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Hydrogenation of Biobased Aldehydes to Monoalcohols Using Bimetallic Catalysts

Giuseppe Bagnato, Michela Signoretto, Cristina Pizzolitto, Federica Menegazzo, Xiaoying Xi, Gert H. ten Brink, Bart J. Kooi, Hero Jan Heeres, and Aimaro Sanna*

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ABSTRACT: A series of monometallic and bimetallic metal catalysts (Pd, Cu, Fe, PdCu, PdFe) supported on ZrO_2 (6–8 nm) were synthesized and tested for the hydrogenation of bio-oil model compounds (furfural, vanillin, glucose) under 50 bar H_2 at 100 °C. The catalysts were fully characterized and their properties related to their catalytic activity. The bimetallic PdFe and PdCu displayed enhanced catalytic performance compared to the monometallic catalysts for aldehyde hydrogenation (furfural, vanillin, glucose). For the best catalyst, 98% vanillin alcohol (VA) and 65.5% furfuryl alcohol (FA) conversion was obtained for 80 min batch-time. PdFe showed high selectivity toward sorbitol (74%) from glucose, though at low conversion (20%). Overall, we have demonstrated that bimetallic Fe- and Cu-based catalysts promoted by Pd show significantly better performance for the partial hydrogenation of bio-oil model compounds than the corresponding monometallic ones. The better performance of the Pd-doped Fe/Cu catalysts is linked to the presence of smaller and better dispersed Pd nanoparticles (STEM) and their lower acidity ($\sim 90 \mu\text{mol/g cat}$) than corresponding monometallic ones ($\sim 167 \mu\text{mol/g cat}$).

KEYWORDS: Hydrogenation, Furfural, Vanillin, Glucose, Bimetallic catalysts

INTRODUCTION

Fast pyrolysis of biomass to bio-oil is an attractive technology due to its low environmental impact, scalability, and cost competitiveness.^{1,2} The current manufacturing costs are estimated at about \$300/t,³ which is higher than for typical fossil-based energy carriers. Moreover, bio-oil aging and phase stability are other main limitations.

The selective hydrogenation of the carbonyl bond of (unsaturated) aldehydes to form the corresponding (unsaturated) alcohols has received high attention because the products are widely used in industry.^{4–6} Moreover, the hydrogenation of aldehydes such as furfural and phenolics such as vanillin can consistently improve the stability of the bio-oil and its aging, due to the reduction of Novolak resins formation.⁷ Furfural is a compound derived from hemicellulose, and its production is estimated at about around 300 kton per annum. Possible products from reactions of furfural with hydrogen in the presence of metal catalysts are shown in Figure 1a.⁸ Partial hydrogenation leads to furfuryl alcohol (FA), which is an important chemical intermediate for the production of chemical products, such as vitamin C, lysine, plasticizers, dispersing agents, and lubricants.^{9,10} Vanillin (VL) can also be partially hydrogenated to vanillin alcohol (Figure 1

b), which finds application in foods, beverages, pharmaceuticals industries, and renewable polymers. VL current production is around 12–14 kton per year.¹¹ Moreover, lignocellulosic biomass-derived bio-oils contain a large amount of sugar-derived compounds such as glucose, levoglucosan, and cellobiose. Glucose represents a platform for the production of numerous chemicals (e.g., sorbitol) by the hydrogenation reaction (Figure 1c).

Numerous heterogeneous catalysts have been reported for the selective hydrogenation of furfural, vanillin, and glucose. Typically, noble metals such as platinum, palladium, rhodium, and ruthenium are used, which are expensive. Recent trends in nanocatalysis have shown that supported bimetallic catalysts show often improved performance compared to their monometallic analogues due to synergistic effects (electronic, geometric, other interfacial effects).¹²

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Figure 1. Catalytic hydrogenation products for (a) furfural, (b) vanillin, and (c) glucose.

When considering furfural hydrogenation to alcohols, the objective of the current study, Cu-based catalysts have shown good performance.¹³ Preferential aldehyde reduction is observed, without competitive hydrogenation of the C=C bonds. Improved bimetallic catalysts, notably with Cr (VI), have been reported, though the use of Cr(VI) is not considered green due to its carcinogenic properties. Recently, Pt, Pd, Ru, Re, and Ni have been shown to be good alternatives to Cr.^{14–17} For instance, Fulajtárova et al. showed that furfural was quantitatively hydrogenated to FA with a selectivity of 86% using a bimetallic Cu (5%)–Pd (1%) catalyst supported on MgO (80 bar H₂, 130 °C, 480 min).¹⁴ Du et al. reported studies on the hydrogenation of furfural using bimetallic Cu (2.66%)–Pd (0.25%) catalysts supported on carbon in 1,4-dioxane (170 °C, 3 h) using formic acid as the H-donor and obtained high selectivity to FA (>96%) at 100% furfural conversion.¹⁵

Bimetallic Ni-based catalysts have also been explored. Sitthisa et al. showed that the addition of Fe to Ni suppresses the decarbonylation activity of Ni,^{18,19} which is a major issue. Shi et al. reported a 74% selectivity to FA at ~97% conversion using a Fe₃₀Ni₅₀/SiO₂ catalyst at 150 °C, 20 bar H₂ (2 h), and isopropanol as the solvent.²⁰ These studies clearly indicate that supported Fe- and Cu-based catalysts promoted with noble metals are of high interest for the hydrogenation of furfural to FA.

