Supplementary information for

Liquid-Phase Catalytic Transfer Hydrogenation and Cyclization of Levulinic Acid and its Esters to γ-valerolactone Over Metal Oxide Catalysts

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Table S1. Catalytic transfer hydrogenation of ethyl levulinate over ZrO₂ in the presence of sec-butyl phenol with varying molar ratios of isopropanol to ester.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>EL (wt%)</th>
<th>SBP (wt%)</th>
<th>Molar ratio IPA:EL</th>
<th>Time (h)</th>
<th>Conv (%)</th>
<th>GVL yield (%)</th>
<th>GVL formation rate (μmol g(^{-1}) min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.6</td>
<td>86.4</td>
<td>1:1</td>
<td>16</td>
<td>28.0</td>
<td>18.1</td>
<td>2.2</td>
</tr>
<tr>
<td>2</td>
<td>8.6</td>
<td>77.1</td>
<td>4:1</td>
<td>16</td>
<td>77.3</td>
<td>72.6</td>
<td>--</td>
</tr>
<tr>
<td>3</td>
<td>7.7</td>
<td>69.7</td>
<td>7:1</td>
<td>1</td>
<td>34.5</td>
<td>33.4</td>
<td>70.1</td>
</tr>
<tr>
<td>4</td>
<td>7.7</td>
<td>69.7</td>
<td>7:1</td>
<td>16</td>
<td>97.3</td>
<td>93.3</td>
<td>--</td>
</tr>
</tbody>
</table>

\(^a\)Batch reactions, mass ratio ZrO₂:EL = 1:2.4, 150 °C, 300 psig He. Only by-product detected was isopropyl levulinate.
Methods and Materials

Catalyst preparation

The $\gamma$-$\text{Al}_2\text{O}_3$ catalyst was used as-received (STREM, $>97\%$, low soda). The MgO/Al$_2$O$_3$ catalyst was obtained by calcination of hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}$·4H$_2$O, Aldrich) in 60 cc (STP)/min flowing air at 723 K for 4 h prior to use in batch experiments. The CeZrO$_x$ and ZrO$_2$ catalysts were prepared by precipitation of Ce(NO$_3$)$_3$·6H$_2$O and ZrO(NO$_3$)$_2$ with NH$_4$OH (Aldrich), according to Serrano-Ruiz et al. Solids were calcined in 60 cc (STP)/min flowing air at 723 K for 4 h prior to use in batch experiments. The MgO/ZrO$_2$ catalyst was prepared by precipitation of Mg(NO$_3$)$_2$·6H$_2$O and ZrOCl$_2$·6H$_2$O with NaOH (Aldrich), according to Aramendia et al. Solids were calcined in 60 cc (STP)/min flowing air at 873 K for 4 h prior to use in batch experiments.

Batch reactor studies

Reactions were carried out using a 50 mL pressure vessel (Hastelloy C-276, Model 4792, Parr Instrument). After loading the reactant solution, catalyst, and magnetic stirrer bar into the reactor, the vessel was sealed, purged with 300 psig He, and pressurized with He (300 psig) to maintain the reaction mixture in the liquid phase. Mechanical stirring was maintained using a magnetic stirrer plate (500 rpm).

Continuous flow reaction experiments

The flow reactor was a 6.4 mm (0.25 inch) outer diameter stainless steel tube with wall thickness of 0.7 mm (0.028 inch). The catalyst bed consisted of calcined catalyst (0.25 g) loaded between a quartz wool plug and fused SiO$_2$ granules (-4+16 mesh, Sigma-Aldrich). The reactor was heated with a furnace composed of close-fitting aluminum blocks externally heated by an insulated furnace (1450 W/ 115 V, Applied Test Systems Series 3210), and temperature was
monitored using a K type thermocouple (Omega) placed outside the reactor immediately next to
the position of catalyst bed. Temperature was controlled with a PID temperature controller (Love
Controls, Series 16A). Liquid feed solution was introduced into the reactor with co-feeding of He
in an up-flow configuration. A HPLC pump (LabAlliance, Series 1) was used to control the
liquid feed rate. Gas flow was controlled with a mass-flow controller (Brooks 5850 model), and
the system pressure was maintained at 300 psig by passing the effluent gas stream through a
back-pressure regulator (GO Regulator, Model BP-60). The effluent liquid was collected in a
gas-liquid separator and drained periodically for analysis by GC. Carbon balances closed within
5% for all data points. Reaction conditions were 5 wt% butyl levulinate in 2-butanol as feed,
WHSV = 0.18 h⁻¹, 150 °C, 300 psig He. The catalyst was regenerated in-situ by calcination in 60
cc (STP)/min flowing air at 723 K for 4 h.

Analytical methods

Quantitative analyses were performed by gas chromatography (Shimadzu GC2010 with
an FID and RTx-5 column). Identification of products was performed using a gas
chromatograph-mass spectrometer (Shimadzu Corp., GCMS-QP2010S) equipped with a SRXI-
5MS capillary column (30 m × 0.25 mm × 0.25 μm).

References

1. J. C. Serrano-Ruiz, J. Luettich, A. Sepúlveda-Escribano and F. Rodríguez-Reinoso,
   Ruiz and F. J. Urbano, Colloids and Surfaces A: Physicochemical and Engineering