cc: Rodiansono Rodiansono <rodiansono@ulm.ac.id>, Maria Dewi Astuti <mdastuti@ulm.ac.id>, Sadang Husain <sadanghusain@ulm.ac.id>, Sutomo Sutomo <sutomo@ulm.ac.id>

Journal Name: Bulletin of Chemical Reaction Engineering & Catalysis
Article Title: The promotion effect of Cu on the Pd/C catalyst in the chemoselective hydrogenation of unsaturated carbonyl compounds
Ms ID: BCREC-2021-10398

Dear Mrs Kamilia Mustikasari,

I am pleased to confirm that your manuscript submitted to Bulletin of Chemical Reaction Engineering & Catalysis entitled: "The promotion effect of Cu on the Pd/C catalyst in the chemoselective hydrogenation of unsaturated carbonyl compounds" has been accepted for publication. Your accepted manuscript will be pre-published soon in the Just Accepted Manuscript and Article In Press (URL: https://ejournal2.undip.ac.id/index.php/bcrec/issue/view/81).

We will send you the galley PDF proof correction soon, as we will ask you for some correction of typesetting.

If you did not send the Copyright Transfer Agreement, please fill and signed originally the Copyright Transfer Agreement (downloadable at: http://bit.ly/bcrec-cta-2020) and then scan and send to the editorial office email (bcrec@live.undip.ac.id).

IMPORTANT NOTE: A GRAPHICAL ABSTRACT of each article is mandatory for this journal. Please read detail guidelines here: https://ejournal2.undip.ac.id/index.php/bcrec/pages/view/graphicalabstract/
This graphic should capture the reader’s attention and, in conjunction with the manuscript title, should give the reader a quick visual impression of the essence of the manuscript without providing specific results.
Choosing/Creating a Graphical Abstract: The graphic should be simple, but informative; The use of color is encouraged; The graphic should uphold the standards of a scholarly, professional publication; The graphic must be entirely original, unpublished artwork created by one of the coauthors; The graphic should not include a photograph, drawing, or caricature of any person, living or deceased; Do not include postage stamps or currency from any country, or trademarked items (company logos, images, and products); Avoid choosing a graphic that already appears within the text of the manuscript. Image size: please provide an image with a size of 500 × 800 pixels (height × width). Preferred file types: TIFF, JPG, PNG, PDF, or MS Office files.

The Graphical Abstracts should be submitted as a separate file during the revised manuscript submission system or otherwise, it can be submitted after acceptance of manuscript by email to: bcrec@live.undip.ac.id

Thank you for submitting your work to this journal. We very welcome your next manuscript submission to this electronic journal or please to encourage your colleague to submit their manuscript to this journal.

With kind regards,

Yours sincerely,

Prof. Dr. Istadi Istadi
Department of Chemical Engineering, Diponegoro University
bcrec@live.undip.ac.id
Twitter: @bcrec_j (https://twitter.com/bcrec_j?s=08)
(Editor in Chief)
Bulletin of Chemical Reaction Engineering & Catalysis
Department of Chemical Engineering, Diponegoro University, Indonesia
Website: http://bcrec.id
Email: bcrec@live.undip.ac.id

5. Bukti Permintaan Proofreading (4 Mei 2021)

Kamilia Mustikasari <kmustikasari@ulm.ac.id>

[BCREC] Proofreading Request (Author) [BCREC-2021-10398]

1 message

Prof. Dr. Istadi Istadi <bcrec@live.undip.ac.id> Tue, May 4, 2021 at 1:52 PM
Reply-To: "Prof. Dr. Istadi Istadi" <bcrec@live.undip.ac.id>
To: Mrs Kamilia Mustikasari <kmustikasari@ulm.ac.id>
Cc: rodiansono@ulm.ac.id, rodian114@gmail.com

Journal Name: Bulletin of Chemical Reaction Engineering & Catalysis
Article Title: The Promotion Effect of Cu on the Pd/C Catalyst in the Chemoselective Hydrogenation of Unsaturated Carbonyl Compounds
Ms ID: BCREC-2021-10398

Dear Mrs Kamilia Mustikasari,

Your submission entitled: "The Promotion Effect of Cu on the Pd/C Catalyst in the Chemoselective Hydrogenation of Unsaturated Carbonyl Compounds" to Bulletin of Chemical Reaction Engineering & Catalysis now needs to be proofread by the following steps.

PLEASE USED THIS UNCORRECTED PROOF DOCUMENT IN PDF FILE TO DO THE PROOFREADING DIRECTLY (as attached or downloaded). Do not convert this PDF file to MS Word or do not use your final revised manuscript MS Word file to do proof reading. Do not major/substantial change of your article . Please check the galley PDF thoroughly and give comments about the proof document directly on the PDF file (using Adobe Reader - Comment Tool) or list in an MS Word correction table.

"Please be noted that you have 1 (one) weeks from now (send date of this email) to check your proof correction.", unless Editorial Office will use this latest version as your final article published version.

1. Click on the Submission URL below.

2. Log into the journal, click Archives, and click taskbar of EDITING (view PROOFING INSTRUCTIONS)

3. Click on VIEW PROOF (IN PDF) in LAYOUT section to download the Uncorrected Proof Document and proof the galley in the one or more formats used

4. Please list corrections (typographical and format) in "Proofreading Corrections" in a table form file (MS Word or others, not on your MS Word manuscript document) according to the PDF Uncorrected Proof Document. Otherwise, you can give comments directly on the PDF proof document.

5. Save and email the correction comments to Editorial Office of BCREC Journal (Email: bcrec@live.undip.ac.id) as an attachment file in MS Word, or PDF file.

6. Otherwise preferably you can also submit it by online at Proof Reading section by copying the comments to "Comment Button" on that section.

7. If you did not send signed Copyright Transfer Agreement, please fill Copyright Transfer Agreement (download at: https://ejournal2.undip.ac.id/index.php/bcrec/pages/view/copyright_bcrec), then send to the editorial office email (bcrec@live.undip.ac.id) and please state the manuscript number in email subject.

8. GRAPHICAL ABSTRACT: A Graphical abstract is "mandatory" for this journal since year 2013 publication. It should summarize the contents of the article in a concise, pictorial form designed to capture the attention of a wide readership online. Authors must provide images that clearly represent the work described in the article. Graphical abstracts should be submitted as a separate file in the online submission system or otherwise can be submitted by email to: bcrec@live.undip.ac.id, after the manuscript has been accepted. Please state the manuscript number in your email subject. Please read guidelines here: https://ejournal2.undip.ac.id/index.php/bcrec/pages/view/graphicalabstract/

Submission URL: https://ejournal2.undip.ac.id/index.php/bcrec/author/submissionEditing/10398
Username: kamilia

Thank you for your contribution to Bulletin of Chemical Reaction Engineering & Catalysis .

Sincerely Yours,

Prof. Dr. Istadi Istadi
Department of Chemical Engineering, Diponegoro University
bcrec@live.undip.ac.id
Twitter: @bcrec_j (https://twitter.com/bcrec_j?s=08)
(Editor in Chief)
Bulletin of Chemical Reaction Engineering & Catalysis
Department of Chemical Engineering, Diponegoro University, Indonesia
Website: http://bcrec.id
Email: bcrec@live.undip.ac.id

bcrec_10398_v16_n2_267-279.pdf
1214K

6. Resubmit Artikel yang sudah di Proofreading dan Graphical Abstract (7 Mei 2021)

Proofreading [BCREC-2021-10398], CTA and Graphical Abstract

1 message

Kamilia Mustikasari <kmustikasari@ulm.ac.id>
To: bcrec@live.undip.ac.id

Fri, May 7, 2021 at 7:19 PM

Journal Name: Bulletin of Chemical Reaction Engineering & Catalysis
Article Title: The Promotion Effect of Cu on the Pd/C Catalyst in the Chemoselective Hydrogenation of Unsaturated Carbonyl Compounds
Ms ID: BCREC-2021-10398

Dear Prof. Dr. Istadi Istadi

The submission entitled: "The Promotion Effect of Cu on the Pd/C Catalyst in the Chemoselective Hydrogenation of Unsaturated Carbonyl Compounds" to Bulletin of Chemical Reaction Engineering & Catalysis was corrected and is attached with this email. T

Thank You.

Sincerely Yours,

Kamilia Mustikasari, M.Si

---

3 attachments

GA-[BCREC-2021-10398].tiff
30K

bcrec_10398_v16_n2_267-279.pdf
1196K

CTA-BCREC-2021-10398.pdf
103K

Available online at BCREC website: https://bcrec.id

Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2) 2021, xxx-xxx

Research Article

The Promotion Effect of Cu on the Pd/C Catalyst in the Chemoselective Hydrogenation of Unsaturated Carbonyl Compounds

Kamilia Mustikasari[1,2], R. Rodiansono[1,2,*)], Maria Dewi Astuti[1,2], Sadang Husain[2,3], S. Sutomo[4]

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Lambung Mangkurat University, Jl. A. Yani Km 36 Banjarbaru South Kalimantan, 70714, Indonesia.
[2]Catalysis for Sustainable Energy and Environment (CATSuRe), Lambung Mangkurat University, Indonesia.
[3]Department of Physics, Faculty of Mathematics and Natural Sciences, Lambung Mangkurat University, Jl. A. Yani Km 36 Banjarbaru, 70714, Indonesia.
[4]Department of Pharmacy, Faculty of Mathematics and Natural Sciences, Lambung Mangkurat University, Jl. A. Yani Km 36 Banjarbaru, 70714, Indonesia.

Received: 17th February 2021; Revised: 28th April 2021; Accepted: 29th April 2021
Available online: 2nd May 2021; Published regularly: June 2021

Abstract

Highly efficient and selective hydrogenation of α,β-unsaturated carbonyl compounds to unsaturated alcohol using bimetallic palladium-copper supported on carbon (denoted as Pd-Cu(3.0)/C; 3.0 is Pd/Cu molar ratio) catalyst is demonstrated. Pd-Cu(3.0)/C catalyst was prepared via a simple hydrothermal route under air atmosphere at 150 °C for 24 h followed by reduction with hydrogen at 400 °C for 1.5 h. The chemoselective hydrogenation of typical α,β-unsaturated carbonyl ketone (2-cyclohexene-1-one) and aldehyde (*trans*-2-hexenaldehyde), and chemoselective hydrogenation of FFald and (E)-non-3-en-2-one mixture demonstrated high productivity, leading to high selectivity of unsaturated alcohols. The presence of bimetallic Pd-Cu alloy phase with relatively high H_2 uptakes was observed, enabling to preferentially hydrogenate C=O rather than to C=C bonds under mild reaction conditions. Pd-Cu(3.0)/C catalyst was found to stable and reusable for at least four reaction runs and the activity and selectivity of the catalyst can be restored to the original after rejuvenation with H_2 at 400 °C for 1.5 h.

