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*

Cite This: ACS Sustainable Chem. Eng. 2020, 8, 11994−12004

ABSTRACT: A series of monometallic and bimetallic metal catalysts (Pd, Cu, Fe, PdCu, PdFe) supported on ZrO2 (6−8 nm) were synthesized and tested for the hydrogenation of bio-oil model compounds (furfural, vanillin, glucose) under 50 bar H2 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 (∼90 μmol/g cat) than corresponding monometallic ones (∼167 μmol/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 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 1b), 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 cellulbiose. 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

Received: April 6, 2020
Revised: July 7, 2020
Published: July 20, 2020
When considering furfural hydrogenation to alcohols, the objective of the current study, Cu-based catalysts have shown good performance. 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. For instance, Fulajtárrova 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). 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.

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, which is a major issue. Shi et al. reported a 74% selectivity to FA at ~97% conversion using a Fe₉₀Ni₁₀/SiO₂ catalyst at 150 °C, 20 bar H₂ (2 h), and isopropanol as the solvent. 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). A number of Pd nanoparticles (NPs) on different supports 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. 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.

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. 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), 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.
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. ZrO2 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 TiO2 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 ≥98% (CAS No. 498-00-0), α-glucose ≥99.5% (CAS No. 50-99-7), and sorbitol ≥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.** Zr(OH)4 was prepared by the dropwise addition of the required amount of aqueous 1 M solution of ZrOCl2·8H2O (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 Zr(OH)4 was isolated by filtration, washed free from chloride (AgNO3 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 ZrO2 support.30

**Catalyst Synthesis.** An incipient wetness (co) impregnation method was applied to prepare the catalyst, due to its suitability for large scale applications. The proper amounts of an aqueous solution of the metal precursor (PdCl2, Fe2O3·9H2O, or Cu(NO3)2·3H2O) were simultaneously added to the ZrO2 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 TecnaiG2 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 NH3-TPD measurements on an AutoChem II system (Micromeritic, USA), and the total acidity was quantified. CO2-TPD was run using a TA Q500. XPS analyses were carried out using a Scienta XPS with an Al Kα (1486.6 eV) monochromatized (ΔE < 300 meV) source. O2/H2 pulse chemisorption measurements28 were performed in the same lab-made equipment used for TPR, while a Thermo Scientific Nicolet iS5 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, Amur 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 H2. The concentration of the model compounds resembled the real overall amount of the specific functional group into WBO from pinewood (BTG bio-ol). 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 H2 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. The reduction of ferrous to metallic ions at 500 °C (as suggested by H2-TPR) was not pursued due to possible interaction of the Fe2+ ions with the ZrO2 support.

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

\[
\text{Conversion}(\%) = \frac{\text{mol reacted}}{\text{initial mole}} \times 100
\]

\[
\text{Selectivity}(\%) = \frac{\text{mole produced}}{\text{mole reacted}} \times \frac{\nu_i}{\nu_j} \times 100
\]

\[
\text{TOF}(\text{h}^{-1}) = \frac{\text{mol}_{\text{metal}}/\text{total mole of metal on catalyst}}{\text{reaction time}}
\]

where \( \nu_i \) and \( \nu_j \) 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 bimetallic catalysts and the sum of the moles of metals for the monometallic 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 (\( \eta_w \)) and internal (\( \eta_i \)) mass transport effectiveness factors were estimated (Supporting Information) by the Damköhler number (\( D_{\text{m}} \)) 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 × 0.2 mm × 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.
The XRD patterns of the catalysts are provided in Figure S3 (Supporting Information). The reflections were identified by using the Crystallography Open Database. 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 ZrO$_2$ 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/ZrO$_2$ and PdCu/ZrO$_2$) were characterized in more detail by STEM-EDX, and the results are given in Figures 2 and 3. Figure 2 shows that the Pd nanoparticles in Pd/ZrO$_2$ have a nanoparticle size of about 5 nm. In contrast, nanoparticles of Pd and Cu were not clearly visible in the bimetallic PdCu/ZrO$_2$ 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 ZrO$_2$, caused by the oxygen vacancies in the zirconia.
latter that play key roles in determining the dispersion of the active metal component.\textsuperscript{35} The adsorption of Cu at ZrO\textsubscript{2} surface hydroxyl sites upon deposition is favored at lower copper surface densities (as used in this work) and facilitates higher levels of Cu dispersion.\textsuperscript{40} Moreover, previous work shows that the addition of Cu into Pd supported on ZrO\textsubscript{2} with a monoclinic crystalline structure results in Cu and Pd particles in intimate contact and highly dispersed in the support.\textsuperscript{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).

