

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

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Research Article

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

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### Abstract

Highly efficient and selective hydrogenation of  $\alpha,\beta$ -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  $\alpha,\beta$ -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<sub>2</sub> 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 be 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<sub>2</sub> at 400 °C for 1.5 h.

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

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### 1. Introduction

The chemoselective hydrogenation of the C=O bond in  $\alpha,\beta$ -unsaturated ketones / alde-

hydes 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].

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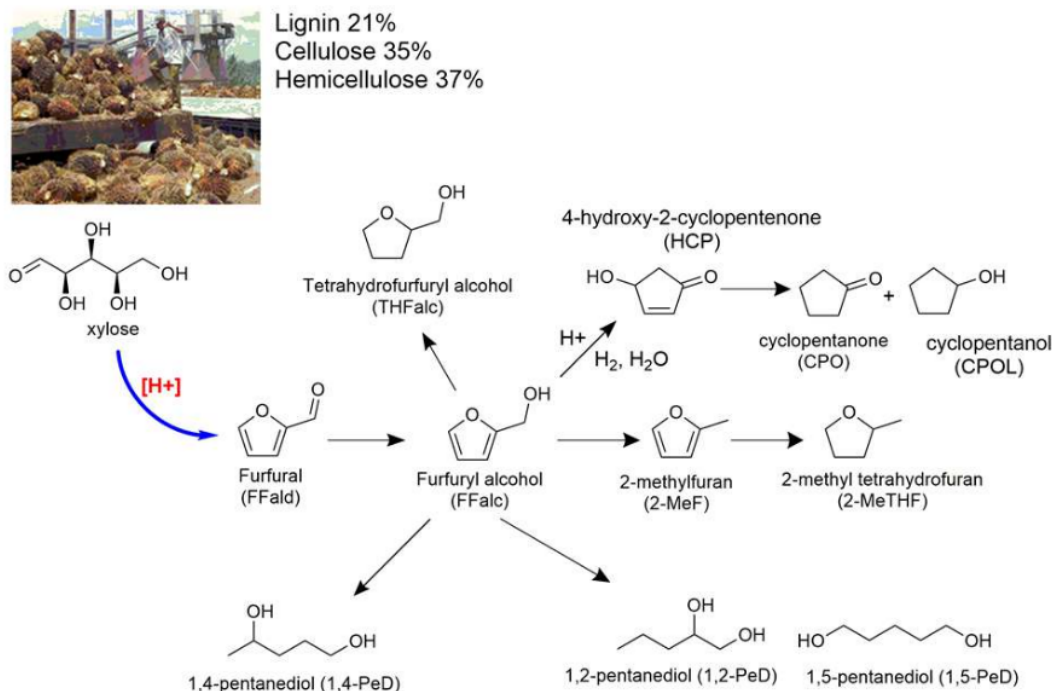
These processes often use costly chemicals and solvents which require separations. In this context, heterogeneous catalysis is viewed as an alternative, more sustainable route for the production of these high-value chemicals at an industrial scale [6–8]. Simple preparation and recovery of heterogeneous 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  $\alpha,\beta$ -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  $\alpha,\beta$ -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 Ni-based catalysts [20,21] due to their intrinsic



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

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<sub>2</sub> 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 active 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 2 h, followed by H<sub>2</sub> treatment at 400 °C for 1.5 h. The promotion effect of Cu on Pd/C catalyst, solvent use and reaction parameters (initial H<sub>2</sub> 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<sub>2</sub>; Tokyo Chemical Industries Co. (TCI)), copper(II) nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O; Merck) were purchased and used as received. Microporous carbon (C, S<sub>BET</sub> = 815 m<sup>2</sup>.g<sup>-1</sup>) was purchased from WAKO Pure Chemical Industries, 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 $\alpha$  radiation ( $\lambda = 0.15444$  nm). XRD operated at 40 kV and 15 mA with solar slit 1.25°, scan step 5° min<sup>-1</sup> and using a Ni K $\beta$  filter. The crystallite size of palladium was estimated by using the Scherrer's equation.