Keywords: bimetallic palladium-copper; chemoselective hydrogenation; unsaturated carbonyl compounds; unsaturated alcohol

How to Cite: K. Mustikasari, R. Rodiansono, M.D. Astuti, S. Husain, S. Sutomo (2021). The Promotion Effect of Cu on the Pd/C Catalyst in the Chemoselective Hydrogenation of Unsaturated Carbonyl Compounds. *Bulletin of Chemical Reaction Engineering & Catalysis*, 16(2), xxx-xxx (doi:10.9767/bcrec.16.2.10398.xxx-xxx)

Permalink/DOI: https://doi.org/10.9767/bcrec.16.2.10398.xxx-xxx

1. Introduction

The chemoselective hydrogenation of the C=O bond in α,β–unsaturated ketones/aldehydes has been extensively studied because the unsaturated alcohols that it forms are important in the production of a variety of fine chemicals, such as pharmaceuticals, perfumes, and flavorings [1,2]. Typically, the chemoselective reduction of the carbonyl group is achieved using reducing agents [3], Meerwin-Ponndorf-Verly [4], or using organometallic cat-

---

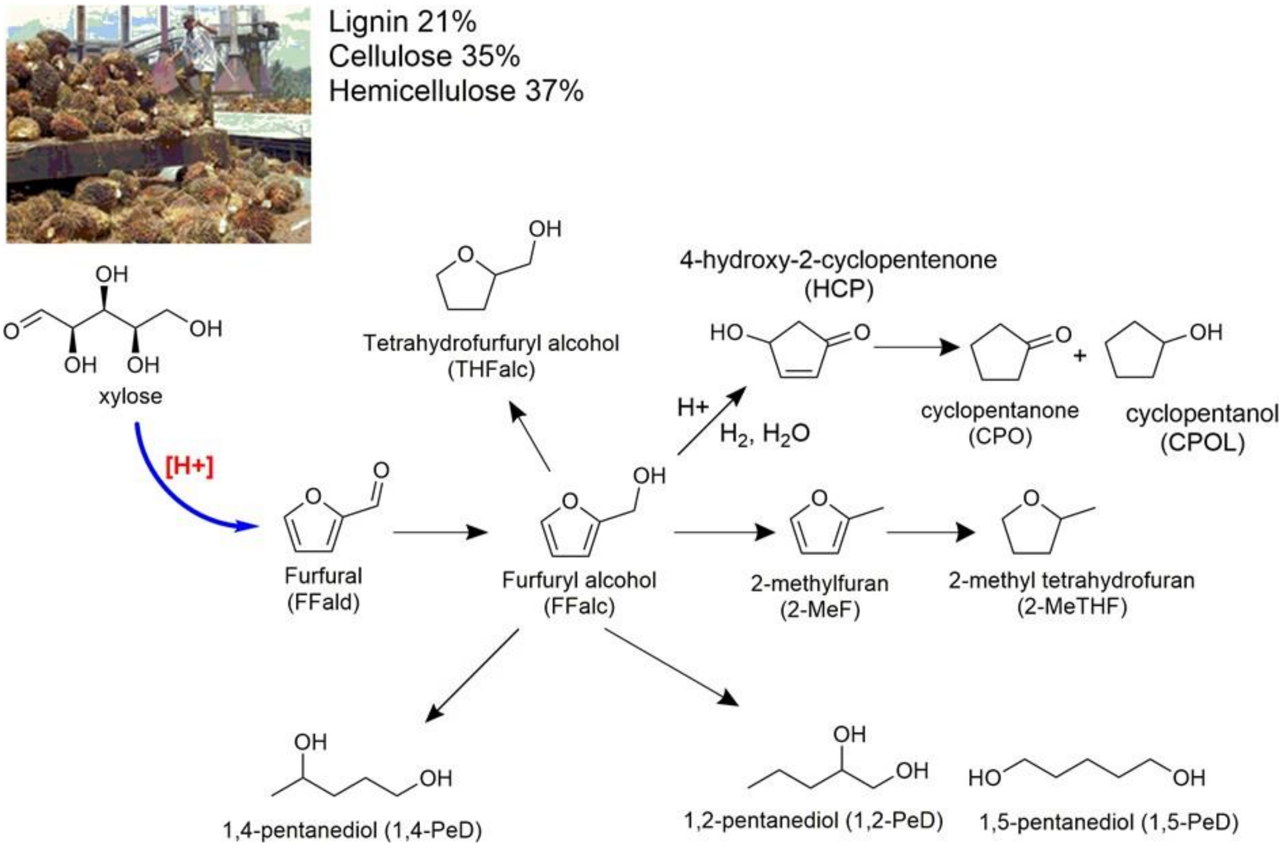
* Corresponding Author.
Email: rodiansono@ulm.ac.id (R. Rodiansono);
Telp. /Fax.: +62 511 477 3112

alysts [5]. These processes often use costly chemicals and solvents which require separations. In this context, heterogeneous catalysis is viewed as an alternative, more sustainable route for the production of these high-value chemicals at an industrial scale [6–8]. Simple preparation and recovery of heterogeneous catalysts are desirable features for the chemical industry.

Recent works indicate that bimetallic catalysts have the potential to enhance the selectivity in the hydrogenation of many different classes of chemicals [9], such as: alkynes, alkenes [10], and carbonyl compounds [11,12] as well as biomass-derived molecules [13–15]. It is well known that the group 9 and 10 metals, such as Rh, Ir, Ni, Pd, and Pt, generally hydrogenate the C=C bond more easily than the C=O bond of α,β–unsaturated aldehydes [16]. To improve the chemoselective hydrogenation of the C=O group, the modification of the above mentioned metals is necessary, *i.e.*, the addition of more electropositive metals [17] or the use of oxide supports that strongly interact with the active metals [18]. In these contexts, we have described previously that the chemoselective behaviors of Ni-based catalysts can be controlled by doping the second metals, such as tin (Sn) or indium (In) to form bimetallic Ni–Sn or Ni-In alloy. Both bulk and supported Ni–Sn and Ni–In alloy catalyst have obviously demonstrated high chemoselectivity in the hydrogenation of α,β-unsaturated ketones/aldehydes toward unsaturated alcohols [19–23].

It is well-known that furfural (FFald), a versatile and biogenic biomass-derived compound, which can be obtained from acidic dehydration of arabinose or xylose of hemicellulosic biomasses [24]. Further catalytic conversion of FFald via chemoselective hydrogenation, hydrogenolysis, hydrogenation-arrangement using both monometallic and bimetallic transition metal catalysts produced a variety of high value chemicals such as furfuryl alcohol (FFalc), tetrahydrofurfuryl alcohol (THFalc), methyl-furan (MeF), methyl tetrahydrofuran (MeTHF), pentanediol (PeD), and cyclopentanone (CPO) or cyclopentanol (CPOL) as shown in Scheme 1 [25–27].

Platinum-group metal (PGM) constitute the most studied catalyst components for hydrogenation of FFald and demonstrated high activity and selectivity towards FFalc, which were included Sn modified Pt-based [28] and



Scheme 1. Conceivable reaction networks for the catalytic transformation of FFald that involve hydrogenation, hydrogenolysis, decarbonylation, ring opening hydrogenation, and hydrogenation-rearrangement pathways.

Ni-based catalysts [20,21] due to their intrinsic high catalytic ability under mild conditions, high selectivity towards a specific product, high stability under various reaction conditions, and tolerance to poisons [29,30]. Although platinum is the most widely used element in catalysis, palladium is receiving increasing attention owing to its similar catalytic properties to platinum and wider availability. However, the catalytic behavior of Pd-based catalyst on the hydrogenation of unsaturated aldehydes/ketones or oxygenated biomass-derived compounds that consisted of C=O and C=C bonds preferentially promoted decarbonylation or decarboxylation reactions. For example, when Pd/C is used as catalyst for hydrogenation of FFald in the presence of H_2 gas, a wide range of competing reactions, such as unselective hydrogenation of furan-ring or aldehyde groups and incomplete hydrodeoxygenation have been reported [31,32]. Therefore, introduction of a secondary metal species or deposition of Pd nanoparticles on the support that strongly interact with the actives metal are frequently adopted as an effective approach to acquire target products in satisfactory yields [30].

In the present report, we have extended our study on the preparation of bimetallic palladium copper catalyst supported on active carbon (denoted as Pd–Cu(3.0)/C; 3.0 is molar ratio of Pd/Cu). Bimetallic Pd–Cu(3.0)/C catalyst was prepared via the hydrothermal treatment of a solution that contained Pd and Cu species at 150 °C for 24 h followed by H_2 treatment at 400 °C for 1.5 h. The promotion effect of Cu on Pd/C catalyst, solvent use and reaction parameters (initial H_2 pressure, reaction temperature) on the activity and selectivity in the hydrogenation of unsaturated carbonyl compounds are also studied.

2. Materials and Methods

2.1 Materials

Palladium(II) chloride ($PdCl_2$; Tokyo Chemical Industries Co. (TCI)), copper(II) nitrate ($Cu(NO_3)_2{\cdot}3H_2O$; Merck) were purchased and used as received. Microporous carbon (C, S_{BET} = 815 $m^2.g^{-1}$) was purchased from WAKO Pure Chemical Industries, Ltd. Ltd. unless otherwise stated. Furfural, furfuryl alcohol, tetrahydrofurfuryl alcohol, *iso*-propanol, ethanol, and authentic organic reactants and products were purchased from Tokyo Chemical Industries Co. (TCI). All organic chemical compounds were purified using standard procedures prior to use.

2.2 Catalyst Characterization

All catalysts were characterized by powder X-ray diffraction (XRD) Miniflex 600 Rigaku with Cu as monochromatic source K a radiation (λ = 0.15444 nm). XRD operated at 40 kV and 15 mA with solar slit 1.25°, scan step 5° min^{-1} and using a Ni Kβ filter. The crystallite size of palladium was estimated by using the Scherrer`s equation.

The Brunauer-Emmet-Teller (BET) surface area (S_{BET}) and pore volume (Vp) were measured using N_2 physisorption at −196 °C on a Belsorp Max (BEL Japan). The samples were degassed at 200 °C 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 [33], while the micropore distribution was estimated by using Horvarth-Kawazoe (HK) approach [34].

The active surface areas were determined by H_2 chemisorption. After the catalyst was heated at 120 °C under vacuum for 30 min, it was heated at 400 °C under H_2 for 30 min and under vacuum for 30 min, followed by evacuation to room temperature for 30 min. The adsorption of H_2 was conducted at 0 °C. The active surface area was calculated from the volume of H_2 desorbed by assuming an H/Pd stoichiometry of one, respectively and the number of Pd atom for the (111) plane is 1.5×10^{15} per cm^2 Pd based on an equal distribution of the three lowest index planes of Pd [35].