Hydrogenation of vanillin is typically performed using monometallic noble metals (Ru and Pd).²¹ A number of Pd nanoparticles (NPs) on different supports^{22–24} have also been reported for vanillin hydrogenation to VA. It was found that their application is limited due to catalyst stability issues associated with leaching of metal nanoparticles. The use of bimetallic Cu–Pd catalysts has been reported recently.²¹ CuPd catalysts on N-rich porous organic polymers were shown to be highly efficient catalysts compared to their monometallic counterparts, providing 99.3% conversion of vanillin with a selectivity of 93.6% for the hydrogenolysis product 2-methoxy-4-methylphenol at 140 °C and 10 bar H₂ in isopropanol.²¹

When considering the selective hydrogenation of the aldehyde moiety in glucose to sorbitol, a number of monometallic catalysts have been developed. Commercially, sorbitol is obtained by using Raney Ni. Ru/C has shown to be a very attractive alternative achieving yields close to 100%; however, it is expensive and prone to coking and sulfur deactivation.²⁵ The addition of Cu NPs to Ru/C resulted in a 50% enhanced catalytic activity in glucose hydrogenation (100 °C, 80 bar H₂, 3 h, 30 mL of 40% glucose in water, 500 mg catalyst),²⁶ while the addition of Fe to Pt enhanced the catalyst activity for the hydrogenation of aldehydes, with TOF increasing from 7.8 min^{−1} (Pt) to 480 min^{−1} (PtFe), which was ascribed to stabilization of adsorbed reactive intermediates on the Pt–Fe interface through bonding with C=O groups.²⁷

The above literature indicates that Fe- and Cu-based catalysts, which are 3 and 2 orders of magnitude cheaper than Pd, are not very effective for aldehyde hydrogenation. However, little is known about the use of bimetallic Fe catalysts promoted with Pd for the hydrogenation of furfural, and also, only one paper is available for a Cu catalyst promoted by Pd for the hydrogenation of vanillin, while none are available for CuPd for glucose and FePd for vanillin and glucose hydrogenation.

We here report an experimental investigation on the use of novel bimetallic catalysts composed of a cheap metal (Fe, Cu) combined with a noble metal, such as Pd due to its high activity at mild conditions, for the aqueous phase hydrogenation of an aldehyde (furfural, vanillin, and glucose), with the aim to obtain alcohols (FA, VA, and sorbitol). Performance of the bimetallic catalysts was compared to that of the monometallic analogues. ZrO_2 was selected as the support for the following reasons: (i) It is known to be stable in aqueous media at elevated temperatures.¹³ (ii) It is less prone to deactivation (compared to TiO_2 and C).^{28,29} The catalysts were characterized in detail, and performance was tested in a batch setup using aqueous solutions of the three model components

■ EXPERIMENTAL DETAILS

Chemicals. Furfural 99% (CAS No. 98-01-1), furfuryl alcohol 98% (CAS No. 98-00-0), vanillin (CAS No. 121-33-5), vanillin alcohol $\geq 98\%$ (CAS No. 498-00-0), D-glucose $\geq 99.5\%$ (CAS No. 50-99-7), and sorbitol $\geq 98\%$ (CAS No. 50-70-4) were purchased from Sigma-Aldrich. Tetrahydrofuran for HPLC (THF, CAS No. 109-99-9) and di-*n*-butyl ether $>99\%$ (DBE, CAS No. 142-96-1) were purchased from Fisher Scientific.

Support Synthesis. $\text{Zr}(\text{OH})_4$ was prepared by the dropwise addition of the required amount of aqueous 1 M solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Aldrich, 99.5%) to water (100 mL). During addition, the pH was kept constant at 8.5 by the dropwise addition of an aqueous solution of ammonia (5 M). After addition, the suspension was aged 20 h at 90 °C. The resulting $\text{Zr}(\text{OH})_4$ was isolated by filtration, washed free from chloride (AgNO_3 test), dried in an oven at 110 °C for 15 h, and subsequently calcined in flowing air (30 mL/min) at 500 °C for 3 h to obtain the ZrO_2 support.³⁰

Catalyst Synthesis. An incipient wetness (co) impregnation method was applied to prepare the catalysts, due to its suitability for large scale applications. The proper amounts of an aqueous solution of the metal precursor (PdCl_2 , $\text{FeN}_3\text{O}_9 \cdot 9\text{H}_2\text{O}$, or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) were simultaneously added to the ZrO_2 support to obtain the desired metal content on the support (5 wt % for Cu and Fe, 1 wt % for Pd). The catalysts were dried in an oven at 110 °C for 15 h and finally calcined in flowing air (30 mL/min) at 500 °C for 3 h.