The Brunauer-Emmet-Teller (BET) surface area (S<sub>BET</sub>) and pore volume (V<sub>p</sub>) were measured using N<sub>2</sub> 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 Horvath-Kawazoe (HK) approach [34].

The active surface areas were determined by H<sub>2</sub> chemisorption. After the catalyst was heated at 120 °C under vacuum for 30 min, it was heated at 400 °C under H<sub>2</sub> for 30 min and under vacuum for 30 min, followed by evacuation to room temperature for 30 min. The adsorption of H<sub>2</sub> was conducted at 0 °C. The active surface area was calculated from the volume of H<sub>2</sub> desorbed by assuming an H/Pd stoichiometry of one, respectively and the number of Pd atom for the (111) plane is 1.5×10<sup>15</sup> per cm<sup>2</sup> 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<sub>2</sub> (0.472 mmol) was dissolved in deionized water (denoted as solution A), and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (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<sub>BET</sub> = 815 m<sup>2</sup>.g<sup>-1</sup>) 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 hydro-



thermal 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<sub>2</sub> was introduced into the reactor with an initial H<sub>2</sub> 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. <sup>1</sup>H and

<sup>13</sup>C NMR spectra were obtained on a JNM-AL400 spectrometer at 400 MHz; the samples for NMR analysis were dissolved in chloroform-*d*<sub>1</sub> with TMS as the internal standard. The products were confirmed by a comparison of their GC retention time, mass, <sup>1</sup>H and <sup>13</sup>C NMR spectra with those of authentic samples. The conversion, yield and selectivity of the products were calculated according to the following equations:

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

$$\text{Yield} = \frac{\text{mol product}}{\Delta F} \times 100\% \quad (2)$$

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

where  $F_0$  is the introduced mol reactant (furfural, FFald),  $F_t$  is the remaining mol reactant, and  $\Delta F$  is the consumed mol reactant (introduced mol reactant- remained mol reactant), which are all obtained from GC analysis using an internal standard technique.

## 3. Results and Discussion

### 3.1 Catalyst Characterization

The N<sub>2</sub>-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 adsorption / desorption of the synthesized Pd-Cu/C samples show a very similar to that of former charcoal support, suggesting that there is no significant

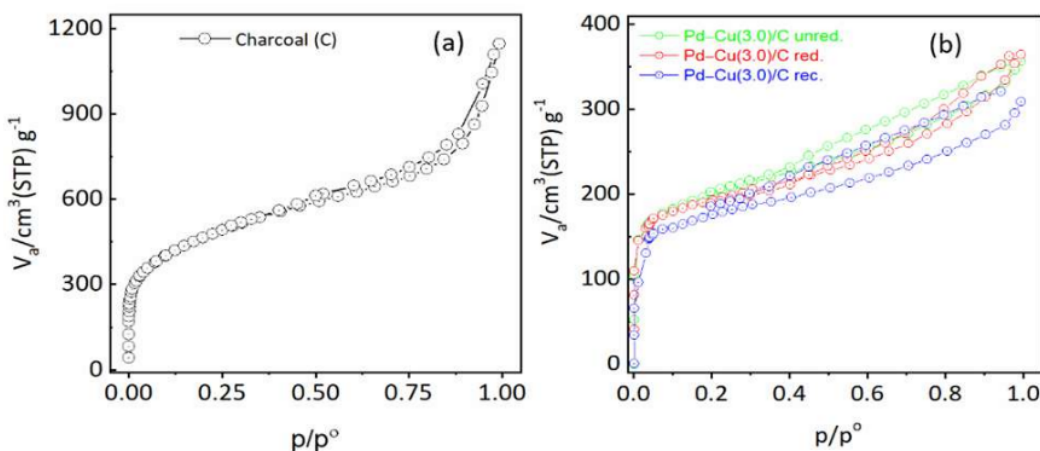


Figure 1. N<sub>2</sub>-adsorption/desorption profiles of (a) charcoal (C) and (b) the synthesized Pd-Cu/C catalyst before and after reduction with H<sub>2</sub> at 400 °C for 1.5 h and recovered sample.

