Supporting Information

Efficient and selective Hydrogenation of Biomass-Derived Furfural to Cyclopentanone Using Ru Catalysts

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Spectra data of CPO
Experimental

1. Materials preparation

MIL-101 was prepared and purified as reported before. Typically, a mixture of 1.2 g (3 mmol) of Cr(NO$_3$)$_3$$\cdot$9H$_2$O, 500 mg of terephthalic acid (H$_2$bdc, 3 mmol), and 0.6 mL of 5 M HF (3 mmol) in 15 mL H$_2$O was heated at 220 °C for 8 h in a Teflon-lined stainless steel bomb. The resulting green solid was passed through a coarse glass filter to remove the unreacted colorless crystals of H$_2$bdc and filtered on the dense paper filter. Then the green raw product was washed in hot DMF (100 °C 8 h, 2 times) and in hot EtOH (80 °C, 8 h, 2 times), filtered off, and dried overnight in an oven at 75 °C.

Synthesis of Ru/MIL-101: a series of supported ruthenium catalysts were synthesized using a simple incipient wetness impregnation method.

Using the synthesis of 1 wt% Ru/MIL-101 as an example, a solution of acetone and activated MIL-101 (300 mg, 6 mL) was first prepared. Then, another freshly prepared mixture of acetone and RuCl$_3$ (1021 mg L$^{-1}$, 6 mL) was added under vigorously stirring. The suspension was stirred for 24 h followed by washing thoroughly with deionized water. The sample was dried at 100 °C under vacuum for 2 h, and finally treated in a stream of H$_2$ at 200 °C for 2 h to yield Ru/MIL-101. The Ru loading on the sample was 1 wt% based on atomic absorption spectroscopy (AAS) analysis. An identical protocol was followed for the preparation for other Ru/MIL-101 catalysts except using different amounts of RuCl$_3$ (12.2, 18.4, 24.5, and 30.7 mg for 2, 3, 4, and 5 wt% Ru, respectively).
2. Materials characterization

Powder XRD patterns of the materials were collected on a Rigaku diffractometer (D/MAX-III A, 3KW) employing Cu Kα radiation (λ = 0.1543 nm) at 40 kV, 30 mA at room temperature. The surface area and porosity were measured by N₂ physisorption at 77 K on a Micromeritics ASAP 2020 instrument. The samples were evacuated at 423 K for 12 h before analysis. The metal contents of the materials were determined quantitatively by atomic absorption spectroscopy (AAS) on a HITACHI Z-2300 instrument.

Transmission Electron Micrographs (TEM) were recorded on a JEOL JEM-2010HR instrument operated at 300 kV. Samples were suspended in ethanol and deposited straightaway on a copper grid prior to analysis.

XPS measurements were performed in a ultra high vacuum (UHV) multipurpose surface analysis system (SpecsTM model, Germany) operating at pressures <10⁻¹⁰ mbar using a conventional X-ray source (XR-50, Specs, Mg Kα, 1253.6 eV) in a “stop-and-go” mode to reduce potential damage due to sample irradiation. Detailed Ru high-resolution spectra (pass energy 25 and 10 eV, step size 1 and 0.1 eV, respectively) were recorded at room temperature with a Phoibos 150-MCD energy analyser. Powdered samples were deposited on a sample holder using double-sided adhesive tape and subsequently evacuated under vacuum (<10⁻⁶ Torr) overnight. Eventually, the sample holder containing the degassed sample was transferred to the analysis chamber for XPS studies. Binding energies were referenced 190 to the C1s line at 284.6 eV from adventitious carbon. Deconvolution curves for
the XPS spectra were obtained using software supplied by the spectrometer manufacturer.

DRIFT experiments were conducted in an FTS 6000 Bio-Rad instrument with a resolution up to 0.15 cm⁻¹. Spectra were scanned at different temperatures in transmittance mode over the wavenumber range of 4000–650 cm⁻¹, with a scan speed of 0.20 209 cm s⁻¹ and 30 accumulations at a resolution of 4 cm⁻¹. A background spectrum of air was scanned under the same instrumental conditions before each series of measurements.

3. Catalytic hydrogenation of furfural

Hydrogenation of furfural was performed in a 10 mL stainless steel autoclave equipped with a magnetic stirrer, a pressure gauge, and an automatic temperature controller. Typically, 500 mg (5.2 mmol) furfural with catalyst (Ru 0.28 mol%) and 5 mL deionized water were loaded into the reactor. Then the autoclave was sealed and purged with hydrogen at low pressure for several times to remove air. After the autoclave was heated to the desired temperature, hydrogen (4 MPa) was charged into the reactor to start the reaction. In order to investigate the reaction kinetics, the liquid phase was sampled at certain time during the reaction process. After reaction, the autoclave was cooled to room temperature. The solid catalyst was isolated from the solution by centrifugation. The liquid phase was collected, then extracted by ethyl acetate, and subsequently analyzed by GC-MS (7890 GC/5975C MS) equipped with a HP-innowax capillary column (30 m × 0.25 mm). ¹H NMR and ¹³C NMR data were
obtained on Bruker Avance III 400 spectrometer using CDCl₃ as solvent and tetrhmethylsilane (TMS) as an internal standard.

