Supporting Information

Efficient Preparation of Biobased N-butane Directly from Levulinic Acid over Pt/C


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The conversion and yield were calculated as following:

LA: Levulinic acid; VA: Valeric acid.

\[
n (LA) = \frac{m (LA)}{116} \\
n (VA) = \frac{m (VA)}{102} \\
n (n\text{-butane}) = \frac{m (n\text{-butane})}{58}
\]

Conversion of LA= \[
\left[1 - \frac{n (LA \text{ after reaction})}{n (LA \text{ before reaction})}\right] \times 100\%
\]

Yield of VA = \[
\frac{n (VA \text{ after reaction})}{n (LA \text{ before reaction})} \times 100\%
\]

Yield of n-butane = \[
\frac{n (n\text{-butane after reaction}) \text{ in organic solvent} + n (n\text{-butane after reaction}) \text{ in gas}}{n (LA \text{ before reaction})} \times 100\%
\]

N-butane in gas (n(n\text{-butane})_g) was calculated as following:

The volume fraction of n-butane (\(\gamma\)) in the reaction gas was estimated by GC.

\[
n(n\text{-butane})_g = \gamma \cdot \frac{pV}{(RT)},\text{ }p\text{ is the reactor pressure after the reaction, } V\text{ is the reactor volume occupied by gas, } T\text{ is room temperature.}
\]

Turnover frequency (TOF) was figured out as following:

Method 1\(^{[1]}\):

Dispersion(Pt)\(_1\) and n(Surface Pt)\(_1\) was estimated by CO titration (Figure S9). Dispersion(Pt)\(_1\): Pt/C - 24.7%; Pt/C(400) - 32.3%; Pt/C(600) - 41.9%; Pt/C(800) - 24.1%.

Method 2\(^{[2]}\):

\[
n(\text{Surface Pt})_2 = \text{Dispersion(Pt)}_2 \times n(\text{Pt}) = \left(\frac{1}{\text{Pt size}}\right) \times 100\% \times n(\text{Pt}), \text{Pt size is the average Pt nanoparticle size (nm) measured by TEM (Figure S8), } n(\text{Pt})\text{ is the amount of Pt used in the reaction.}\text{ Dispersion(Pt)}_2: \text{Pt/C} - 66.7%; \text{Pt/C}(400) - 38.5%; \text{Pt/C}(600) - 31.3%; \text{Pt/C (800) - 18.2%}.
\]

TOF\(_1\) = \[
\frac{[n (LA \text{ after reaction}) - n (LA \text{ before reaction})]}{[n(\text{Surface Pt})_1 \times t]},
\]

\[\]

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TOF₂ = [n(LA after reaction) - n(LA before reaction)] / [n(Surface Pt) × t],

where t is the reaction time.

**Figure S1** XRD profiles of Pt/ZrO₂, Pt/Nb₂O₅, Pt/Al₂O₃, Pt/C(OH⁻) and Pt/C.
Table S1 Physicochemical properties of various catalysts in this work

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m$^2$/g)</th>
<th>Pore diameter (nm)</th>
<th>Pore volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$V_{\text{total}}$</td>
</tr>
<tr>
<td>Pt/C</td>
<td>1171.9</td>
<td>3.51</td>
<td>1.03</td>
</tr>
<tr>
<td>Pt/C(OH$^-$)</td>
<td>704.0</td>
<td>3.36</td>
<td>0.59</td>
</tr>
<tr>
<td>Pt/C(400)</td>
<td>1295.4</td>
<td>3.50</td>
<td>1.12</td>
</tr>
<tr>
<td>Pt/C(600)</td>
<td>1253.1</td>
<td>3.80</td>
<td>1.19</td>
</tr>
<tr>
<td>Pt/C(800)</td>
<td>1111.4</td>
<td>3.96</td>
<td>1.10</td>
</tr>
<tr>
<td>Pt/Al$_2$O$_3$</td>
<td>157.1</td>
<td>5.48</td>
<td>0.22</td>
</tr>
<tr>
<td>Pt/ZrO$_2$</td>
<td>369.8</td>
<td>3.71</td>
<td>0.34</td>
</tr>
<tr>
<td>Pt/Nb$_2$O$_3$</td>
<td>301.3</td>
<td>3.36</td>
<td>0.25</td>
</tr>
</tbody>
</table>
Figure S2 TEM images of (a) Pt/C, (b) Pt/Al$_2$O$_3$, (c) Pt/Nb$_2$O$_5$ and (d) Pt/ZrO$_2$. 

![TEM images of Pt/C, Pt/Al$_2$O$_3$, Pt/Nb$_2$O$_5$, and Pt/ZrO$_2$.](image)
Figure S3 GC signals (Panna, A91 PLUS) (a) TCD profiles of mixed gas standard sample, (b) TCD profiles of gas product from LA to n-butane, (c) FID
profiles of n-butane standard sample, (d) FID profiles of gas product from LA to n-butane. H₂ is the carrier gas; hexane is the organic solvent.

Note:

The mole of CO₂ was calculated as following:

The volume fraction of CO₂ (χ) in the reaction gas was estimated by GC.

\[ pV = \frac{n(\text{CO}_2)}{\chi}*RT \]

\( p \) is the reactor pressure after the reaction, \( V \) is the reactor volume occupied by gas, \( T \) is room temperature.

\( n(\text{CO}_2) = 4.2 \text{ mmol} \), \( n(\text{n-butane}) = 3.8 \text{ mmol} \).

Reaction conditions: LA 4 mmol, 5wt% Pd/C(OH\(_2\)) 0.09 g, hexane 6 mL, H\(_2\)O 12 mL, initial pressure of H\(_2\) 100 psi, 300°C, 4 h, 600 rpm.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>GVL VA n-butane</td>
</tr>
<tr>
<td>1</td>
<td>100.0</td>
<td>0.0 0.0 95.5</td>
</tr>
<tr>
<td></td>
<td>100.0</td>
<td>0.1</td>
</tr>
<tr>
<td>---</td>
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</tr>
<tr>
<td>3</td>
<td>100.0</td>
<td>0.1</td>
</tr>
</tbody>
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Reaction conditions: LA 4 mmol, 5wt% Pd/C(OH⁻) 0.09 g, hexane 6 mL, H₂O 12 mL, initial pressure of H₂ 100 psi, 300°C, 4 h, 600 rpm.
Figure S4 NH₃ titration profiles of (a) Pt/C, (b) Pt/C(OH⁻) and (c) Pt/C(H⁺)
Figure S5 NH$_3$ titration profiles of (a) Pt/C, (b) Pt/C(400), (c) Pt/C(600) and (d) Pt/C(800).
Figure S6 XRD profiles of Pt/C, Pt/C(400), Pt/C(600) and Pt/C(800).
Figure S7 CO titration profiles of (a) Pt/C, (b) Pt/C(400), (c) Pt/C(600) and (d) Pt/C(800).
Table S3 Physicochemical properties of Pt/C(OH\(^{-}\)) and Pt/C(OH\(^{-}\)) (Spent)

<table>
<thead>
<tr>
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<td>Pt/C(OH(^{-}))</td>
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<td>3.36</td>
<td>0.59</td>
</tr>
<tr>
<td>Pt/C(OH(^{-}))(Spent)</td>
<td>661.1</td>
<td>3.15</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Figure S8 XRD profiles of Pt/C(OH\(^{-}\)) and Pt/C(OH\(^{-}\))(spent).
Figure S9 TEM images of (a) Pt/C(OH⁻) and (b) Pt/C(OH⁻)(spent).
Reference