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  $\geq 0.66$  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  $2\theta = 39.96^\circ$ ,  $46.16^\circ$ ,  $67.6^\circ$  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  $2\theta = 40.8^\circ$

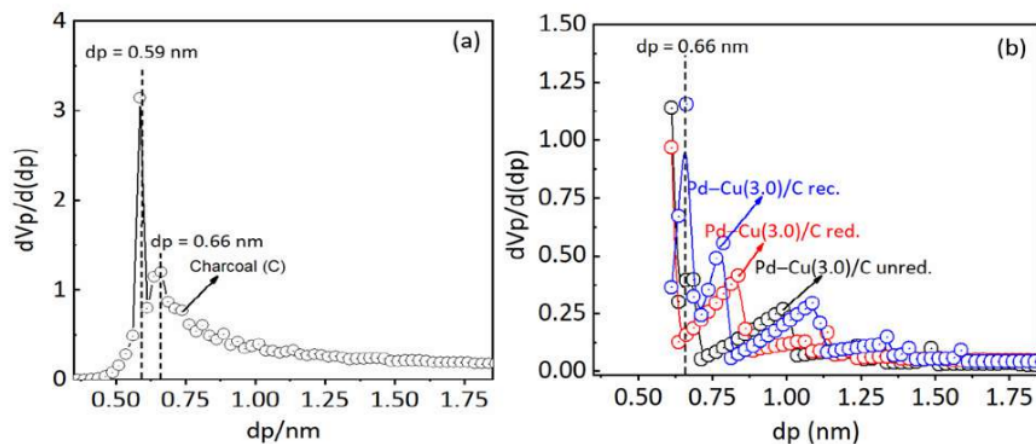


Figure 2. Pore distribution of (a) charcoal (C) and the synthesized bimetallic Pd-Cu(3.0)/C catalysts using HK approach.

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

Entry	Catalyst <sup>a</sup>	$S_{BET}^b$ ( $m^2.g^{-1}$ )	Pore Vol. <sup>b</sup> ( $m^3.g^{-1}$ )	Pore Diameter <sup>b</sup> (nm)		$H_2$ uptakes <sup>d</sup> ( $mmol.g^{-1}$ )
				BJH <sup>b</sup>	HK <sup>c</sup>	
1	Charcoal (C)	815	1.762	1.22	0.59	nd
2 <sup>e</sup>	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 <sup>f</sup>	Pd-Cu(3.0)/C recovered	601	0.428	2.85	0.71	27.8

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

become broadened, which can be attributed as the formation of bimetallic Pd-Cu alloy after reduction with H<sub>2</sub> 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 3c). A small peak at 2θ = 29.6° which can be assigned as the Cu<sub>2</sub>O(110) species (JCPDS# 78-2076) was also observed both in the as prepared and reduced Pd-Cu(3.0)/C samples (Figure 3b-c). Additionally, the broadened peak at 2θ = 21.3° can be at-

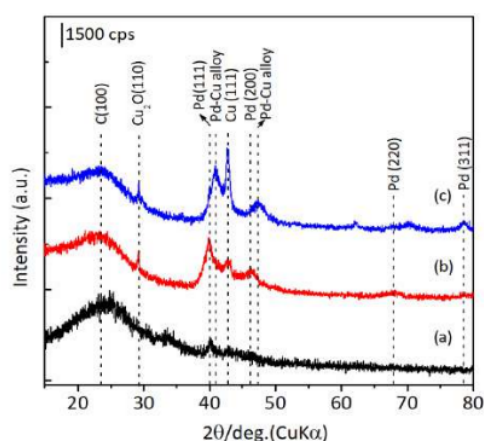


Figure 3. XRD patterns of (a) commercial Pd/C (5%wt Pd), (b) as prepared Pd-Cu(3.0)/C and (c) after reduction with H<sub>2</sub> at 400 °C for 1.5 h.

tributed 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 THFald (90%) 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<sub>2</sub>, the conversion of FFald was only 56% and yielded 28% FFalc, 15% THFald, 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<sub>2</sub> 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 THFald 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