2.3 Preparation of Pd-Cu(3.0)/C Catalysts

A typical procedure of the synthesis of bimetallic palladium-copper supported on carbon (denoted as Pd-Cu(3.0)/C (Pd = 5wt%; 3.0 molar ratio of Pd/Cu)) catalyst is described as follows [20]: $PdCl_2$ (0.472 mmol) was dissolved in deionized water (denoted as solution A), and $Cu(NO_3)_2{\cdot}3H_2O$ (0.156 mmol) was dissolved in ethanol/2-methoxy ethanol (2:1) (denoted as solution B) at room temperature. Solutions A and B were mixed at room temperature and a 1.0 g carbon (C, S_{BET} = 815 $m^2.g^{-1}$) was subsequently added; the temperature was 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 reduced with hydrogen at 400 °C for 1.5 h.

2.4 Catalytic Reactions

2.4.1 Hydrogenation of FFald

Pd–Cu(3.0)/C catalyst (0.05 g), FFald (1.1 mmol), *trans*-decahydronaphthalene (decalin) (0.2 mmol), and *iso*-PrOH (3 mL) as solvent were placed into a glass reaction tube, which fitted inside a stainless-steel reactor. After H_2 was introduced into the reactor with an initial H_2 pressure of 3.0 MPa at room temperature, the temperature of the reactor was increased to 130 °C. After 1.5 h (90 min), the conversion of FFald and the yield of FFalc were determined by GC analysis using an internal standard technique. The Pd–Cu(3.0)/C catalyst was easily separated using either simple centrifugation or filtration. The solvent was removed in vacuo, and the residue was purified via silica-gel column chromatography.

2.4.2 Product Analysis

GC analysis of the reactant (FFald) and products (FFalc and THFalc) was performed on a Shimadzu GC-8A equipped with a flame ionization detector and silicone OV-101 packing. 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. ^{1}H and ^{13}C NMR spectra were obtained on a JNM-AL400 spectrometer at 400 MHz; the samples for NMR analysis were dissolved in chloroform-d_1 with TMS as the internal standard. The products were confirmed by a comparison of their GC retention time, mass, ^{1}H and ^{13}C NMR spectra with those of authentic samples. The conversion, yield and selectivity of the products were calculated according to the following equations:

$$Conversion = \frac{introduced\ mol\ reactant\ (Fo) - remained\ mol\ reactant\ (Ft)}{introduced\ mol\ reactant\ (Fo)} \times 100\% \tag{1}$$

$$Yield = \frac{mol\ product}{consumed\ mol\ reactant\ (DF)} \times 100\% \tag{2}$$

$$Selectivity = \frac{mol\ product}{total\ mol\ product} \times 100\% \tag{3}$$

where F_0 is the introduced mol reactant (furfural, FFald), F_t is the remaining mol reactant, and ΔF 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 Characterization

The N_2-adsorption/desorption of charcoal (C) support and the synthesized bimetallic Pd-Cu/C was performed and the profiles are shown in Figure 1. The hysteresis loop of adsorptio/desorption of the synthesized Pd-Cu/C samples show a very similar to that of former charcoal support, suggesting that there is no significant change of the pore structure of catalyst support during the introducing Pd metal or thermal activation using N_2 or H_2 at 400 °C. It

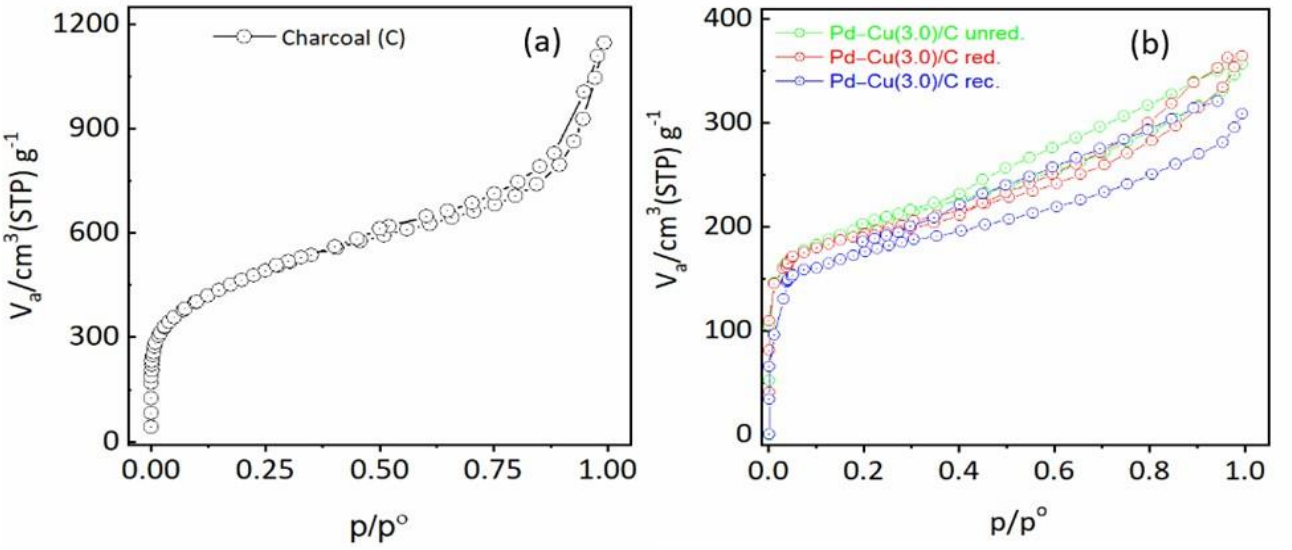


Figure 1. N_2-adsorption/desorption profiles of (a) charcoal (C) and (b) the synthesized Pd-Cu/C catalyst before and after reduction with H_2 at 400 °C for 1.5 h and recovered sample.

has been reported that carbon support has high thermal and chemical stability at the range of 300-500 °C under H_2 or N_2 atmosphere [36,37].

To determine the pore size distribution of C support and the synthesized catalysts, the plot of volume of adsorbed-N_2 versus pore distribution using Horvarth-Kawazoe (HK) approach were performed as shown in Figure 2. As expected, the charcoal (C) support shows the microstructure of carbon with narrow pore size distribution of 0.59-0.66 nm (Figure 2a). After introduction of Pd-Cu, the shift of pore size distribution at ≥0.66 nm for after and before reduction and recovered samples are clearly observed. However, there is no clear evidence for the shift of pore size distribution towards small pore sizes or big pore sizes after introducing the Pd-Cu species or thermal activation using N_2 or H_2 at 400 °C.

The physico-chemical properties (*e.g.* specific surface area BET (S_{BET}), pore volume, pore diameter, and H_2 uptakes) of the synthesized bimetallic Pd-Cu(3.0)/C catalysts are summarized in Table 1.

The S_{BET} of as prepared, H_2-reduced, and recovered Pd-Cu(3.0)/C was 637, 712, and 601 $m^2.g^{-1}$, respectively, which are lower than that of the S_{BET} of the carbon support (C, S_{BET} = 815 $m^2.g^{-1}$). The incorporation of metal species into pore structure of carbon will significantly reduce the specific surface area (S_{BET}) due the pore blocking or collapsed the structure by chemical or thermal treatment during the catalyst preparation [38]. The decrease in S_{BET} is consistent with the shift of pore size distribution as has been mentioned above.

Figure 3 shows the XRD pattern of commercial Pd/C(5%wt), as-prepared and pre-reduced bimetallic Pd-Cu(3.0)/C catalysts. In the case of as-prepared Pd-Cu(3.0)/C catalyst, the typical diffraction peaks at 2θ = 39.96°, 46.16°, 67.6° were clearly observed, which can be attributed to the metallic species of Pd(111), Pd(200), and Pd(020) (JCPDS#05-0681), respectively [39]. The diffraction peak of Pd(111) at 2θ = 40.8° become broadened, which can be attributed as the formation of bimetallic Pd-Cu alloy after reduction with H_2 at 400 °C for 90 min [40]. By

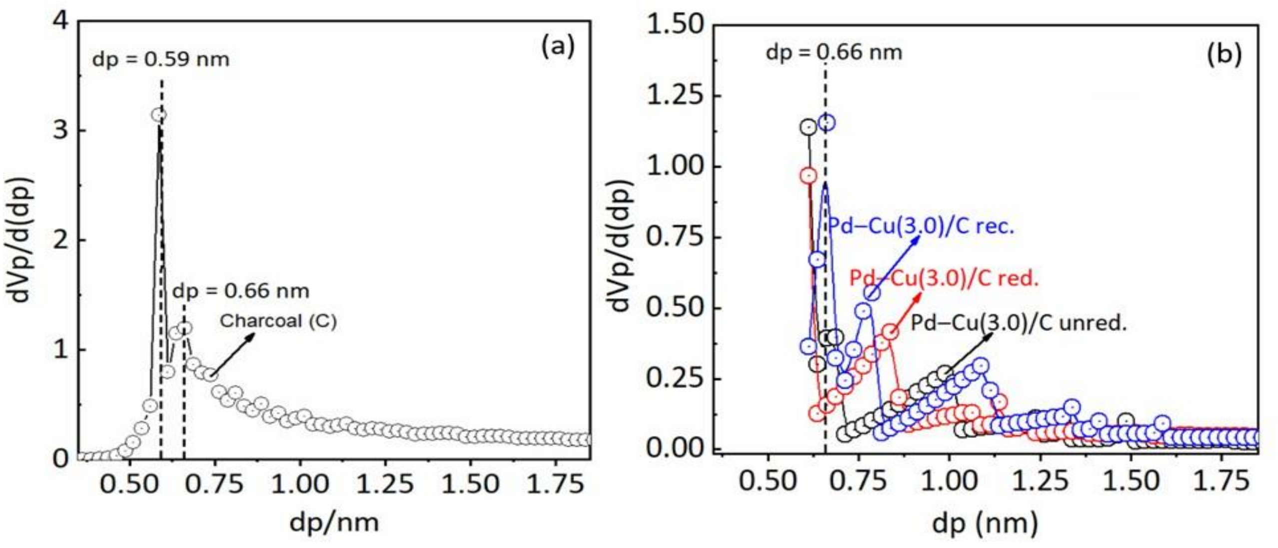


Figure 2. Pore distribution of (a) charcoal (C) and the synthesized bimetallic Pd–Cu(3.0)/C catalysts using HK approach.

Table 1. Physico-chemical properties of bimetallic Pd-Cu(3.0)/C catalyst.