Catalysts Characterization. A detailed description of the methods used for the catalysts' characterization is reported in the Supporting Information. The metal amount on the catalyst was determined by atomic absorption spectroscopy (AAS) using a PerkinElmer Analyst 100. TEM analyses were carried out using a CM12 microscope (Philips), operating at 120 keV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained with a ThemisZ microscope (Thermo Fischer Scientific). Energy dispersive X-ray spectroscopy (EDX mapping) results were achieved with a Dual X EDX system (Bruker). TPR measurements were carried out using a homemade device. Nitrogen physisorption analyses were performed using a Tristar II Plus Micromeritics analyzer. TPO was applied to characterize the carbon species on spent catalysts using a homemade device. The surface acidity of the catalysts was determined using NH_3 -TPD measurements on an AutoChem II system (Micromeritics, USA), and the total acidity was quantified. CO_2 -TPD was run using a TA Q500. XPS analyses were carried out using a Scienta XPS with an Al

$K\alpha$ (1486.6 eV) monochromatized ($\Delta E < 300$ meV) source. O_2/H_2 pulse chemisorption measurements³¹ were performed in the same lab-made equipment used for TPR, while a Thermo Scientific Nicolet 155 model with a 1D7 ATR attachment was used for Fourier-transform infrared spectroscopy (FTIR).

Catalysts Testing Protocols. The hydrogenation reactions were carried out in a batch reactor (stainless steel, 50 mL, Amar Equipment LTD, model no. 1233). The reactor was equipped with a heating jacket to allow operation at a constant temperature. The reactor was loaded with 200 mg of catalyst and 30 mL of an aqueous solution of the model component (0.519, 0.204, and 1.07 mol/L for furfural, vanillin and glucose, respectively) and subsequently pressurized using H_2 . The concentration of the model compounds resembled the real overall amount of the specific functional group into WBO from pinewood (BTG bio-oil). All reactions were carried out at 100 °C, 50 bar, and under continuous stirring (600 rpm). Before each experiment, the catalyst was activated overnight in the presence of H_2 at 20 bar at 100 °C (PdFe and Pd), 200 °C (PdCu and Cu), or 300 °C (Fe). The reduction temperatures were determined by TPR analysis. The overnight procedure was chosen in order to have a complete reduction of the active metals as suggested by previous authors.³² The reduction of ferrous to metallic ions at 500 °C (as suggested by H_2 -TPR) was not pursued due to possible interaction of the Fe^{2+} ions with the ZrO_2 support.³³

To evaluate the performance of the catalysts, the conversion, selectivity, and TOF were calculated for the *i*-model compound using eqs 1 and 2.

$$\text{Conversion}_i(\%) = \frac{\text{mol reacted}_i}{\text{initial mole}_i} \times 100 \quad (1)$$

$$\text{Selectivity}_j(\%) = \frac{\text{mole produced}_j}{\text{mole reacted}_i} \times \frac{\nu_i}{\nu_j} \times 100 \quad (2)$$

$$\text{TOF}(\text{h}^{-1}) = \frac{\text{mole}_i|_{t=0} - \text{mole}_i|_{t=\text{reaction time}}}{\text{total mole of metal on catalyst} \times \text{reaction time}} \quad (3)$$

where ν_i and ν_j represent the stoichiometric coefficients of *i* and *j* compounds, and the total moles of metal on the catalyst are the moles of Cu, Pd, and Fe for the monometallic catalysts and the sum of the moles of metals for the bimetallic ones. Conversion levels below 20% of the maximum equilibrium conversion were employed to calculate furfural and glucose TOFs to minimize possible issues associated with excess of catalyst, undesired catalyst deactivation, and surface coverage. However, this was not possible for vanillin, since the initial conversion was already higher than 20% of the equilibrium conversion, so that the TOFs in this case were estimated by curves fitting at conversion less than 20%.

To evaluate if the system was operating free of mass transport limitations, the external (η_{ex}) and internal (η_{in}) mass transport effectiveness factors were estimated (Supporting Information) by the Damköhler number ($D_{\text{II,b}}$) and observed Thiele modulus, respectively.

Product Characterization. The glucose concentration was determined by HPLC using a Hewlett-Packard 1050 system equipped with a Bio-Rad Organic Acid column (Aminex HPX-87H) and a Waters 410 differential refractometer. Aqueous sulfuric acid (5 mmol/L) was used as the mobile phase (0.55 mL/min). The column was maintained at 60 °C. Furfural and vanillin hydrogenation products were analyzed by a Shimadzu GC-2010A gas chromatograph equipped with a FID detector using a CPWAX 57-CB column (25 m $\times$ 0.2 mm $\times$ 0.2 μm).