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

Entry	Catalyst <sup>a</sup>	Composition (mmol.g <sup>-1</sup> )		Temp. (°C)	Conv. <sup>b</sup> (%)	Yield <sup>b</sup> (%)			
		Pd	M			FFalc	THFald	2-MeF	Others <sup>c</sup>
1	Pd/C <sup>d</sup>	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 <sup>e</sup>	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

<sup>a</sup>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<sub>2</sub> pressure (3.0 MPa); reaction time (1.5 h). <sup>b</sup>Conversion and yields of FFalc, THFald, and 2-MeF were determined by GC using an internal standard technique. <sup>c</sup>Others consist of condensation product of FFald or FFalc according to GC/GC-MS data. <sup>d</sup>Commercially available Pd/C (5%wt Pd). <sup>e</sup>The reaction time was 3 h.



Pd-Cu(3.0)/C catalyst. Sitthisa *et al.* [32] have noticed that the presence of Cu in Pd-Cu/SiO<sub>2</sub> catalyst to form Pd-Cu alloy phase greatly enhanced the affinity of Pd towards η<sup>2</sup>(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<sub>2</sub> 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 quantita-

tively 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<sub>2</sub>O solvent, therefore we furtherly evaluated the catalytic reaction both in H<sub>2</sub>O solvent only and the alcohols/1,4-dioxane-H<sub>2</sub>O mixture solvent and the results are also summarized in Table 3. In ethanol : H<sub>2</sub>O (1.5:2.0 v/v), 2-propanol:H<sub>2</sub>O (1.5:2.0 v/v), and 1,4-dioxane : H<sub>2</sub>O (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<sub>2</sub>O (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<sub>2</sub>O mixture solvent was used. These results are very consistent with the previous work of Dewi Astuti *et al.* [27] using bimetallic Ni-Fe(3.0)/TiO<sub>2</sub> catalysts under the identical reaction conditions. Therefore, further investigation on the hydrogenolysis of FFald using bimetallic Pd-based catalysts will be reported in our upcoming manuscript.

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

Entry	Solvent	Conv. <sup>a</sup> (%)	Yield <sup>a</sup> (%)			
			FFalc	THFalc	2-MeF	Others <sup>b</sup>
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 <sup>c</sup>
6	Toluene	56	43	13	0	0
7	H <sub>2</sub> O	67	27	13	7	20
8	Ethanol: H <sub>2</sub> O (1.5: 2.0 v/v)	98	53	18	5	32 <sup>c</sup>
9	2-Propanol/H <sub>2</sub> O (1.5: 2.0 v/v)	99	57	15	5	22
10	1,4-Dioxane/H <sub>2</sub> O (1.5: 2.0 v/v)	99	38	15	2	44 <sup>c</sup>

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



### 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 tempera-

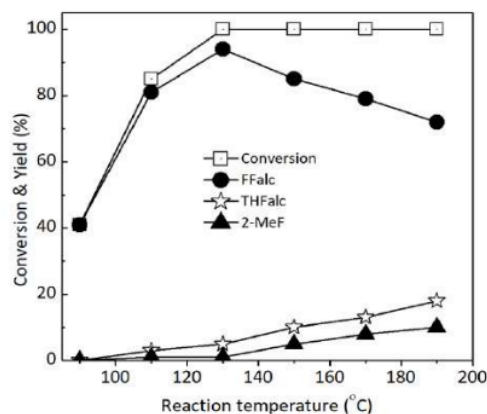


Figure 4. Effect of reaction temperature on the FFald conversion and product distribution over bimetallic Pd-Cu(3.0)/C catalyst. Reaction conditions: catalyst, 0.05 g; FFald, 1.1 mmol; iso-PrOH, 3 mL; H<sub>2</sub>, 3.0 MPa, 1.5 h.