Entry	Catalyst[a]	S_{BET}[b] ($m^2.g^{-1}$)	Pore Vol.[b] ($m^3.g^{-1}$)	Pore Diameter[b] (nm)		H_2 uptakes[d] ($mmol.g^{-1}$)
				BJH[b]	HK[c]	
1	Charcoal (C)	815	1.762	1.22	0.59	nd
2[e]	Pd-Cu(3.0)/C unred.	637	0.494	3.10	0.61	38.4
3	Pd-Cu(3.0)/C red.	712	0.548	3.08	0.65	39.6
4[f]	Pd-Cu(3.0)/C recovered	601	0.428	2.85	0.71	27.8

[a] The value in the parenthesis is Pd/Cu molar ratio. [b] S_{BET} was determined by N_2 adsorption at -196 °C (77 K), pore volume and pore diameter were calculated according to BJH approach. [c] Pore diameter was calculated using HK method. [d] Based upon total the H_2 uptake at 0 °C (after corrections for physical and chemical adsorption). [e] The as prepared Pd-Cu(3.0)/C without pre reduced with H_2. [f] The recovered Pd-Cu(3.0)/C after the third reaction run.

using the Scherrer`s equation, the average crystallite sizes of Pd(111) in as prepared Pd-Cu(3.0)/C were 4.2 nm, whereas in Pd-Cu(3.0)/C was unable to calculate due to the overlapping diffraction peaks of Pd(111) and Pd-Cu alloy phase (Figure 1c). A small peak at 2θ = 29.6° which can be assigned as the $Cu_2O(110)$ species (JCPDS# 78-2076) was also observed both in the as prepared and reduced Pd-Cu(3.0)/C samples (Figure 1b-c). Additionally, the broadened peak at 2θ = 21.3° can be attributed to the diffraction peaks of C(111) of carbon support [41].

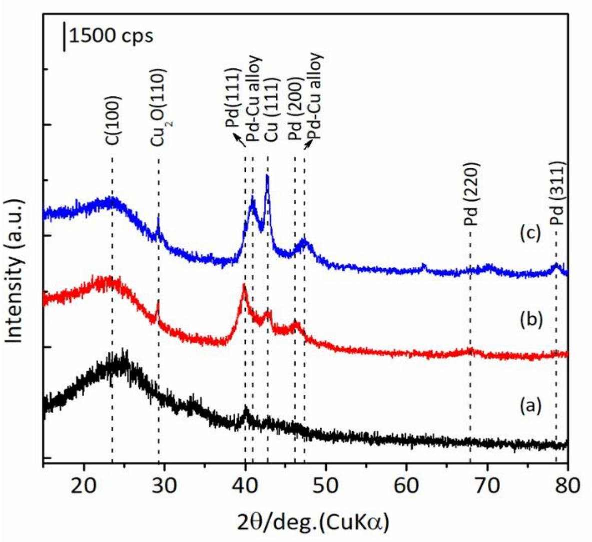


Figure 3. XRD patterns of (a) commercial Pd/C (5%wt Pd), (b) as prepared Pd-Cu(3.0)/C and (c) after reduction with H_2 at 400 °C for 1.5 h.

3.2 Catalytic Reactions

3.2.1 Screening of second metal

In the first set experiments, the catalytic hydrogenation of biomass-derived FFald using various bimetallic Pd-based catalysts were performed and the results are summarized in Table 2. By using commercial Pd/C (5%wt Pd) catalyst, the main product was THFalc (80%) s the result of total hydrogenation of both C=C and C=O bonds in FFald with small amount yields of FFalc (2%) and 2-MeF (8%) at 100% conversion of FFald (entry 1). Using Pd-Cu(3.0)/C catalyst without pre-reduction with H_2, the conversion of FFald was only 56% and yielded 28% FFalc, 15% THFalc, and 13% others (others consist of furfural condensation according to GC and GC-MS data) (entry 2) [42]. After a small amount of Cu (0.156 mmol; Pd/Cu molar ratio ≅ 3.0) was introduced and Pd-Cu(3.0)/C catalyst was pre-reduced with H_2 at 400 °C, the product selectivity remarkably shifted to FFalc (68% in yield) at 73% conversion of FFald (entry 3). An increase in the reaction temperature from 100 °C to 130 °C gave a remarkable increase in FFalc yield from 68% to 94%, respectively (entries 3 and 4). After reaction time was extended to 3 h, the yield of FFalc slightly decreased to 92% while THFalc and 2-MeF yield remained unchanged at >99% conversion of FFald (entry 5). This result suggests that further hydrogenation of C=C furan ring was significantly inhibited over bimetallic Pd-Cu(3.0)/C catalyst. Sitthisa *et al* have noticed that the presence of Cu in Pd-Cu/SiO_2 catalyst to form Pd-Cu alloy phase greatly enhanced the affinity of Pd towards η^2(C–O)-

Table 2. Results of selective hydrogenation of FFald using various bimetallic Pd-based catalysts.

Entry	Catalyst[a]	Composition (mmol.g⁻¹)		Temp. (°C)	Conv.[b] (%)	Yield[b] (%)			
		Pd	M			FFalc	THFalc	2-MeF	Others[c]
1	Pd/C[d]	0.50	-	100	100	2	90	8	0
2	Pd-Cu(3.0)/C *unred.*	0.472	0.156	100	56	28	15	0	13
3	Pd-Cu(3.0)/C	0.472	0.156	100	73	68	3	2	0
4	Pd-Cu(3.0)/C	0.472	0.156	130	>99	94	5	1	0
5[e]	Pd-Cu(3.0)/C	0.472	0.156	130	>99	92	6	3	0
6	Pd-Sn(3.0)/C	0.461	0.152	130	53	16	5	2	20
7	Pd-Co(3.0)/C	0.464	0.151	130	43	12	15	6	10
8	Pd-Ni(3.0)/C	0.481	0.161	130	13	6	6	1	0
9	Pd-Fe(3.0)/C	0.560	0.187	130	78	43	25	5	15

[a] The value in the parenthesis is Pd/M molar ratio (M = Cu, Sn, Co, Ni, and Fe); the bulk composition was determined by ICP-OES. Reaction conditions: catalyst (5 mg); FFald (2 mmol); solvent (2-propanol, 5 mL); temperature (130 °C); initial H_2 pressure (3.0 MPa); reaction time (1.5 h). [b] Conversion and yields of FFalc THFalc, and 2-MeF were determined by GC using an internal standard technique. [c] Others consist of condensation product of FFald or FFalc according to GC/GC-MS data. [c] Commercially available Pd/C (5%wt Pd). [e] The reaction time was 3 h.

furfural interaction, facilitated the formation of hydroxyalkyl species then easily hydrogenated to FFalc. On the other hand, the further hydrogenation of C=C or decarbonylation rate is greatly reduced on bimetallic Pd-Cu system [32]. Furthermore, investigation of the effect of various second metals, such as: tin (Sn), cobalt (Co), nickel (Ni), and iron (Fe), on the conversion of FFald and yield of FFalc was also performed and the results are also summarized in Table 2. Those Pd-M/C (M = Sn, Co, Ni, and Fe) catalysts were synthesized using a similar procedure to that of Pd-Cu(3.0)/C catalyst. However, those bimetallic Pd-M/C (M = Sn, Co, Ni, and Fe) catalysts gave unsatisfied results both conversion of FFald and yield of FFalc under the same reaction conditions (entries 6-9). Therefore, the catalytic reaction of FFald in the presence of bimetallic Pd-Cu(3.0)/C catalyst will be furtherly investigated, including the effect of solvent used, reaction temperature, initial H_2 pressure, time profiles, and reusability test.

3.2.2 Effect of Solvent

The solvent screening for FFald hydrogenation using Pd-Cu(3.0)/C catalyst on the conversion and yield was performed and the results are summarized in Table 3. Alcohols, such as: 2-propanol (*iso*-PrOH), 1-propanol, ethanol, and methanol, and 1,4-dioxane (typical cyclic ether) are superior to other solvents, giving quantitatively high yields of FFalc (entries 1-5). On the other hand, FFald hydrogenation did not proceed effectively in toluene, giving only a 43% FFalc yield at the same conditions (entry 6). These results are very good agreement with the catalytic reaction results over bimetallic Ni-Sn alloy catalysts as reported previously [19,21]. The formation of 1,2-, 1,5-, and 1,4-pentanediol as the hydrogenolyzed products or condensation product was firstly observed in H_2O solvent, therefore we furtherly evaluated the catalytic reaction both in H_2O solvent only and the alcohols/1,4-dioxane-H_2O mixture solvent and the results are also summarized in Table 3. In ethanol : H_2O (1.5:2.0 v/v), 2-propanol:H_2O (1.5:2.0 v/v), and 1,4-dioxane : H_2O (1.5 : 2.0 v/v) mixture solvents, the reaction not only hydrogenation of C=O and C=C bonds of reactant but also hydrogenolysis of furan ring, giving significantly high yield of pentanediol (entries 8-10). These results are in accordance with our results in the hydrogenolysis of FFald to 1,4-pentanediol in ethanol:H_2O (1.5:2.0 v/v) mixture solvent using bulk Ni-Sn alloy catalyst as reported previously [43]. Additionally, a notable high yield of cyclopentanone (CPO) and cyclopentanol (CPOL) was obtained when 1,4-dioxane or 1,4-dioxane-H_2O mixture solvent was used. These results are very consistent with the previous work of Dewi Astuti et al. using bimetallic Ni-Fe(3.0)/TiO_2 catalysts under the identical reaction conditions [27]. Therefore, further investigation on the hydrogenolysis of FFald using bimetallic Pd-based catalysts will be reported in our upcoming manuscript.

3.2.3 Effect of reaction temperature

The effect of temperature on the catalytic hydrogenation of FFald to FFalc was evaluated over Pd-Cu(3.0)/C catalyst at range tempera-

Table 3. Results of solvent screening for FFald hydrogenation over Pd-Cu(3.0)/C catalyst.

Entry	Solvent	Conv.[a] (%)	Yield[a] (%)			
			FFalc	THFalc	2-MeF	Others[b]
1	1-Propanol	>99	90	8	2	0
2	2-Propanol	>99	94	5	1	0
3	Ethanol	96	94	2	0	0
4	Methanol	90	80	7	3	0
5	1,4-Dioxane	67	94	3	0	27[c]
6	Toluene	56	43	13	0	0
7	H_2O	67	27	13	7	20
8	Ethanol: H_2O (1.5: 2.0 v/v)	98	53	18	5	32[c]
9	2-Propanol/H_2O (1.5: 2.0 v/v)	99	57	15	5	22
10	1,4-Dioxane/H_2O (1.5: 2.0 v/v)	99	38	15	2	44[c]

Reaction conditions: catalyst (5 mg); FFald (2 mmol); solvent (3.5 mL); temperature (130 °C); initial H_2 pressure (3.0 MPa); reaction time (1.5 h). [a]Conversion and yields of FFalc THFalc, and 2-MeF were determined by GC using an internal standard technique. [b]Others consist of the hydrogenolysis products such as 1,2-pentanediol, 1,5-pentanediol, and 1,4-pentanediol. [c]The main product of others using 1,4-dioxane solvent was cyclopentanone (CPO) and cyclopentanol (CPOL).

ture of 90-190 °C in batch system for 1.5 h and the results are shown in Figure 4.

