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Supplementary on-line information

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

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<u>Figure S1</u>: Schematic representation of the millifluidic set-up for the synthesis of Au_xPd_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.











<u>Figure S2:</u> 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 .











<u>Figure S3:</u> 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 .







<u>Figure S4</u>: 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.



<u>Figure S5</u>: 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.



<u>Figure S6:</u> Au4f 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.



<u>Figure S7</u>: Pd3d XPS analysis of the batch-prepared catalysts. (a) Pd/TiO₂, (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 Pd⁰, while the blue fitting represents the Pd²⁺; the green fitting represents the satellite Au 4d peaks.



<u>Figure S8</u>: Au4f XPS analysis of the continuous-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.



<u>Figure S9</u>: Pd3d XPS analysis of the continuous-prepared catalysts. (a) Pd/TiO₂, (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 Pd⁰, while the blue fitting represents the Pd²⁺; the green fitting represents the satellite Au 4d peaks.



<u>Figure S10</u>: XPS survey scans for the batch-prepared catalysts. (a) Pd/TiO₂, (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 .



<u>Figure S11</u>: XPS survey scans for the continuous-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 .



<u>Figure S12</u>: Au4f XPS analysis of the continuous-prepared $Au_{75}Pd_{25}/TiO_2$ 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.



<u>Figure S13</u>: Pd3d XPS analysis of the continuous-prepared $Au_{75}Pd_{25}/TiO_2$ catalysts heat treated at different temperature. (a) untreated, (b) 200 °C, (c) 300 °C and (d) 400 °C. The red fitting represents the Pd⁰, while the blue fitting represents the Pd²⁺; the green fitting represents the satellite Au 4d peaks.



<u>Figure S14</u>: XPS survey scans for the continuous-prepared $Au_{75}Pd_{25}/TiO_2$ catalysts heat treated at different temperature. (a) untreated, (b) 200 °C, (c) 300 °C and (d) 400 °C.

<u>Table S1</u>: Au:Pd molar ratio and Au $4f_{7/2}$ and Pd $3d_{5/2}$ binding energy of the catalysts prepared in in continuous (Au₇₅Pd₂₅/TiO₂-C) heat treated at different temperature. The ratios are calculated from XPS quantification.

Catalyst	Au:Pd ratio (mol/mol)	Binding Energy (eV)	
		Au 4f _{7/2}	Pd 3d _{5/2}
Au ₇₅ Pd ₂₅ /TiO ₂ -C	76 : 24	83.2	334.7
Au ₇₅ Pd ₂₅ /TiO ₂ -C-200	72 : 28	83.1	334.7
Au ₇₅ Pd ₂₅ /TiO ₂ -C-300	70 : 30	83.1	334.6
Au ₇₅ Pd ₂₅ /TiO ₂ -C-400	71 : 29	83.2	334.8