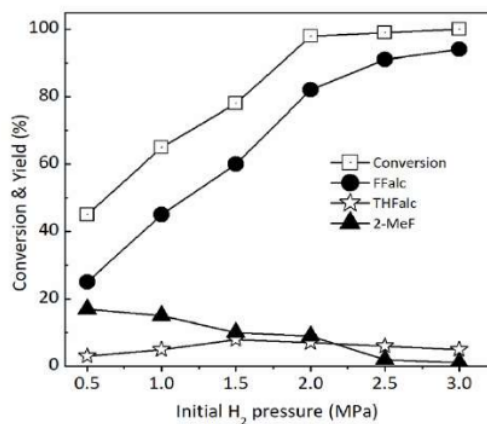


Figure 5. Effect of the initial H<sub>2</sub> pressure on the FFald conversion over bimetallic Pd-Cu(3.0)/C catalyst. Reaction conditions: catalyst, 0.05 g; FFald, 1.1 mmol; iso-PrOH, 3 mL; 130 °C, 1.5 h.

ture 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 unchanged 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<sub>2</sub> pressure

The effect of the initial H<sub>2</sub> pressure on the FFald conversion and product selectivity as shown in Figure 5. The FFald conversion and FFalc selectivity gradually increased as the initial H<sub>2</sub> pressure increased, whereas the THFalc increased at initial H<sub>2</sub> pressure of 0.5-1.0 MPa and remained unchanged at the higher initial H<sub>2</sub> pressure. On the other hand, yield of 2-MeF

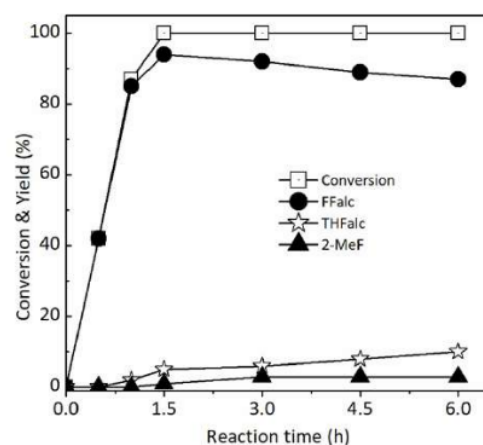


Figure 6. Time profiles of the hydrogenation of FFald over bimetallic Pd-Cu(3.0)/C catalyst. Reaction conditions: catalyst, 0.05 g; FFald, 1.1 mmol; iso-PrOH, 3 mL; 130 °C.

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 6. At the early reaction time (0.5 h), FFald conversion was 42% to produce 100% FFalc selectivity, indicating that C=O hydrogenation was taken 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 $\alpha,\beta$ -Unsaturated Ketone and Aldehyde

A substrate scope of the presence of Pd-Cu(3.0)/C catalyst in the hydrogenation of  $\alpha,\beta$ -unsaturated ketone and aldehyde was exam-

Table 4. Results of selective hydrogenation of typical  $\alpha,\beta$ -unsaturated ketone using Pd-Cu(3.0)/C catalyst.

Entry	Catalyst <sup>a</sup>	Reaction temp. (°C)	Reaction time (h)	Conv. <sup>b</sup> (%)	Selectivity <sup>b</sup> (%)		
					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. <sup>a</sup>The value in the parenthesis is Pd/Cu molar ratio, determined by ICP-OES. <sup>b</sup>Conversion and yield were determined by GC using an internal standard technique.

Table 5. Results of selective hydrogenation of typical  $\alpha,\beta$ -unsaturated aldehyde using Pd-Cu(3.0)/C catalyst

Entry	Catalyst <sup>a</sup>	Reaction temp. (°C)	Reaction time (h)	Conv. <sup>b</sup> (%)	Selectivity <sup>b</sup> (%)	
					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. <sup>a</sup>The value in the parenthesis is Pd/Cu molar ratio, determined by ICP-OES. <sup>b</sup>Conversion and yield were determined by GC using an internal standard technique

ined 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  $\alpha,\beta$ -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).