Differences in the conversion of FFald and product distributions at different temperature are clearly observed. At lower temperature (90-110 °C), the maximum conversion of FFald was around 87% with selectivity of FFalc was nearly 100%. An increase of the reaction temperature from 100 °C to 130 °C gave a notable increase in FFalc yield from 68% to 94%, respectively followed by a slight increase of THFalc from 3% to 5%. At those of reaction temperatures, the enhancement of decarbonylation reaction rate of FFald did not occur as indicated by remained unchange of 2-MeF yield. Moreover, further increase of reaction temperature to 150-190 °C promoted the hydrogenation of C=C bond as well as the decarbonylation reactions, giving increase in yields of THFalc and 2-MeF, respectively. It has been reported that the decarbonylation reaction of FFald corresponding to 2-MeF using catalyst of platinum metal groups (Pd, Pt, and Ir) is favourably occurred at relatively high reaction temperature (190-220 °C) [44] or vapor phase hydrogenation [31]. The presence of second metals, such as: Cu or Fe, was significantly inhibited the further reaction of FFald or FFalc, such as: total hydrogenation of C=C/C=O bonds or decarbonylation/decarboxylation, therefore the selectivity of desired product FFalc maintained along with the wide range reaction conditions [32].

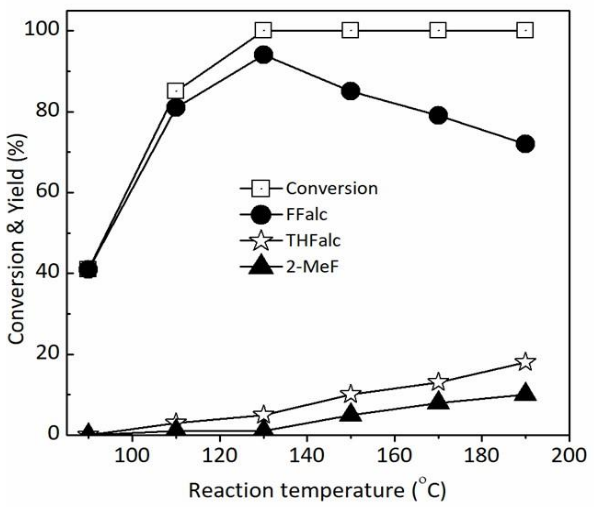


Figure 4. Effect of reaction temperature on the FFald conversion and product distribution over bimetallic Pd-Cu(3.0)/C catalyst. Reaction conditions: catalyst, 0.05 g; FFald, 1.1 mmol; *iso*-PrOH, 3 mL; H_2, 3.0 MPa, 1.5 h.

3.2.4 Effect of initial H_2 pressure

The effect of the initial H_2 pressure on the FFald conversion and product selectivity in shown in Figure 5. FFald conversion and FFalc selectivity gradually increased as the initial H_2 pressure increased, whereas the THFalc increased at initial H_2 pressure of 0.5-1.0 MPa and remained unchanged at the higher initial H_2 pressure. On the other hand, yield of 2-MeF decreased to 0% at initial pressure between 2.5 MPa and 3.0 MPa.

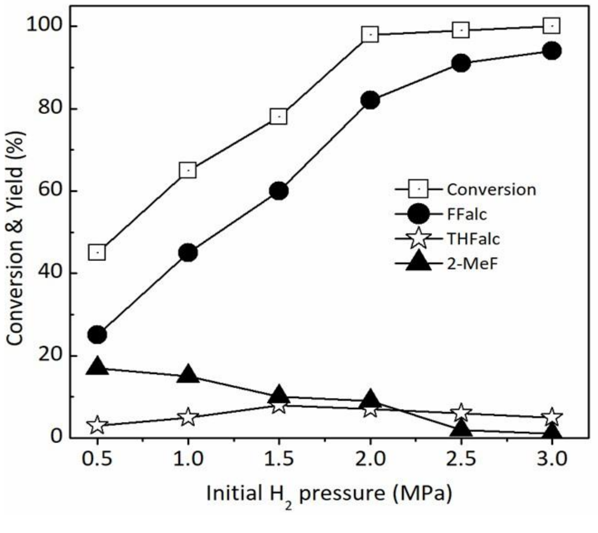


Figure 5. Effect of the initial H_2 pressure on the FFald conversion over bimetallic Pd-Cu(3.0)/C catalyst. *Reaction conditions:* catalyst, 0.05 g; FFald, 1.1 mmol; *iso*-PrOH, 3 mL; 130 °C, 1.5 h.

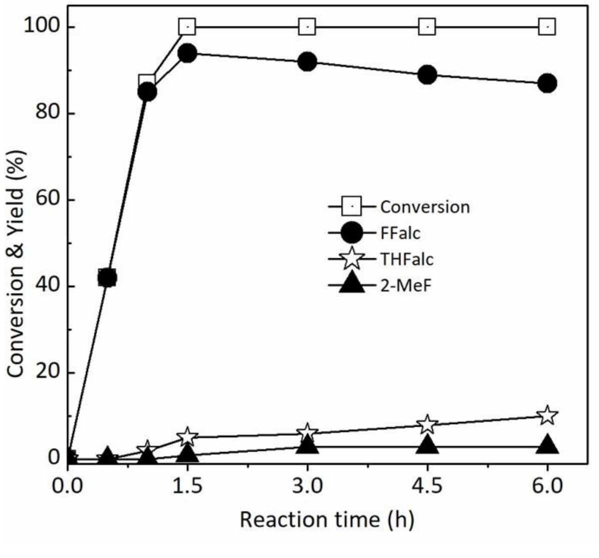


Figure 6. Time profiles of the hydrogenation of FFald over bimetallic Pd-Cu(3.0)/C catalyst. *Reaction conditions:* catalyst, 0.05 g; FFald, 1.1 mmol; *iso*-PrOH, 3 mL; 130 °C.

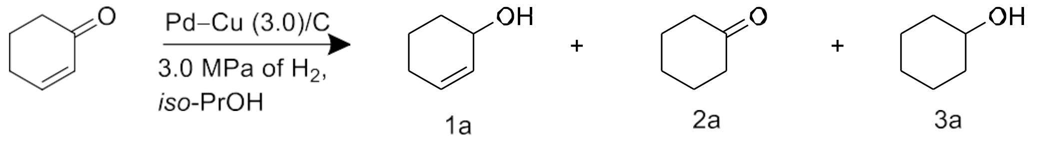
3.3 Time Profiles

The reaction profiles of FFald hydrogenation at 130 °C on the bimetallic Pd-Cu(3.0)/C catalyst are shown in Figure 6. At the early reaction time (0.5 h), FFald conversion was 42% to produce 100% FFalc selectivity, indicating that C=O hydrogenation was took place easily using bimetallic Pd-Cu(3.0)/C catalyst. After reaction was prolonged to 1.0 h, a notable increase of FFald was obtained (87%) with yields of FFalc and THFalc were 85% and 2%, respectively. It has been reported that Pd exhibits a low rate for hydrogenation of the C=O bond compared with other metals commonly used for hydrogenation [45]. Our current results show that a great enhancement both conversion of FFald and selectivity of FFalc which can be attributed to the promotional effect of the second metal Cu as has already described in previous reports [31,32]. The maximum yield of FFalc (94%) was achieved after a reaction time of 1.5 h at full conversion of FFald. When the reaction time was extended to 3-6 h, further hydrogenation reaction of C=C bond obviously occurred as indicated by the increase of THFalc yield. On the other hand, the yield of 2-MeF was almost unchanged after a reaction time of 6 h (3%), suggesting the decarbonylation of FFald or FFalc did not occur effectively using bimetallic Pd-Cu(3.0)/C catalyst under the current operating conditions as mentioned previously.

3.4 Hydrogenation of α,β-Unsaturated Ketone and Aldehyde

A substrate scope of the presence of Pd-Cu(3.0)/C catalyst in the hydrogenation of α,β-unsaturated ketone and aldehyde was examined and the results are summarized in Table 4 and Table 5. In the case of hydrogenation of ketone, 2-cyclohexene-1-one was selected as a

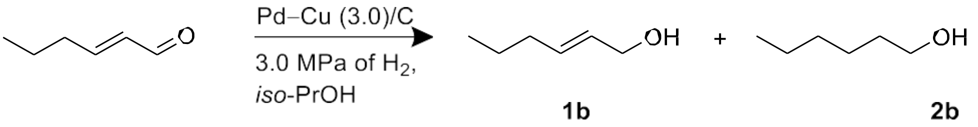
Table 4. Results of selective hydrogenation of typical α,β-unsaturated ketone using Pd-Cu(3.0)/C catalyst.



Entry	Catalyst[a]	Reaction temp. (°C)	Reaction time (h)	Conv.[b] (%)	Selectivity[b] (%)		
					1a	**2a**	**3a**
1	Pd/C (5%wt)	130	1.5	33	0	24	76
2	Pd-Cu(3.0)/C	100	1.5	54	96	0	4
3	Pd-Cu(3.0)/C	130	1.5	94	90	0	10
4	Pd-Cu(3.0)/C	130	3.0	>99	68	0	32

Reaction conditions: catalyst, 0.05 g; substrate, 1.1 mmol; *iso*-PrOH, 3 mL. [a]The value in the parenthesis is Pd/Cu molar ratio, determined by ICP-OES. [b]Conversion and yield were determined by GC using an internal standard technique.