■ RESULTS AND DISCUSSION

Catalysts Characterization. The textural properties of the catalysts and the actual metal contents are reported in Table 1 and are discussed in the Supporting Information.

Table 1. Relevant Catalyst Properties

	Metal content ^a (%)				Pore volume ^c (cm ³ /g)	Specific surface area ^b (m ² /g)	Mean support pore diameter ^b (nm)	Mean support particles diameter ^d (nm)	H ₂ uptake (μmol/g)	Weak acid sites ^{e,f} (μmol NH ₃ /g cat)	Strong acid sites ^{e,g} (μmol NH ₃ /g cat)	Total acidity (μmol NH ₃ /g cat)	Total basicity (μmol CO ₂ /g cat)
	Pd	Fe	Cu										
Pd/ZrO ₂	1.11	—	—	—	0.27	66	19.9	7.3 ± 0.5	350	167	165	332	—
PdFe/ZrO ₂	1.00	4.11	—	—	0.25	68	18.6	8.4 ± 0.6	98	91	78	169	190
PdCu/ZrO ₂	1.05	—	4.68	—	0.26	60	18.3	6.1 ± 0.4	290	92	88	180	120
Fe/ZrO ₂	—	5.05	—	—	0.24	64	18.8	7.4 ± 0.6	280	111	119	260	160
Cu/ZrO ₂	—	—	4.28	—	0.25	61	18.4	8.0 ± 0.5	280	109	152	261	90

^aFrom atomic absorption spectroscopy analyses. ^bFrom N₂ physisorption analyses. ^cBJH. ^dFrom the Scherrer equation. ^eBy peak deconvolution from data obtained by AutoChem II system (Figure S5). ^fWeak acid sites temperature range 100–210 °C. ^gStrong acid sites temperature range 210–400 °C.

The XRD patterns of the catalysts are provided in Figure S3 (Supporting Information). The reflections were identified by using the Crystallography Open Database.³⁴ In all the samples, reflections of the zirconia support were clearly detected and showed that presence of mostly monoclinic crystallites. Application of the Scherrer equation for major ZrO₂ reflections revealed a particle size range of about 6–8.4 nm (Table 1), which is slightly smaller than found using TEM. Fe, Cu, and Pd were mainly present in the oxidic form.

Two of the catalysts (Pd/ZrO₂ and PdCu/ZrO₂) were characterized in more detail by STEM-EDX, and the results are given in Figures 2 and 3. Figure 2 shows that the Pd

Figure 2. STEM-EDX image of Pd/ZrO₂.

nanoparticles in Pd/ZrO₂ have a nanoparticle size of about 5 nm. In contrast, nanoparticles of Pd and Cu were not clearly visible in the bimetallic PdCu/ZrO₂ catalyst. EDX mapping shows that Pd and Cu are well dispersed. The dispersion of Cu on the zirconia surface derives from the intimate contact between Cu and ZrO₂, caused by the oxygen vacancies in the

Figure 3. STEM-EDX image of PdCu/ZrO₂.

latter that play key roles in determining the dispersion of the active metal component.³⁵ The adsorption of Cu at ZrO₂ surface hydroxyl sites upon deposition is favored at lower copper surface densities (as used in this work) and facilitates higher levels of Cu dispersion.³⁶ Moreover, previous work shows that the addition of Cu into Pd supported on ZrO₂ with a monoclinic crystalline structure results in Cu and Pd particles in intimate contact and highly dispersed in the support.³⁷ This is consistent with the STEM-EDX results showing good Pd dispersion. These distinct differences are expected to have impacts on catalyst performance (vide infra).

H₂-TPR data for the different catalysts are provided in Table 1 and the Supporting Information (Figure S4). The studied catalysts present similar H₂ uptake (~280–350 μmol/g), the only exception being FePd/ZrO₂ (98 μmol/g). For the monometallic Pd/ZrO₂ catalyst, only one clear peak is observed at around 100 °C, which is attributed to Pd metal formation from the oxide phase.^{38–40} Zr⁴⁺ reduction does not take place in the measured temperature range (max 700 °C), in line with literature data.⁴¹ The monometallic Cu/ZrO₂ catalyst shows two peaks, one at about 200 °C assigned to the reduction of CuO to Cu₂O and a broad peak between 250 and 400 °C assigned to the consecutive reduction of Cu₂O to Cu⁰. The presence of the two overlapping peaks can be attributed to the different CuO species that are differently interacting with the support.^{42,43} The H₂-TPR spectrum of the bimetallic CuPd/ZrO₂ shows one clear band from Cu (~230 °C) and a shoulder (~300 °C) assigned to reduction of Cu₂O to Cu⁰. The peak from Cu reduction is shifted to higher temperatures compared to monometallic Cu/ZrO₂, indicating a Cu–Pd interaction.¹⁵ The Fe/ZrO₂ catalyst shows clear peaks at about 300, 400, and 520 °C, associated with several reduction steps (Fe₂O₃ → Fe₃O₄ → Fe).⁴⁴ In the bimetallic Fe–Pd catalyst, the main reduction peaks of Fe₂O₃ are shifted to lower temperature, indicating a much stronger capability of FePd/ZrO₂ (compared to FeZrO₂) in adsorbing H₂ at low temperature.