H\textsubscript{2}-TPR data for the different catalysts are provided in Table 1 and the Supporting Information (Figure S4). The studied catalysts present similar H\textsubscript{2} uptake (∼280–350 μmol/g), the only exception being FePd/ZrO\textsubscript{2} (98 μmol/g). For the monometallic Pd/ZrO\textsubscript{2} catalyst, only one clear peak is observed at around 100 °C, which is attributed to Pd metal formation from the oxide phase.\textsuperscript{38–40} Zr\textsuperscript{4+} reduction does not take place in the measured temperature range (max 700 °C), in line with literature data.\textsuperscript{41} The monometallic Cu/ZrO\textsubscript{2} catalyst shows two peaks, one at about 200 °C assigned to the reduction of CuO to Cu\textsubscript{2}O and a broad peak between 250 and 400 °C assigned to the consecutive reduction of Cu\textsubscript{2}O to Cu. The presence of the two overlapping peaks can be attributed to the different CuO species that are differently interacting with the support.\textsuperscript{32,43} The H\textsubscript{2}-TPR spectrum of the bimetallic CuPd/ZrO\textsubscript{2} shows one clear band from Cu (∼230 °C) and a shoulder (∼300 °C) assigned to reduction of Cu\textsubscript{2}O to Cu. The peak from Cu reduction is shifted to higher temperatures compared to monometallic Cu/ZrO\textsubscript{2}, indicating a Cu–Pd interaction.\textsuperscript{15} The Fe/ZrO\textsubscript{2} catalyst shows clear peaks at about 300, 400, and 520 °C, associated with several reduction steps (Fe\textsubscript{2}O\textsubscript{3} → Fe\textsubscript{2}O\textsubscript{4} → Fe).\textsuperscript{44} In the bimetallic Fe–Pd catalyst, the main reduction peaks of Fe\textsubscript{2}O\textsubscript{3} are shifted to lower temperature, indicating a much stronger capability of FePd/ZrO\textsubscript{2} (compared to FeZrO\textsubscript{2}) in adsorbing H\textsubscript{2} at low temperature.

Figure S5 shows the NH\textsubscript{3}-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. NH\textsubscript{3}-TPD reveals that the bimetallic catalysts are less acidic than the monometallic ones (Table 1), with acidity similar to that of bare ZrO\textsubscript{2} (∼160 μmol NH\textsubscript{3}/g cat).\textsuperscript{45} The monometallic Pd/ZrO\textsubscript{2} catalyst was the most acidic, with 332 μmol NH\textsubscript{3}/g\textsubscript{cat} desorbed, while PdFe/ZrO\textsubscript{2} was the least acidic (169 μmol NH\textsubscript{3}/g cat). XPS spectra for the monometallic Fe/ZrO\textsubscript{2} catalyst (Figure S6) show two Fe 2p binding energy (BE) bands from Fe\textsubscript{2}O\textsubscript{3} (711 and 715 eV) and one for Fe\textsubscript{3}O\textsubscript{4} (725 eV). In the bimetallic FePd/ZrO\textsubscript{2} catalyst, these bands shift to higher BEs, which suggests the presence of Fe–Pd interactions. XPS spectra for monometallic Cu/ZrO\textsubscript{2} (Figure S7) indicate the presence two peaks corresponding to Cu\textsuperscript{0} (934.4 and 952 eV).\textsuperscript{46} For the bimetallic Cu-based catalyst, the shakeup features of Cu 2p\textsubscript{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 H\textsubscript{2}-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 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/ZrO\textsubscript{2} catalyst (∼70% after 80 min), which is considerably higher than for the monometallic Cu/ZrO\textsubscript{2}. 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, H\textsubscript{2} chemisorption for Fe/ZrO\textsubscript{2} and PdFe/ZrO\textsubscript{2} was carried out. Chemisorption of O\textsubscript{2} (at 25 °C) followed by H\textsubscript{2} titration (at 60 °C) resulted in 0.17 and 2.03 mL H\textsubscript{2}/g\textsubscript{cat} chemisorbed, respectively, on Fe and PdFe/ZrO\textsubscript{2}. 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/ZrO\textsubscript{2} presents a distinct Pd nanoparticle with a size of about 5 nm, there was a better dispersion of Pd for PdCu/ZrO\textsubscript{2} 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 η1 (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 differential resistances were not observed (Table S8). The catalysts performances are shown in Table 3 and Figure 5. Reproducibility was evaluated running two tests 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

<table>
<thead>
<tr>
<th>Vanillin conversion (%)</th>
<th>Vanillin alcohol selectivity (%)</th>
<th>TOF[^a] (h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 wt % Cu/ZrO₂</td>
<td>51.4</td>
<td>99</td>
</tr>
<tr>
<td>1/5 wt % PdCu/ZrO₂</td>
<td>98.2</td>
<td>99</td>
</tr>
<tr>
<td>5 wt % Fe/ZrO₂</td>
<td>39.3</td>
<td>99</td>
</tr>
<tr>
<td>1/5 wt % PdFe/ZrO₂</td>
<td>99.2</td>
<td>99</td>
</tr>
<tr>
<td>1 wt % Pd/ZrO₂</td>
<td>71.6</td>
<td>99</td>
</tr>
</tbody>
</table>

[^a]: Estimated 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 with 71.6% conversion, while neither cresol nor guaiacol was detected. For other catalysts, the conversion varied from 18.1% to 51.4%.