Table 5. Results of selective hydrogenation of typical α,β-unsaturated aldehyde using Pd-Cu(3.0)/C catalyst



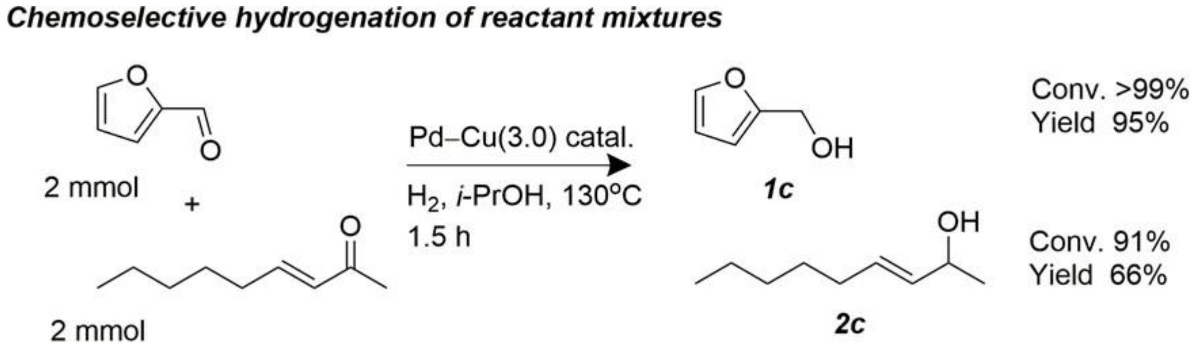
Entry	Catalyst[a]	Reaction temp. (°C)	Reaction time (h)	Conv.[b] (%)	Selectivity[b] (%)	
					1a	**2a**
1	Pd/C (5%wt)	130	1.5	65	0	100
2	Pd-Cu(3.0)/C	100	1.5	87	96	4
3	Pd-Cu(3.0)/C	130	1.5	90	90	10
4	Pd-Cu(3.0)/C	130	3.0	>99	83	17

Reaction conditions: catalyst, 0.05 g; substrate, 1.1 mmol; iso-PrOH, 3 mL. [a]The value in the parenthesis is Pd/Cu molar ratio, determined by ICP-OES. [b]Conversion and yield were determined by GC using an internal standard technique typical α,β-unsaturated ketone substrate. Using a commercial Pd/C (5%wt Pd) catalyst, 33% conversion of 2-cyclohexene-1-one was obtained with the selectivities of product 2a and 3a were 24% and 76%, respectively without the formation of product 1a (entry 1). A remarkably high selectivity of product 1a (96%) was obtained over Pd-Cu(3.0)/C catalyst at temperature of 100 °C for 1.5 h at 54% conversion (entry 2). This is a result of promoting effect of Cu on Pd/C, leading to high affinity toward C=O bond rather than C=C bond of the substrate. An increase reaction temperature from 100 °C to 130 °C not only enhanced the conversion to 94% but also caused further hydrogenation C=C bond, therefore the selectivity to 3a increased significantly (entry 3). Moreover, the extent of reaction time to 3.0 h gave a completed reaction (>99% conversion) with product selectivities of 1a and 3a were 68% and 32%, respectively (entry 4).

Next, we examined the catalytic reaction of typical α,β-unsaturated aldehyde (*trans*-2-hexenaldehyde) using bimetallic Pd-Cu(3.0)/C catalyst and the results are summarized in Table 5. Using Pd/C catalyst at 130 °C and 1.5 h, 65% conversion of *trans*-2-hexenaldehyde was achieved and yielded 100% selectivity of n-hexanol (1b), which means both C=C and C=O bonds of reactant were simultaneously hydrogenated under the reaction conditions (entry 1). Interestingly, bimetallic Pd-Cu(3.0)/C catalyst gave a remarkable selectivity to 2-henxene-ol (1a) (96%) at 87% conversion at 100 °C for 1.5 h (entry 2). When the reaction temperature was increased to 130 °C or reaction time was extended to 3 h, the selectivity of saturated alcohol significantly increased indicating the further hydrogenation of C=C was obviously occurred (entries 3 and 4).

3.5 Chemoselective Hydrogenation of Reactant Mixtures

To complete our investigation in the selective hydrogenation of C=O bond rather than C=C bond, the catalytic reaction of a mixture of FFald (typical unsaturated aldehyde) and (E)-non-3-en-2-one (typical unsaturated ketone) (molar ratio to 1.0) was examined using bimetallic Pd-Cu(3.0)/C catalysts and the results showed in Scheme 2. Under the current operating conditions, at a full conversion of FFald with 95% yield of FFalc (**1c**) was obtained. On



Scheme 2. Chemoselective hydrogenation of aldehyde (FFald) and ketone ((E)-non-3-en-2-one) reactant mixtures. Reaction conditions: catalyst, 0.05 g; substrate, 2.0 mmol; *iso*-PrOH, 3.5 mL, 3.0 MPa H_2, 130 °C, 1.5 h.

Table 6. Results of the selective hydrogenation of FFald to FFalc over bimetallic Pd-Cu(3.0)/C catalyst after four consecutive reaction runs.

Entry	Reaction run-	Conversion[a] (%)	Yield[a] (%)		
			FFalc	THFalc	2-MeF
1	1st	>99	94	5	1
2	2nd	82	76	5	1
3	3rd	73	66	6	1
4[b]	4th	>99	95	4	1

Reaction conditions: catalyst (0.05 g); FFald (1.1 mmol); solvent (*iso*-PrOH, 3.5 ml); temperature (130 °C); initial H_2 pressure (3.0 MPa); reaction time (1.5 h). [a]Conversion and yields of FFalc THFalc, and 2-MeF were determined by GC using an internal standard technique. [b]The used Pd-Cu(3.0)/C catalyst was reduced with H_2 at 400 °C for 1.5 h before reaction.

the other hand, the conversion of (E)-non-3-en-2-one was 91% with moderate yield of unsaturated alcohol (**2c**) (66%). These results suggest that the bimetallic Pd-Cu(3.0)/C catalyst can be applied for selective hydrogenation of α,β-unsaturated ketone and aldehyde to corresponding unsaturated alcohol from moderate to high yield.

3.6 Reusability Test

A reusability test was performed on the Pd-Cu(3.0)/C catalyst in the selective hydrogenation of FFald and the results are summarized in Table 6. The used Pd-Cu(3.0)/C catalyst was easily separated by either simple centrifugation or filtration after the reaction. The activity of the catalyst decreased while the selectivity was maintained for at least four consecutive reaction runs. The catalytic activity and selectivity of the used Pd-Cu(3.0)/C catalyst can be restored to the original by simple reduction with H_2 at 400 °C for 1.5 h.

4. Conclusions

We have described the promotional effect of second metal Cu on Pd/C catalyst in the chemoselective hydrogenation of biobased furfuraldehyde (FFald) and typical α,β-unsaturated ketones/aldehydes. The presence of Cu (0.012 mmol) in Pd/C to form bimetallic Pd-Cu alloy phases obviously enhanced the selectivity of Pd towards C=O rather than C=C bonds in furfural or typical α,β-unsaturated ketones/aldehydes, leading to high yield of unsaturated alcohols. The formation of bimetallic Pd-Cu alloy phase in Pd-Cu(3.0)/C catalyst was clearly observed after reduction with H_2 at 400 °C for 1.5 h, which plays a pivotal role during the chemoselective hydrogenations. Pd-Cu(3.0)/C catalyst was found to stable and reusable for at least four reaction runs and the activity and selectivity of the catalyst can be restored to the original after rejuvenation with H_2 at 400 °C for 1.5 h.

Acknowledgments

The authors acknowledge the RISET DASAR (contract number DIPA-042.06-1.401516/2020) from Ministry of Education and Culture, Indonesian Government, which all financially supported this work. We would also like thank to Professor Shogo Shimazu for kind help in XRD, H_2-chemisorption, and N_2-adsorption/desorption-BET measurements.

References

[1] Hoydonckx, H.E., Van Rhijn, W.M., Van Rhijn, M., De Vos, D.E., Jacobs, P.A. (2012). Furfural and Derivatives, in: *Ullmann's Encyclopedia of Industrial Chemistry* , Wiley-VCH Verlag GmbH & Co. KGaA, pp. 285–309. DOI: 10.1002/14356007.a12_119.pub2.

[2] Kimura, H. (2011). Progress in one-step amination of long-chain fatty alcohols with dimethylamine development of key technologies for industrial applications, innovations, and future outlook. *Catalysis Reviews-Science and Engineering*, 53, 1–90. DOI: 10.1080/01614940.2011.556913.

[3] Pasumansky, L., Goralski, C.T., Singaram, B. (2006). Lithium aminoborohydrides: Powerful, selective, air-stable reducing agents. *Organic Process Research & Development*, 10, 959–970. DOI: 10.1021/op0600759.

[4] Cha, J.S. (2006). Recent developments in Meerwein-Ponndorf-Verley and related reactions for the reduction of organic functional groups using aluminum, boron, and other metal reagents: A review. *Organic Process Research & Development,* 10, 1032–1053. DOI: 10.1021/op068002c.

[5] Ohkuma, T., Kurono, N., Arai, N. (2019). Development of asymmetric reactions catalyzed by ruthenium complexes with two kinds of ligands. *Bulletin of the Chemical Society of Japan*, 92, 475–504. DOI: 10.1246/bcsj.20180328.

[6] Gallezot, P., Richard, D. (1998). Selective Hydrogenation of a,b-Unsaturated Aldehydes. *Catalysis Reviews-Science and Engineering*, 40, 81–126. DOI: 10.1080/01614949808007106.

[7] Mäki-Arvela, P., Salmi, T., Holmbom, B., Willför, S., Murzin, D.Y. (2011). Synthesis of sugars by hydrolysis of hemicelluloses- A review. *Chemical Reviews*, 111, 5638–5666. DOI: 10.1021/cr2000042.

[8] Claus, P. (1998). Selective hydrogenation of alpha,beta-unsaturated aldehydes and other C=O and C=C bonds containing compounds. *Topics in Catalysis*, 5, 51–62. DOI: 10.1023/a:1019177330810.

[9] Luneau, M., Lim, J.S., Patel, D.A., Sykes, E.C.H., Friend, C.M., Sautet, P. (2020). Guidelines to Achieving High Selectivity for the Hydrogenation of α,β-Unsaturated Aldehydes with Bimetallic and Dilute Alloy Catalysts: A Review. *Chemical Reviews*, 120(23), 12834–12872. DOI: 10.1021/acs.chemrev.0c00582.

[10] Lucci, F.R., Liu, J., Marcinkowski, M.D., Yang, M., Allard, L.F., Flytzani-

Stephanopoulos, M., Sykes, E.C.H. (2015). Selective hydrogenation of 1,3-butadiene on platinum-copper alloys at the single-atom limit. *Nature Communications*, 6, 1–8. DOI: 10.1038/ncomms9550.

[11] Guo, Z., Xiao, C., Maligal-Ganesh, R.V., Zhou, L., Goh, T.W., Li, X., Tesfagaber, D., Thiel, A., Huang, W. (2014). Pt Nanoclusters Confined within Metal–Organic Framework Cavities for Chemoselective Cinnamaldehyde Hydrogenation. *ACS Catalysis*, 4, 1340–1348. DOI: 10.1021/cs400982n.

[12] Silva, A.M., Santos, O.A.A., Mendes, M.J., Jordão, E., Fraga, M.A. (2003). Hydrogenation of citral over ruthenium-tin catalysts. *Applied Catalysis A: General*, 241, 155–165. DOI: 10.1016/S0926-860X(02)00463-5.