The conversions and selectivities were evaluated on the basis of the amounts of furfural. The conversion of furfural (mol%), products yield (mol%) and cyclopentanone selectivity (mol%) were calculated using the following equations:

\[
\text{Furfural conversion} = \left(1 - \frac{\text{Moles of furfural}}{\text{Moles of furfural loaded}}\right) \times 100\%
\]

\[
\text{Product selectivity} = \frac{\text{Moles of product}}{\text{Moles of furfural converted}} \times 100\%
\]

\[
\text{Cyclopentanone yield} = \frac{\text{Moles of cyclopentanone}}{\text{Moles of furfural loaded}} \times 100\%
\]

\[
\text{Carbon balance} = \frac{\text{Moles of products}}{\text{Moles of furfural converted}} \times 100\%
\]

4. Effect of stirring speed on furfural hydrogenation

In a liquid-phase heterogeneous catalytic system, the stirring speed is too important to be ignored because it could decrease external diffusion limitations between the different phases and also influence the reaction rate and production selectivity. In order to rule out the effect of potential external mass transfer on the reaction, the hydrogenation of furfural over 3 wt% Ru/MIL-101 was carried out at 120 °C and 4 MPa H₂ under different stirring speeds. The results indicated that when the stirring speed was over 1200 rpm, there was no significant improvement in reaction rate when further increasing the stirring speed. Thus, we choose the stirring
speed of 1200 rpm for all the tests performed in this work.

5. Effect of water filling on furfural hydrogenation

The furfural hydrogenation was carried out at 160 °C and 4 MPa $\text{H}_2$ using the 3% Ru/MIL-101 catalyst (0.28 mol% Ru) with 5.2 mmol FFA dissolved in different quantities of water (3 mL, 5 mL, and 7 mL). The reaction performed in 5 mL water obtained the highest furfural conversion and CPO selectivity within 2.5 h. Therefore, 5 mL water was selected as the optimized condition for the hydrogenation reactions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Water filling (mL)</th>
<th>Conv. (%)</th>
<th>Selectivity (%)</th>
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<tr>
<td></td>
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<tr>
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<td>2</td>
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<td>3</td>
<td>7</td>
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References:


Table S1. Characterization results of Ru/MIL-101 materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ru content measured (wt%)</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$S_{Langmuir}$ (m$^2$ g$^{-1}$)</th>
<th>$V_{pore}$ (cm$^3$ g$^{-1}$)</th>
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<td>MIL-101</td>
<td>-</td>
<td>2863</td>
<td>3623</td>
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<td>2 wt% Ru/MIL-101</td>
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<td>4 wt% Ru/MIL-101</td>
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<td>5 wt% Ru/MIL-101</td>
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<td>1.12</td>
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<td>3 wt% Ru/MIL-101 reused for 6 times</td>
<td>3.1</td>
<td>2304</td>
<td>3190</td>
<td>1.15</td>
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</table>
Figure S1. Powder XRD patterns of MIL-101 (a); 1 wt% Ru/MIL-101 (b); 2 wt% Ru/MIL-101 (c); 3 wt% Ru/MIL-101 (d); 5 wt% Ru/MIL-101 (e); and 3 wt% Ru/MIL-101 after catalytic reaction (f).
**Figure S2.** Nitrogen adsorption isotherms of MIL-101(▲); 1 wt% Ru/MIL-101(◇); 2 wt% Ru/MIL-101(○); 3 wt% Ru/MIL-101(■), 5 wt% Ru/MIL-101(◆), and 3 wt% Ru/MIL-101 after catalytic reaction (●).
Figure S3. XPS spectra of Ru3p for 3 wt% Ru/MIL-101.
Figure S4. TEM images of Ru/MIL-101 samples with 4 wt% Ru (a), and 5 wt% Ru (b), respectively.
Figure S5. Activity profile for the conversion of FFA; with catalyst (◆), and with filtration (◇). Reaction conditions: FFA (5.2 mmol), catalyst (Ru 0.28 mol%), water (5 mL), 160 °C, 4 MPa H₂, 2.5 h.
$^1$H NMR and $^{13}$C NMR spectra of CPO.