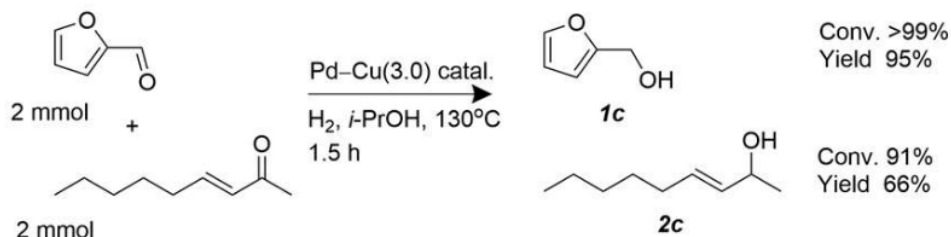
Next, we examined the catalytic reaction of typical  $\alpha,\beta$ -unsaturated aldehyde (*trans*-2-hexenaldehyde) using bimetallic Pd-Cu(3.0)/C catalyst and the results are summarized in Ta-

ble 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-hexene-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

#### Chemoselective hydrogenation of reactant mixtures



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<sub>2</sub>, 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 <sup>a</sup> (%)	Yield <sup>a</sup> (%)		
			FFalc	THFalc	2-MeF
1	1 <sup>st</sup>	>99	94	5	1
2	2 <sup>nd</sup>	82	76	5	1
3	3 <sup>rd</sup>	73	66	6	1
4 <sup>b</sup>	4 <sup>th</sup>	>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<sub>2</sub> pressure (3.0 MPa); reaction time (1.5 h). <sup>a</sup>Conversion and yields of FFalc THFalc, and 2-MeF were determined by GC using an internal standard technique. <sup>b</sup>The used Pd-Cu(3.0)/C catalyst was reduced with H<sub>2</sub> at 400 °C for 1.5 h before reaction.

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  $\alpha,\beta$ -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 or 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  $\alpha,\beta$ -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  $\alpha,\beta$ -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 be 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.

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### 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  $\alpha,\beta$ -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  $\alpha,\beta$ -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 nish 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 Ni<sub>3</sub>Sn<sub>2</sub> 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 TiO<sub>2</sub> 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., Salmikov, O.G., Khudorozhkov, A.K., Bukhtiyarov, A.V., Prosvirin, I.P., Gerasimov, E.Y., Bukhtiyarov, V.I., Koptuyug, I.V. (2015). Strong Metal-Support Interactions for Pd Supported on TiO<sub>2</sub> Catalysts in Heterogeneous Hydrogenation with Parahydrogen. *ChemCatChem*, 7, 2581–2584. DOI: 10.1002/cctc.201500618.
- [31] Pino, N., Siththisa, S., Tan, Q., Souza, T., López, D., Resasco, D.E. (2017). Structure, activity, and selectivity of bimetallic Pd-Fe/SiO<sub>2</sub> and Pd-Fe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts for the conversion of furfural. *Journal of Catalysis*, 350, 30–40. DOI: 10.1016/j.jcat.2017.03.016.
- [32] Siththisa, S., Prasomsri, T.P., Sooknoi, T., Mallinson, R.G., Resasco, D.E. (2011). Conversion of furfural and 2-methylpentanal on Pd/SiO<sub>2</sub> and Pd-Cu/SiO<sub>2</sub> 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  $\gamma$ -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 C<sub>5</sub>-furan into 1,4-pentanediol over bulk Ni-Sn alloy catalysts in an ethanol/H<sub>2</sub>O 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., Ponc, V. (1995). Activity and selectivity in the reactions of substituted  $\alpha,\beta$ -Unsaturated aldehydes. *Journal of Catalysis*, 151, 431–438. DOI: 10.1006/jcat.1995.1045.

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

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Leahy. "Hydrogenation of Furfural with a Pt-Sn Catalyst: The Suitability to Sustainable Industrial Application", Organic Process Research & Development, 2016

Publication

---

8

Takamichi Oishi. "Heterogeneously Catalyzed Efficient Alkyne-Alkyne Homocoupling by Supported Copper Hydroxide on Titanium Oxide", Chemistry - A European Journal, 08/03/2009

Publication

---

9

Kim, B.J.. "Optimization of the pore structure of nickel/graphite hybrid materials for hydrogen storage", International Journal of Hydrogen Energy, 201101

Publication

---

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Mandal, Kaustab, Debaleena Bhattacharjee, Partha Sarathi Roy, Swapan Kumar Bhattacharya, and Subrata Dasgupta. "Room temperature synthesis of Pd-Cu nanoalloy catalyst with enhanced electrocatalytic activity for the methanol oxidation reaction", Applied Catalysis A General, 2015.

Publication

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