**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 differential resistances were not observed (Table S8). The catalysts performances are reported in Table 4 and Figure 6. The conversion of glucose 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 was dispersed.
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 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 7. Selectivity of glucose hydrogenation at 100 °C and 50 bar after 120 min.

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 < FeZrO2 < PdZrO2 < CuZrO2 < 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 S5 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 deposit is not present on the catalysts when analyzed by TPO.

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).

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).
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. However, if the TPO data are compared to the conversion ones (Figure 4), deactivation by coking can be excluded, since Fe/ZrO$_2$ and Cu/ZrO$_2$ 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 lower metal leaching levels. Rietveld refinement (Figure S9) also confirmed the loss of Cu from the Cu/ZrO$_2$ 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.

Table 5. EA of Spent Catalysts

<table>
<thead>
<tr>
<th>Spent catalyst</th>
<th>C (wt %)</th>
<th>H (wt %)</th>
<th>H/C ratio (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/ZrO$_2$</td>
<td>2.01</td>
<td>0.14</td>
<td>0.07</td>
</tr>
<tr>
<td>Cu/ZrO$_2$</td>
<td>3.52</td>
<td>0.19</td>
<td>0.05</td>
</tr>
<tr>
<td>Fe/ZrO$_2$</td>
<td>2.94</td>
<td>0.14</td>
<td>0.05</td>
</tr>
<tr>
<td>PdCu/ZrO$_2$</td>
<td>4.54</td>
<td>0.29</td>
<td>0.06</td>
</tr>
<tr>
<td>PdFe/ZrO$_2$</td>
<td>1.94</td>
<td>0.13</td>
<td>0.07</td>
</tr>
</tbody>
</table>

However, if the TPO data are compared to the conversion ones (Figure 4), deactivation by coking can be excluded, since Fe/ZrO$_2$ and Cu/ZrO$_2$ 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 lower metal leaching levels. Rietveld refinement (Figure S9) also confirmed the loss of Cu from the Cu/ZrO$_2$ 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

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).

AUTHOR INFORMATION

Corresponding Author
Aimaro Sanna — Advanced Biofuels Lab, Institute of Mechanical, Process and Energy Engineering, School of Engineering & Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, United Kingdom; orcid.org/0000-0002-0311-4105; Phone: +44(0)1314518108; Email: A.Sanna@hw.ac.uk

Authors
Giuseppe Bagnato — Advanced Biofuels Lab, Institute of Mechanical, Process and Energy Engineering, School of Engineering & Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, United Kingdom; Department of Chemical Engineering, Engineering and Technology Institute Groningen, University of Groningen, 9747 AG Groningen, The Netherlands; orcid.org/0000-0002-6576-9625

Michela Signoretto — CATMAT Lab, Department of Molecular Sciences and Nanosystems, Ca’ Foscari University Venice and INSTM-RU Ve, 30172 Venezia Mestre, Italy; orcid.org/0000-0002-0051-2968

Cristina Pizzolitto — CATMAT Lab, Department of Molecular Sciences and Nanosystems, Ca’ Foscari University Venice and INSTM-RU Ve, 30172 Venezia Mestre, Italy; orcid.org/0000-0002-8268-4682

Federica Menegazzo — CATMAT Lab, Department of Molecular Sciences and Nanosystems, Ca’ Foscari University Venice and INSTM-RU Ve, 30172 Venezia Mestre, Italy; orcid.org/0000-0002-8032-6379

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful to the Erasmus plus training program. Also, the authors thank M. B. Figueirêdo, L. Rohrbach, and Dr. Z. Tang, Department of Chemical Engineering, Engineering and Technology Institute Groningen, University of Groningen, for technical support and TEM analysis.

REFERENCES


(2) Bagnato, G.; Boulet, F.; Sanna, A. Effect of Li-LSX zeolite, NiCe/Al₂O₃, and NiCe/ZrO₂ on the production of drop-in bio-fuels by pyrolysis and hydrotreating of Nannochloropsis and isochrysis microalgae. Energy 2019, 179, 199–213.


(26) Vedyagin, A. A.; Volodin, A. M.; Kenzhin, R. M.; Chesnokov, V. V.; Mishakov, I. V. CO Oxidation over Pd/ZrO2 Catalysts: Role of Support’s Donor Sites. Molecules 2016, 21 (10), 1289.