Figure S5 shows the NH₃-TPD profiles of the catalysts studied in this work. For all the samples, an overlap of weak (160–210 °C) and strong acid peaks (240–340 °C) was observed. NH₃-TPD reveals that the bimetallic catalysts are less acidic than the monometallic ones (Table 1), with acidity similar to that of bare ZrO₂ (~160 μmol NH₃/g_{cat}).⁴⁵ The monometallic Pd/ZrO₂ catalyst was the most acidic, with 332 μmol NH₃/g_{cat} desorbed, while PdFe/ZrO₂ was the least acidic (169 μmol NH₃/g_{cat}). XPS spectra for the monometallic Fe/ZrO₂ catalyst (Figure S6) show two Fe 2p binding energy (BE) bands from Fe₃O₄ (711 and 715 eV) and one for Fe₂O₃ (725 eV). In the bimetallic FePd/ZrO₂ catalyst, these bands shift to higher BEs, which suggests the presence of Fe–Pd interactions. XPS spectra for monometallic Cu/ZrO₂ (Figure S7) indicate the presence two peaks corresponding to Cu⁰ (934.4 and 952 eV).⁴⁶ For the bimetallic Cu-based catalyst, the shakeup features of Cu 2p_{3/2} were very similar to those of the monometallic Cu catalyst but with lower binding energy, suggesting interaction between Cu and Pd, as found by the H₂-TPR analysis.

Furfural Hydrogenation. The hydrogenation of furfural using the monometallic and bimetallic catalysts was performed in a batch autoclave at 100 °C and 50 bar hydrogen, using water as the solvent. Mass-transfer resistances (external and internal diffusion limitations) were absent in the presence of furfural, as both the internal and external effectiveness were ~1

(Table S8). The concentration of furfural was 0.519 M, and the substrate–catalyst ratio was set at 7.48 g/g. The catalyst performance data are given in Table 2 and Figure 4. Some

Table 2. Hydrogenation of Furfural at 100 °C, 50 bar, Furfural 0.519 mol/L, and 200 mg Catalyst after 80 min

Catalyst	Furfural conversion (%)	Furfuryl alcohol selectivity (%)	TOF(h ^{−1})
5 wt % Cu/ZrO ₂	29.5	99	5.3
1/5 wt % PdCu/ZrO ₂	66.1	99	6.9
5 wt % Fe/ZrO ₂	26.1	99	6.5
1/5 wt % PdFe/ZrO ₂	54.7	99	2.1
1 wt % Pd/ZrO ₂	43.7	99	14

Figure 4. Hydrogenation of furfural at 100 °C, 50 bar, 30 mL of furfural 0.519 mol/L, and 200 mg of catalyst (furfural:catalyst wt ratio 7.48:1).

experiments were performed in duplicate, and the error in the conversion was shown to be about 7%. All catalysts gave close to quantitative selectivity to FA and neither ring hydrogenation nor decarbonylation, well-known side reactions, were observed. The highest furfural conversion was obtained with the bimetallic PdCu/ZrO₂ catalyst (~70% after 80 min), which is considerably higher than for the monometallic Cu/ZrO₂. A similar trend, i.e. the higher activity of the bimetallic PdFe catalyst compared the monometallic Fe one, was found for the Fe based catalysts.

A possible explanation is the better dispersion of the metals for the bimetallic catalysts compared to the monometallic ones, as was illustrated using STEM-EDX for the Pd- and Cu-based catalysts (Figure 2). To verify this, H₂ chemisorption for Fe/ZrO₂ and PdFe/ZrO₂ was carried out. Chemisorption of O₂ (at 25 °C) followed by H₂ titration (at 60 °C) resulted in 0.17 and 2.03 mLH₂/g_{cat} chemisorbed, respectively, on Fe and PdFe/ZrO₂. These data well corroborate the STEM-EDX finding of a better metal dispersion for the bimetallic catalysts.

