Supplementary on-line information

Continuous flow synthesis of bimetallic AuPd catalysts for the selective oxidation of 5-hydroxymethylfurfural to 2,4-furandicarboxylic acid

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Figure S1: Schematic representation of the millifluidic set-up for the synthesis of Au$_x$Pd$_y$/TiO$_2$ catalysts in continuous mode. (a) Peristaltic pump, (b) PFA T-shape connection, (c) image of the PFA T-shape connection and (d) suspension of TiO$_2$ in water.
Figure S2: Representative BF-TEM images and (inset) respective particle size distributions of the various catalysts prepared in continuous mode: (a) Au/TiO$_2$, (b) Au$_{75}$Pd$_{25}$/TiO$_2$, (c) Au$_{50}$Pd$_{50}$/TiO$_2$, (d) Au$_{25}$Pd$_{75}$/TiO$_2$ and (e) Pd/TiO$_2$. 

(a) 3.2 ± 0.9 nm

(b) 3.7 ± 0.7 nm

(c) 3.2 ± 0.9 nm

(d) 3.3 ± 0.8 nm

(e) 3.1 ± 1.0 nm

Relative Frequency (%) vs. Particle Size (nm)
Figure S3: Representative BF-TEM images and (inset) the respective particle size distribution of the various catalysts prepared in batch mode: (a) Au/TiO$_2$, (b) Au$_{75}$Pd$_{25}$/TiO$_2$, (c) Au$_{50}$Pd$_{50}$/TiO$_2$, (d) Au$_{25}$Pd$_{75}$/TiO$_2$ and (e) Pd/TiO$_2$. 
Figure S4: Representative BF-TEM images and (inset) the respective particle size distributions of the Au$_{75}$Pd$_{25}$/TiO$_2$ catalyst prepared in continuous mode and subjected to thermal calcination treatment at (a) 200 °C, (b) 300 °C and (c) 400 °C.
Figure S5: Representative BF-TEM image of the Au$_{75}$Pd$_{25}$/TiO$_2$ catalyst prepared in continuous mode and heat treated at 200 °C after the 5th catalysis run. The particle size distribution is shown in the inset.
Figure S6: Au 4f XPS analysis of the batch-prepared catalysts. (a) Au$_{25}$Pd$_{75}$/TiO$_2$, (b) Au$_{50}$Pd$_{50}$/TiO$_2$, (c) Au$_{75}$Pd$_{25}$/TiO$_2$ and (d) Au/TiO$_2$. The red fitting represents the Au$^0$, while the blue fitting represents the satellite Pd 4s peak.

Figure S7: Pd 3d XPS analysis of the batch-prepared catalysts. (a) Pd/TiO$_2$, (b) Au$_{25}$Pd$_{75}$/TiO$_2$, (c) Au$_{50}$Pd$_{50}$/TiO$_2$ and (d) Au$_{75}$Pd$_{25}$/TiO$_2$. The red fitting represents the Pd$^0$, while the blue fitting represents the Pd$^{2+}$; the green fitting represents the satellite Au 4d peaks.
Figure S8: Au 4f XPS analysis of the continuous-prepared catalysts. (a) $\text{Au}_{25}\text{Pd}_{75}/\text{TiO}_2$, (b) $\text{Au}_{50}\text{Pd}_{50}/\text{TiO}_2$, (c) $\text{Au}_{75}\text{Pd}_{25}/\text{TiO}_2$ and (d) $\text{Au}/\text{TiO}_2$. The red fitting represents the Au$^0$, while the blue fitting represents the satellite Pd 4s peak.

Figure S9: Pd 3d XPS analysis of the continuous-prepared catalysts. (a) $\text{Pd}/\text{TiO}_2$, (b) $\text{Au}_{25}\text{Pd}_{75}/\text{TiO}_2$, (c) $\text{Au}_{50}\text{Pd}_{50}/\text{TiO}_2$ and (d) $\text{Au}_{75}\text{Pd}_{25}/\text{TiO}_2$. The red fitting represents the Pd$^0$, while the blue fitting represents the Pd$^{2+}$; the green fitting represents the satellite Au 4d peaks.
Figure S10: XPS survey scans for the batch-prepared catalysts. (a) Pd/TiO$_2$, (b) Au$_{25}$Pd$_{75}$/TiO$_2$, (c) Au$_{50}$Pd$_{50}$/TiO$_2$, (d) Au$_{75}$Pd$_{25}$/TiO$_2$ and (e) Au/TiO$_2$. 
Figure S11: XPS survey scans for the continuous-prepared catalysts. (a) Pd/TiO₂, (b) Au₂5Pd₇5/TiO₂, (c) Au₅₀Pd₅₀/TiO₂, (d) Au₇₅Pd₂₅/TiO₂ and (e) Au/TiO₂.
Figure S12: Au4f XPS analysis of the continuous-prepared Au75Pd25/TiO2 catalysts heat treated at different temperature. (a) untreated, (b) 200 °C, (c) 300 °C and (d) 400 °C. The red fitting represents the Au\(^{0}\), while the blue fitting represents the satellite Pd 4s peak.

Figure S13: Pd3d XPS analysis of the continuous-prepared Au75Pd25/TiO2 catalysts heat treated at different temperature. (a) untreated, (b) 200 °C, (c) 300 °C and (d) 400 °C. The red fitting represents the Pd\(^{0}\), while the blue fitting represents the Pd\(^{2+}\); the green fitting represents the satellite Au 4d peaks.
Figure S14: XPS survey scans for the continuous-prepared Au$_{75}$Pd$_{25}$/TiO$_2$ catalysts heat treated at different temperatures. (a) untreated, (b) 200 °C, (c) 300 °C and (d) 400 °C.
Table S1: Au:Pd molar ratio and Au 4f\textsubscript{7/2} and Pd 3d\textsubscript{5/2} binding energy of the catalysts prepared in in continuous (Au\textsubscript{75}Pd\textsubscript{25}/TiO\textsubscript{2}-C) heat treated at different temperature. The ratios are calculated from XPS quantification.

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<th>Catalyst</th>
<th>Au:Pd ratio (mol/mol)</th>
<th>Binding Energy (eV)</th>
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<tr>
<td></td>
<td></td>
<td>Au 4f\textsubscript{7/2}</td>
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<tr>
<td>Au\textsubscript{75}Pd\textsubscript{25}/TiO\textsubscript{2}-C</td>
<td>76 : 24</td>
<td>83.2</td>
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<td>Au\textsubscript{75}Pd\textsubscript{25}/TiO\textsubscript{2}-C-200</td>
<td>72 : 28</td>
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<td>83.1</td>
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<tr>
<td>Au\textsubscript{75}Pd\textsubscript{25}/TiO\textsubscript{2}-C-400</td>
<td>71 : 29</td>
<td>83.2</td>
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