[13] Gupta, K., Rai, R.K., Dwivedi, A.D., Singh, S.K. (2017). Catalytic Aerial Oxidation of Biomass-Derived Furans to Furan Carboxylic Acids in Water over Bimetallic Nickel–Palladium Alloy Nanoparticles. *ChemCatChem*, 9, 2760–2767. DOI: 10.1002/cctc.201600942.

[14] Sankar, M., Dimitratos, N., Miedziak, P.J., Wells, P.P., Kiely, C.J., Hutchings, G.J. (2012). Designing bimetallic catalysts for a green and sustainable future. *Chemical Society Reviews*, 41, 8099–8139. DOI: 10.1039/c2cs35296f.

[15] Alonso, D.M., Wettstein, S.G., Dumesic, J.A. (2012). Bimetallic catalysts for upgrading of biomass to fuels and chemicals. *Chemical Society Reviews,* 41, 8075–8098. DOI: 10.1039/c2cs35188a.

[16] Mäki-Arvela, P., Hájek, J., Salmi, T., Murzin, D.Y. (2005). Chemoselective hydrogenation of carbonyl compounds over heterogeneous catalysts. *Applied Catalysis A: General*, 292, 1–49. DOI: 10.1016/j.apcata.2005.05.045.

[17] Altmann, L., Wang, X., Borchert, H., Kolny-Olesiak, J., Zielasek, V., Parisi, J., Kunz, S., Bäumer, M. (2015). Influence of Sn content on the hydrogenation of crotonaldehyde catalysed by colloidally prepared PtSn nanoparticles. *Physical Chemistry Chemical Physics*, 17, 28186–28192. DOI: 10.1039/c5cp00280j.

[18] Liang, S., Hao, C., Shi, Y. (2015). The Power of Single-Atom Catalysis. *ChemCatChem*, 7, 2559–2567. DOI: 10.1002/cctc.201500363.

[19] Rodiansono, R., Hara, T., Ichikuni, N., Shimazu, S. (2012). A novel preparation method of nisn alloy catalysts supported on aluminium hydroxide: Application to chemoselective hydrogenation of unsaturated carbonyl compounds. *Chemistry Letters*, 41, 769–771. DOI: 10.1246/cl.2012.769.

[20] Rodiansono, R., Khairi, S., Hara, T., Ichikuni, N., Shimazu, S. (2012). Highly efficient and selective hydrogenation of unsaturated carbonyl compounds using Ni-Sn alloy catalysts. *Catalysis Science & Technology*, 2, 2139–2145. DOI: 10.1039/c2cy20216f.

[21] Rodiansono, R., Hara, T., Ichikuni, N., Shimazu, S. (2014). Development of Nanoporous Ni-Sn Alloy and Application for Chemoselective Hydrogenation of Furfural to Furfuryl Alcohol. *Bulletin of Chemical Reaction Engineering & Catalysis*, 9, 53–59. DOI: 10.9767/bcrec.9.1.5529.53-59.

[22] Rodiansono, R., Astuti, M.D., Khairi, S., Shimazu, S. (2016). Selective Hydrogenation of Biomass-derived Furfural over Supported Ni3Sn2 Alloy: Role of Supports. *Bulletin of Chemical Reaction Engineering & Catalysis,* 11, 1–9. DOI: 10.9767/bcrec.11.1.393.1-9.

[23] Rodiansono, R., Astuti, M.D., Mujiyanti, D.R., Santoso, U.T., Shimazu, S. (2018). Novel preparation method of bimetallic Ni-In alloy catalysts supported on amorphous alumina for the highly selective hydrogenation of furfural. *Molecular Catalysis*, 445, 52–60. DOI: 10.1016/j.mcat.2017.11.004.

[24] Dutta, S., De, S., Saha, B., Alam, M.I. (2012). Advances in conversion of hemicellulosic biomass to furfural and upgrading to biofuels. *Catalysis Science & Technology*, 2, 2025–2036. DOI: 10.1039/C2CY20235B.

[25] Lange, J.-P., van der Heide, E., van Buijtenen, J., Price, R. (2012). Furfural—A Promising Platform for Lignocellulosic Biofuels. *ChemSusChem*, 5, 150–166. DOI: 10.1002/cssc.201100648.

[26] Chen, S., Wojcieszak, R., Dumeignil, F., Marceau, E., Royer, S. (2018). How Catalysts and Experimental Conditions Determine the Selective Hydroconversion of Furfural and 5-Hydroxymethylfurfural. *Chemical Reviews*, 118, 11023–11117. DOI: 10.1021/acs.chemrev.8b00134.

[27] Astuti, M.D., Kristina, D., Rodiansono, R., Mujiyanti, D.R. (2020). One-pot Selective Conversion of Biomass-derived Furfural into Cyclopentanone/Cyclopentanol over TiO2 Supported Bimetallic Ni-M (M = Co, Fe) Catalysts. *Bulletin of Chemical Reaction Engineering & Catalysis*, 15, 231–241. DOI: 10.9767/bcrec.15.1.6307.231-241.

[28] O'Driscoll, Á., Curtin, T., Hernández, W.Y., Van Der Voort, P., Leahy, J.J. (2016). Hydrogenation of Furfural with a Pt-Sn Catalyst: The Suitability to Sustainable Industrial Application. *Organic Process Research & Development*, 20, 1917–1929. DOI: 10.1021/acs.oprd.6b00228.

[29] Liao, F., Lo, T.W.B., Tsang, S.C.E. (2015). Recent Developments in Palladium-Based Bimetallic Catalysts. *ChemCatChem*, 7, 1998–2014. DOI: 10.1002/cctc.201500245.

[30] Kovtunov, K.V., Barskiy, D.A., Salnikov, O.G., Khudorozhkov, A.K., Bukhtiyarov, A.V., Prosvirin, I.P., Gerasimov, E.Y., Bukhtiyarov, V.I., Koptyug, I.V. (2015). Strong Metal-Support Interactions for Pd Supported on TiO2 Catalysts in Heterogeneous Hydrogenation with Parahydrogen. *ChemCatChem*, 7, 2581–2584. DOI: 10.1002/cctc.201500618.

[31] Pino, N., Sitthisa, S., Tan, Q., Souza, T., López, D., Resasco, D.E. (2017). Structure, activity, and selectivity of bimetallic Pd-Fe/SiO2 and Pd-Fe/γ-Al2O3 catalysts for the conversion of furfural. *Journal of Catalysis*, 350, 30–40. DOI: 10.1016/j.jcat.2017.03.016.

[32] Sitthisa, S., Prasomsri, T.P., Sooknoi, T., Mallinson, R.G., Resasco, D.E. (2011). Conversion of furfural and 2-methylpentanal on Pd/SiO2 and Pd–Cu/SiO2 catalysts. *Journal of Catalysis*, 280, 17–27. DOI: 10.1016/j.jcat.2011.02.006.

[33] Lowell, S., Shields, J.E., Thomas, M.A., Thommes, M. (2004). *Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density*. Dordrecht, The Netherlands: Kluwer Academic Publishers. DOI: 10.1007/978-1-4020-2303-3.

[34] Storck, S., Bretinger, H., Maier, W.F. (1998). Characterization of micro- and mesoporous solids by physisorption methods and pore-size analysis. *Applied Catalysis A: General*, 174, 137–146. DOI: 10.1016/S0926-860X(98)00164-1.

[35] Aben, P.C. (1968). Palladium areas in supported catalysts. Determination of palladium surface areas in supported catalysts by means of hydrogen chemisorption. *Journal of Catalysis*, 10, 224–229. DOI: 10.1016/S0021-9517(68)80002-8.

[36] Xu, Q., Kharas, K.C., Croley, B.J., Datye, A.K. (2011). The Sintering of Supported Pd Automotive Catalysts. *ChemCatChem*, 3, 1004–1014. DOI: 10.1002/cctc.201000392.

[37] Lu, J., Fu, B., Kung, M.C., Xiao, G., Elam, J.W., Kung, H.H., Stair, P.C. (2012). Coking- and sintering-resistant palladium catalysts achieved through atomic layer deposition. *Science*, 335, 1205–1208. DOI: 10.1126/science.1212906.

[38] Gong, S., Chen, N., Nakayama, S., Qian, E.W. (2013). Isomerization of n-alkanes derived from jatropha oil over bifunctional catalysts. *Journal of Molecular Catalysis A: Chemical,* 370, 14–21. DOI: 10.1016/j.molcata.2012.11.019.

[39] JCPDS-ICDD. (1991). Powder diffraction files, JCPDS-International center for diffraction data (JCPDS-ICDD).

[40] Chen, D., Sun, P., Liu, H., Yang, J. (2017). Bimetallic Cu-Pd alloy multipods and their highly electrocatalytic performance for formic acid oxidation and oxygen reduction. *Journal of Materials Chemistry A*, 5, 4421–4429. DOI: 10.1039/c6ta10476b.

[41] Wei, Z., Lou, J., Su, C., Guo, D., Liu, Y., Deng, S. (2017). An Efficient and Reusable Embedded Ru Catalyst for the Hydrogenolysis of Levulinic Acid to Γ-Valerolactone. *ChemSusChem*, 10, 1720–1732. DOI: 10.1002/cssc.201601769.

[42] Gandini, A. (2010). Furans as offspring of sugars and polysaccharides and progenitors of a family of remarkable polymers: a review of recent progress. *Polymer Chemistry*, 1, 245–251. DOI: 10.1039/B9PY00233B.

[43] Rodiansono, R., Astuti, M.D., Hara, T., Ichikuni, N., Shimazu, S. (2019). One-pot selective conversion of C5-furan into 1,4-pentanediol over bulk Ni-Sn alloy catalysts in an ethanol/H2O solvent mixture. *Green Chemistry*, 21, 2307–2315. DOI: 10.1039/c8gc03938k.

[44] Date, N.S., Hengne, A.M., Huang, K.W., Chikate, R.C., Rode, C.V. (2018). Single pot selective hydrogenation of furfural to 2-methylfuran over carbon supported iridium catalysts. *Green Chemistry*, 20, 2027–2037. DOI: 10.1039/c8gc00284c.

[45] Marinelli, T.B.L.W., Nabuurs, S., Ponec, V. (1995). Activity and selectivity in the reactions of substituted α,β-Unsaturated aldehydes. *Journal of Catalysis*, 151, 431–438. DOI: 10.1006/jcat.1995.1045.