To establish a potential relation between the NPs size and the furfural conversion, Pd and PdCu NPs were studied by scanning TEM (STEM)-EDX mapping (shown in Figures 2 and 3). The figures clearly indicate that while Pd/ZrO₂ presents a distinct Pd nanoparticle with a size of about 5 nm, there was a better dispersion of Pd for PdCu/ZrO₂, with

less agglomeration and smaller particles. Therefore, the better performance of the bimetallic PdCu is possibly related to the distinct difference in Pd NPs size that resulted in a better dispersion for the bimetallic PdCu.

Moreover, adding Pd to Cu can modify the structure and surface electronic properties of the Cu catalysts, which will affect the stability of intermediates and the adsorption capacity of Cu.⁴⁷ Since Cu has a half empty 4s band that can act as an electron donor or acceptor depending on the valence band of the different metal, while Pd has a fully filled 4d band, the electrons will flow from the Pd 4d band into the Cu 4s band, stabilizing the latter, where furfural is adsorbed via the η^1 (O)-aldehyde binding with consequent hydrogenation of the C=O bond to form FA.^{48,49}

Considering the TOF, the best results were obtained using Pd/ZrO₂ (TOF = 14 h⁻¹). Regarding selectivity, all the zirconia-supported catalysts resulted in 99% selectivity toward FA. A recent work suggested that selectivity to FA is related to Cu content in PdCu/C, with 2.66%–5.33% being the best content, while Pd content resulted in not being linked to FA selectivity.¹⁵ Such correlation was not found in our work, since also Pd alone achieved 99% selectivity to FA, suggesting that the operating conditions are the driver for high selectivity.

Vanillin Hydrogenation. The hydrogenation of vanillin was studied under the same conditions used for furfural but with a concentration of 0.204 M and a substrate–catalyst ratio of 4.65 g/g. Both internal and external diffusional resistances were not observed (Table S8). The catalysts performances are shown in Table 3 and Figure 5. Reproducibility was evaluated running two testes in triplicate with an average error of 2.2%.

Table 3. Hydrogenation of Vanillin at 100 °C, 50 bar, 30 mL of Vanillin 0.204 mol/L, and 200 mg Catalyst at 10 min^a

	Vanillin conversion (%)	Vanillin alcohol selectivity (%)	TOF ^a (h ⁻¹)
5 wt % Cu/ZrO ₂	51.4	99	22
1/5 wt % PdCu/ZrO ₂	98.2	99	41
5 wt % Fe/ZrO ₂	39.3	99	10
1/5 wt % PdFe/ZrO ₂	99.2	99	49
1 wt % Pd/ZrO ₂	71.6	99	250

^aEstimated at conversion: <20%.

The catalysts show a 99% selectivity for partial hydrogenation to vanillin alcohol, and neither cresol (C–O bond cleavage) or guaiacol (C–C bond cleavage) were detected. The highest conversion of VL was obtained for PdFe/ZrO₂ (99.2%) and PdCu/ZrO₂ (98.2%) after 40 and 80 min, respectively, which was 2-folds (Cu/ZrO₂) and 2.5-folds (Fe/ZrO₂) higher than for the monometallic zirconia catalysts.

A synergic effect is exhibited by the bimetallic catalyst and, in particular, the PdFe catalyst. A previous study reported that the Fe surface serves as the catalytic site for the activation of phenolic compounds, and Pd stabilized Fe by its electronic interaction with Fe surface atoms.⁵⁰

Rezaei et al. reported that the oxophilicity of the Fe metal causes repulsion to the phenolic ring, and in turn, a strong interaction with the carbonyl group, facilitating its selective hydrogenation to the corresponding alcohol.⁵¹ Moreover, the H₂-chemisorption tests indicate that the addition of Pd to Fe reduces the barrier to H₂ chemisorption of Fe. Furthermore, the addition of 1% Pd to 5% Cu (and possibly to Fe) is beneficial to the dispersion of the Pd nanoparticles as indicated

Figure 5. Hydrogenation of vanillin at 100 °C, 50 bar, 30 mL of vanillin 0.204 mol/L, and 200 mg catalyst (vanillin:catalyst wt ratio 4.65:1).

by the H₂-chemisorption and TEM analyses, which can be linked to the enhanced hydrogenation activity of the bimetallic species (Figure 5).

Previous works suggest that the partial hydrogenation of VL to VA is favored in the presence of basic sites.^{19,22,23} All the ZrO₂-based catalysts possess basic sites as reported in Table 1, which can be linked to the high VA selectivity.

The comparison of the VL and FU conversion data indicates that the aldehyde group of vanillin is more reactive than the aldehyde group of furfural. This could be due to differences in interactions between either the substrate or product with the catalyst.^{24,48}

Glucose Hydrodeoxygenation. The hydrogenation of glucose with an initial concentration of 1.07 M and a substrate–catalyst ratio of 28.9 g/g was studied in the water phase under the same conditions used for FU and VL. Under these conditions, internal and external diffusional resistances were not observed (Table S8). The catalysts performances are reported in Table 4 and Figure 6. The conversion of glucose

Table 4. Hydrogenation of Glucose at 100 °C, 50 bar, 30 mL of Glucose 1.07 mol/L, and 200 mg Catalyst at 120 min^a

	Glucose conversion (%)	Sorbitol selectivity (%)	TOF (h ⁻¹)
5 wt % Cu/ZrO ₂	18	34	0.7×10^{-2}
1/5 wt % PdCu/ZrO ₂	20	52	0.6×10^{-2}
5 wt % Fe/ZrO ₂	16	49	0.6×10^{-2}
1/5 wt % PdFe/ZrO ₂	19	74	0.6×10^{-2}
1 wt % Pd/ZrO ₂	18	58	1.6×10^{-2}

^aGlucose:catalyst wt ratio 28.9:1.

was relatively low (16%–20%), possibly due to a high substrate–catalyst ratio used in comparison to previous works.^{52–54} The TOF decreases in the following order Pd/ZrO₂ > PdFe/ZrO₂ > Fe/ZrO₂ > PdCu/ZrO₂ > Cu/ZrO₂. Similarly to FU and VL, the highest glucose conversion (~20%) was achieved with the bimetallic catalysts, even if the conversion difference with the monometallic counterparts was less marked, which supports the finding that more dispersed Pd

Figure 6. Hydrogenation of glucose at 100 °C, 50 bar, 30 mL of glucose solution (1.07 mol/L), and 200 mg catalyst (glucose:catalyst wt. ratio 28.9:1).

NPs (Figures 2 and 3) in the bimetallic species have a positive effect on the biosubstrate conversion.

Contrary to FU and VL, the hydrogenation of glucose led to several products (Figure 7) denoting the coexistence of

Figure 7. Selectivity of glucose hydrogenation at 100 °C and 50 bar after 120 min.

multiple reactions under the studied conditions. The aldehyde group of glucose was hydrogenated to produce sorbitol, achieving a selectivity around 74% for PdFe/ZrO₂, while the lowest value (about 34%) was detected for the Cu-containing catalysts. The catalyst selectivity for sorbitol decreased in the order PdFe/ZrO₂ > Pd/ZrO₂ > Fe/ZrO₂ > PdCu/ZrO₂ > Cu/ZrO₂, suggesting that the dispersion of the Pd NPs were not linked to the product's selectivity. The different products distribution could be linked to the catalysts acidity.⁴⁹ Figure 8 shows the relation between the acidity of the catalysts and the selectivity toward sorbitol. As can be seen, excluding Pd, there is a clear trend, where the least acid catalyst (PdFe) resulted in

Figure 8. Sorbitol selectivity vs catalysts acidity at 40 min for hydrogenation of glucose at 100 °C, 50 bar, 30 mL of glucose 1.07 mol/L, and 200 mg catalyst (glucose:catalyst wt. ratio 28.9:1).

the highest selectivity to sorbitol. Cu/ZrO₂ and in less extent CuPd/ZrO₂ favor the further hydrogenation or retro-aldol condensation of sorbitol to form glycerol and the hydrolysis to EG and PG, and this explains its low selectivity toward sorbitol.⁵⁴

Zhang et al. obtained a 60% and 75% selectivity to sorbitol, respectively, at 40 and 60 bar at 140 °C using 1.5% Pt-SBA-15 (calculated at 5% glucose conversion).⁵⁵ In the same study, it was shown that the catalyst activity increased 3-folds when the temperature was increased from 100 to 140 °C. This latter data can be used to compare the conversion obtained in our work, since similar metal loadings and H₂ pressure were used. Despite Ru and Pt being typically employed for the hydrogenation of glucose,⁵⁵ here we show that Fe promoted by Pd has a good selectivity toward sorbitol.

Catalysts Deactivation Study. Since the conversion versus batch time profiles for the reactants (Figure 4) showed signs of deactivation for the monometallic catalysts, TPO was carried out to evaluate the presence of organic deposits on the catalysts' surfaces. Figure 9a and Table S7 indicate that poisoning by organic species (in terms of mg O₂ consumed/g catalyst) occurred during the reaction and increased in the following order for furfural: PdFe/ZrO₂ < Fe/ZrO₂ < Pd/ZrO₂ < Cu/ZrO₂ < PdCu/ZrO₂. The TPO analyses of the spent catalysts from the vanillin hydrogenation instead suggest deposition of organics on the catalyst surface, mainly for the bimetallic catalysts, which are the most active (Figure 9b). Finally, the TPO analysis of spent catalysts from glucose hydrogenation (Figure 9c) shows low oxygen consumption due to the low activity of the catalysts in hydrogenating glucose. The peak between 200 and 400 °C can be ascribed to coke, while the peak at about 180 °C, which is present in PdFe/ZrO₂ and PdCu/ZrO₂, can be assigned to unreacted glucose.