5. Bukti Konfirmasi Artikel published online (11 Mei 2021)

Kamilia Mustikasari <kmustikasari@ulm.ac.id>

Your article (DOI: 10.9767/bcrec.16.2.10398.267-279) has been published in Bull. Chem. React. Eng. Catal. (Volume 16 Issue 2 Year 2021, regular publication of 30 June 2021)

1 message

BCREC Group <bcrec@live.undip.ac.id> Tue, May 11, 2021 at 2:46 PM
Reply-To: bcrec@live.undip.ac.id
To: "Cc:" <rodiansono@ulm.ac.id>
Cc: kmustikasari@ulm.ac.id, mdastuti@ulm.ac.id, sadanghusain@ulm.ac.id, sutomo@ulm.ac.id

Dear Authors,

It is glad to inform you that your article (DOI: 10.9767/bcrec.16.2.10398.267-279) has been published in a new issue of **Bulletin of Chemical Reaction Engineering & Catalysis (Bull. Chem. React. Eng. Catal., ISSN: 1978-2993) (Volume 16 Issue 2 Year 2021, regular publication of 30th June 2021 and available online since 2nd May 2021).** The URL of the published issue is here: https://ejournal2.undip.ac.id/index.php/bcrec/issue/view/714. The PDF full text or metadata of all articles in this issue will be included soon in reputable databases (Scopus, EI-Compendex, Web of Science Core Collection Database (ESCI), EBSCO, ProQuest, etc.).

Please be noted that citations to these journal articles on your next publication is greatly appreciated, especially from other reputable journals. Your articles following focus and scopes and following high quality standards of BCREC journal are very welcome.

Thank you for your great contribution to this reputable journal.

NOTE:
Here are **the four reasons why is the right platform for your next paper to be published in Bulletin of Chemical Reaction Engineering & Catalysis**:

1. Bulletin of Chemical Reaction Engineering & Catalysis has been indexed in the following databases: **Engineering Village - Compendex**, **SCOPUS**, **Clarivate Analytics' Emerging Sources Citation Index (ESCI) - Web of Science**, so that your published articles are guaranteed maximum visibility.
2. Fulltext PDFs of Bulletin of Chemical Reaction Engineering & Catalysis have been distributed by the following major aggregators: **EBSCO Publishing** and **ProQuest Databases**, so that your published article is guaranteed maximum visibility.
3. Bulletin of Chemical Reaction Engineering & Catalysis has a CiteScore™ (2019) of 1.8 (Scopus®, 2020), **SJR of 0.256 (2019)**, and Q3-ranked in Scimago Journal Ranking 2020. **Current Tracking of CiteScore (April 2021): 2.2** with **Current Acceptance Rate 40%**.
4. Bulletin of Chemical Reaction Engineering & Catalysis has a good current tracking predicted Impact Factor (IF) of Clarivate Analytics' Emerging Sources Citation Index (ESCI) in **March 2021**: 253 citations in 2018-2020 which were cited to 138 articles of (2018-2019).

If you are looking for the ideal home for your next paper, we invite you to submit to **Bulletin of Chemical Reaction Engineering & Catalysis**.

>>> **Editorial Boards of Bulletin of Chemical Reaction Engineering & Catalysis**:

- Editor in Chief: Prof. Dr. I. Istadi
- Regional Editor for Europe and Africa: Prof. Dr. Dmitry Yu Murzin
- Regional Editor for Asia-Pacific: Prof. Dr. Bunjerd Jongsomjit; and Prof. Dr. Hadi Nur

>>> **Link to Editorial Boards**
>>> **Find out more this journal**
>>> **Submit your paper here** or **Author Guidelines 2020**
>>> **Browse All Issues here**
>>> **BCREC Profile on Scopus**

>>> **BCREC Profile on Web of Science (Clarivate)**
>>> **BCREC Profile on Twitter (please follow)**.

Table of Contents (22 Articles):

1. Elgubbi, H. M., Othman, S. S., Harun, F. W. (2021). Comparative Study on Lipase Immobilized onto Organo-Cation Exchanged Kaolin and Metakaolin: Surface Properties and Catalytic Activity. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 214-233 (doi:10.9767/bcrec.16.2.10230.214-233)
2. Arboui, F., Amzert, S. A., Boucherit, M. N., Hanini, S., Ghezali, K. (2021). Evaluation of Corrosion Inhibition of 316L Stainless Steel by Permanganate Ions in Chloride Solution. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 234-243 (doi:10.9767/bcrec.16.2.10504.234-243)
3. Mohadi, R., Palapa, N. R., Lesbani, A. (2021). Preparation of Ca/Al-Layered Double Hydroxides/Biochar Composite with High Adsorption Capacity and Selectivity toward Cationic Dyes in Aqueous. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 244-252 (doi:10.9767/bcrec.16.2.10211.244-252)
4. Yudha S, S., Falahudin, A., Wibowo, R. H., Hendri, J., Wicaksono, D. O. (2021). Reduction of 4-nitrophenol Mediated by Silver Nanoparticles Synthesized using Aqueous Leaf Extract of Peronema canescens. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 253-259 (doi:10.9767/bcrec.16.2.10426.253-259)
5. Wang, L., Kong, F., Tai, X. (2021). Crystal Structure and Catalytic Activity of Poly[bis(3-bromo-2-hydroxybenzaldehyde)-2-aminopyrimidinemagnesium(II)] for Hydrogenation of 1,3-Butadiene. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 260-266 (doi:10.9767/bcrec.16.2.10421.260-266)
6. Mustikasari, K., Rodiansono, R., Astuti, M. D., Husain, S., Sutomo, S. (2021). The Promotion Effect of Cu on the Pd/C Catalyst in the Chemoselective Hydrogenation of Unsaturated Carbonyl Compounds. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 267-279 (doi:10.9767/bcrec.16.2.10398.267-279)
7. Malahayati, M., Yufita, E., Ismail, I., Mursal, M., Idroes, R., Jalil, Z. (2021). Hydrogen Desorption Properties of MgH_2 + 10 wt% SiO_2 + 5 wt% Ni Prepared by Planetary Ball Milling. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 280-285 (doi:10.9767/bcrec.16.2.10220.280-285)
8. Kuntari, K. (2021). Kinetic and Isotherm Studies of Nitrate Adsorption in Salt Water Using Modified Zeolite. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 286-292 (doi:10.9767/bcrec.16.2.10312.286-292)
9. Aritonang, A. B., Pratiwi, E., Warsidah, W., Nurdiansyah, S. I., Risko, R. (2021). Fe-doped TiO_2/Kaolinite as an Antibacterial Photocatalyst under Visible Light Irradiation. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 293-301 (doi:10.9767/bcrec.16.2.10325.293-301)
10. Rahmah, A. U., Harimurti, S., Kurnia, K. A., Omar, A. A., Murugesan, T. (2021). Oxytetracycline Mineralization inside a UV/H_2O_2 System of Advanced Oxidation Processes: Inorganic By-Product. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 302-309 (doi:10.9767/bcrec.16.2.10308.302-309)
11. Kurniawan, Y. S., Yuliati, L. (2021). Activity Enhancement of P25 Titanium Dioxide by Zinc Oxide for Photocatalytic Phenol Degradation. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 310-319 (doi:10.9767/bcrec.16.2.10319.310-319)
12. Dini, F. W., Helmiyati, H., Krisnandi, Y. K. (2021). Cellulose and TiO_2–ZrO_2 Nanocomposite as a Catalyst for Glucose Conversion to 5-EMF. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 320-330 (doi:10.9767/bcrec.16.2.10320.320-330)
13. Fatmawati, A., Anggoro, A., Muslim, K. A., Widjaja, A., Nurtono, T., Sangian, H. F. (2021). Mathematical Modelling of Alkaline and Ionic Liquid Pretreated Coconut Husk Enzymatic Hydrolysis. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 331-341 (doi:10.9767/bcrec.16.2.10306.331-341)
14. AlMohamadi, H., Aljabri, A., Mahmoud, E. R., Khan, S. Z., Aljohani, M. S., Shamsuddin, R. (2021). Catalytic Pyrolysis of Municipal Solid Waste: Effects of Pyrolysis Parameters. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 342-352 (doi:10.9767/bcrec.16.2.10499.342-352)
15. Nadir, N., Wahid, Z., Shafie, A. A., Ahmad, F. B., Zainuddin, M. T. (2021). Investigating Photochromic Behavior of Organic Dyes in Solution Form using Multilevel Factorial Design. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 353-365 (doi:10.9767/bcrec.16.2.10496.353-365)
16. Ruhaimi, A. H., Teh, C. C., Aziz, M. A. A. (2021). Mesoporous Magnesium Oxide Adsorbent Prepared via Lime (Citrus aurantifolia) Peel Bio-templating for CO_2 Capture. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 366-373 (doi:10.9767/bcrec.16.2.10505.366-373)
17. Zaidi, A. A., Khan, S. Z., Almohamadi, H., Mahmoud, E. R. I., Naseer, M. N. (2021). Nanoparticles Synergistic Effect with Various Substrate Pretreatment and their Comparison on Biogas Production from Algae Waste. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 374-382 (doi:10.9767/bcrec.16.2.10637.374-382)
18. Rasid, N. S. A., Shamjuddin, A., Amin, N. A. S. (2021). Chemical and Structural Changes of Ozonated Empty Fruit Bunch (EFB) in a Ribbon-Mixer Reactor. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 383-395 (doi:10.9767/bcrec.16.2.10506.383-395)
19. Nuhma, M. J., Alias, H., Jazie, A. A., Tahir, M. (2021). Role of Microalgae as a Source for Biofuel Production in the Future: A Short Review. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 396-412 (doi:10.9767/bcrec.16.2.10503.396-412)
20. Ahmad, I., Abdullah, N., Koji, I., Yuzir, A., Mohamad, S. (2021). Potential of Microalgae in Bioremediation of Wastewater. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 413-429 (doi:10.9767/bcrec.16.2.10616.413-429)
21. Abbas, T., Tahir, M., Amin, N. A. S. (2021). Electrochemical Generation of Hydrogen and Methanol using ITO Sheet Decorated with Modified-Titania as Electrode. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 430-439 (doi:10.9767/bcrec.16.2.10514.430-439)
22. Inayat, A., Ahmad, M. A. B., Raza, M., Ghenai, C., Naqvi, S. R., Ayoub, M. (2021). Development of Reaction Kinetics Model for the Production of Synthesis Gas from Dry Methane Reforming. Bulletin of Chemical Reaction Engineering & Catalysis, 16 (2): 440-445 (doi:10.9767/bcrec.16.2.10510.440-445)

Best regards

Prof. Dr. I. Istadi (Editor-in-Chief)
Bulletin of Chemical Reaction Engineering & Catalysis (ISSN 1978-2993)
ScopusID: 6506850769
Publons: https://publons.com/researcher/1722596/istadi-istadi/
Website: http://bcrec.undip.ac.id
E-mail: bcrec@live.undip.ac.id