EA of bare and spent catalysts (from furfural tests) were also carried out for coke quantification. Table 5 shows that PdFe/ZrO₂ had the least coke on the surface, while PdCu/ZrO₂ resulted in the highest coke yield, in agreement with the TPO analysis. Coke deposition does not seem to be linked to the catalysts' deactivation, possibly due to the fact that coke

Figure 9. TPO analyses of spent catalysts after (a) furfural, (b) vanillin, and (c) glucose hydrogenation reactions.

Table 5. EA of Spent Catalysts

Spent catalyst	C (wt %)	H (wt %)	H/C ratio (wt %)
Pd/ZrO ₂	2.01	0.14	0.07
Cu/ZrO ₂	3.52	0.19	0.05
Fe/ZrO ₂	2.94	0.14	0.05
PdCu/ZrO ₂	4.54	0.29	0.06
PdFe/ZrO ₂	1.94	0.13	0.07

formed at low temperature is less poisonous than more condensed coke generated at high temperature.⁵⁶

To elucidate if the found organic deposits were made of coke or resulted from the deposition of unreacted furfural, FTIR of the spent catalysts (Figure S8) was performed. The broad peaks between 3000 and 3400 cm⁻¹ and 1530–1630 cm⁻¹ are assigned, respectively, to weak C–H and C=C stretching vibration of aromatic groups.⁵⁷ The absence of strong transmittance bands in the range of 1000–1300 cm⁻¹, which represent the C–O–C bending vibration, indicates the absence of unconverted furfural or presence of produced furfuryl alcohol.⁵⁷ Presence of peaks at ~1400 cm⁻¹ and the narrow bands caused by the C–H out-of-plane bending mode in the range of 650–900 cm⁻¹ can be also associated to PAH molecules.⁵⁸ The H/C ratio (Table 5) of the coke on the catalysts surface somehow matches those of 2-ring PAH. Instead, H-depleted species that are typically formed at higher temperature seem to be absent on the catalysts surface,⁵⁷ as confirmed by presence of H in the EA.

However, if the TPO data are compared to the conversion ones (Figure 4), deactivation by coking can be excluded, since Fe/ZrO₂ and Cu/ZrO₂ do not present the highest organic deposits, which instead seem to be proportional to the catalysts' activity. This also suggests that other causes such as metal sintering or leaching could be linked to the monometallic deactivation. To elucidate the presence of metal leaching and sintering, AAS and XRD analyses of the spent catalysts were carried out. The AAS indicates that monometallic Fe and Cu catalysts suffered major leaching, with Fe almost disappearing from the catalyst surface and Cu decreasing from ~5% to ~3%. On the contrary, the bimetallic catalysts showed good stability, related to low metal leaching levels. Rietvel refinement (Figure S9) also confirmed the loss of Cu from the Cu/ZrO₂ spent catalyst, while metal sintering was excluded due to the unchanged in Pd and Cu peaks shape/intensities. Therefore, the deactivation of the monometallic catalysts shown in Figure 4 can be prevalently ascribed to metal leaching under the studied conditions. Further studies are required to evaluate the long-term stability of the proposed catalysts.

CONCLUSIONS

The aim of this study was to investigate the effect of adding Pd as promoter to non-noble metals such as iron and copper for the hydrogenation of the aldehyde group of different model compounds representative of pyrolysis bio-oils. Therefore, Cu,

Fe, Pd, PdCu, and PdFe supported on ZrO₂ were prepared by a wetness impregnation technique, characterized by different techniques, and used in hydrogenation experiments. For furfural and vanillin, a 99% selectivity was obtained for monoalcohols (FA and VA). The bimetallic PdFe and PdCu displayed enhanced catalytic performance in terms of reactant conversion toward VA and FA and to a less extent sorbitol, compared to the monometallic catalysts. A better dispersion of the metals for the bimetallic catalysts compared to the monometallic ones, as was illustrated using STEM-EDX, is probably the main reason behind the higher conversion of the bimetallic catalysts. Interaction of the well-dispersed Pd with Cu and Fe in the bimetallic catalysts was linked to their superior performance, due to their favorable H₂ adsorption at low temperature.

This work shows that supported non-noble metal-based catalysts containing Fe and Cu have high potential for the partial hydrogenation (or stabilization) of bio-oil model compounds by promotion with (1 wt %) of Pd. Studies on the hydrogenation of lignocellulosic biomass-derived bio-oils with the catalysts reported here and their stability are in progress and will be reported in due course.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.0c02623>.

Experimental details on catalysts characterization; results for catalysts characterization, surface analysis, TEM, XRD, H₂-TPR, NH₃-TPD, XPS, and FTIR; Rietveld refinement of bare and spent catalysts; selectivity for HDO of glucose; external and internal mass transfer limitations assessment; and pseudo-first-order reaction model of reactants conversion data (PDF)

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Notes

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