Supporting Information

Synthesis of jet fuel range high-density polycycloalkanes with polycarbonate waste

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1. Materials

In this work, pure PC pellets (2 mm length × 2 mm diameter) from Luxi Chemical Group Co., Ltd. were used as a model of waste PC. In hydrodeoxygenation (HDO) tests, the bisphenol A \( (i.e. \ 1A) \) was bought from Aladdin company, while the 4,4’-(ethane-1,1-diyl)diphenol \( (i.e. \ 2A) \) and 4,4’-methylenediphenol \( (i.e. \ 3A) \) were purchased from Tokyo Chemical Industry (TCI) Co., Ltd.. The activated carbon loaded noble metal (denoted as M/C, \( M = \text{Pt, Pd or Ru} \)) catalysts were obtained from Aladdin company. We chose Pt, Pd and Ru as active metals because they are often used catalysts in many hydrogenation reactions. The H-ZSM-5, H-β and H-MOR zeolite were purchased from Nankai University. According to the information from the supplier, the SiO\(_2\)/Al\(_2\)O\(_3\) molar ratios of these zeolites were 25, 160 and 24, respectively.

2. Characterization

The specific BET surface areas of the activated carbon loaded noble metal (denoted as M/C, \( M = \text{Pt, Ru or Pd} \)) and zeolite catalysts (see Table S1) used in the HDO of bisphenols were determined by \( \text{N}_2 \)-physisorption at 77 K using a Micromeritics ASAP 2010 apparatus.

The XRD patterns of M/C catalysts were obtained with a PW3040/60X’ Pert PRO (PANalytical) diffractometer equipped with Cu \( K_\alpha \) radiation source \( (\lambda = 0.15432 \ \text{nm}) \) at 40 kV and 40 mA. Based on the XRD results, the average particle sizes of catalysts (see Table S1) were estimated by Debye-Scherrer equation.

The metal dispersions in M/C catalysts (see Table S1) were measured with a Micromeritics AutoChem II 2920 Automated Catalyst Characterization System based on the molar ratios of CO chemisorption and noble metals in the catalysts. These values correspond to the ratios of
surface metal atoms to total metal atoms assuming that the stoichiometry of adsorbed CO to surface metal atom is one. Before the tests, the samples were dried in helium flow at 393 K for 0.5 h and cooled down to 323 K. After the stabilization of baseline, the CO adsorption was carried out at 323 K by the pulse adsorption of 5% CO in He.

The acid amounts and acid strengths of the zeolites were characterized by NH$_3$-chemisorption and NH$_3$-TPD. Before each test, 0.1 g sample was placed in a quartz reactor, pretreated in He flow at 773 K for 0.5 h and cooled down in He flow to 373 K. After the stabilization of base line, pulses of NH$_3$ (1 mL) were dosed in the reactor until saturation. The amount of acid sites on the catalyst was calculated by the adsorptions of NH$_3$ during the test. Subsequently, the desorption of NH$_3$ was conducted in He flow from 373 K to 1073 K at a heating rate of 10 K min$^{-1}$. The desorbed NH$_3$ molecules were detected by a mass spectrometry (MS) OminiStar equipped with the software quadstar.

3. **Activity test**

3.1 *Alcoholysis and glycolysis of PC waste*

The alcoholysis and glycolysis reactions of PC waste were carried out in a batch reactor in a 100 mL stainless steel batch reactor (Parr 4848) under nitrogen atmosphere. For each test, 1 g PC waste and 40 mL alcohol (or polyol) were used. After purging the reactor with nitrogen for three times, the mixture was stirred at 413-473 K for 3 h, then quenched to room temperature with cool water. Subsequently, an excess amount of methanol was added to into the reaction system. According to the saturated solutions of bisphenol A (*i.e.* IA in Scheme 2) and carbonates at room temperature, the amount of methanol used in this work was more than enough to dissolve them even when they were produced at 100% yield. The residual PC
waste is unsolvable in methanol. Therefore, it was easily separated from the alcoholysis product by filtration, dried at 343 K overnight and weighted to calculate the conversion of PC waste. The \( \text{1A} \) generated during the alcoholysis (or glycolysis) of PC waste was solved in methanol and quantificationally analyzed by an Agilent 7890A GC. The PC waste conversions and the \( \text{1A} \) yields in the alcoholysis (or glycolysis) tests were calculated according to following equations.

**Conversion of PC waste (%)**

\[
\text{Conversion of PC waste} \% = \left( \frac{\text{Initial weight of PC waste} - \text{the weight of residual PC waste}}{\text{Initial weight of PC waste}} \right) \times 100\%
\]

**Yield of \( \text{1A} \) (%)**

\[
\text{Yield of \( \text{1A} \) \( \% \)}} = \left( \frac{\text{Mole of \( \text{1A} \) generated during the alcoholysis (or glycolysis) test}}{\text{Theoretical mole of \( \text{1A} \) which should be produced from the complete conversion of the PC waste}} \right) \times 100\%
\]

3.2 **Hydrodeoxygenation (HDO) of bisphenols**

The HDO of bisphenols was carried out in a 100 mL stainless steel batch reactor (Parr 4848). For each test, 5 mmol bisphenol, 40 mL cyclohexane, 0.04 g M/C catalyst and 0-0.6 g zeolite were used. After purging the reactor and filling it with hydrogen, the reaction system was heated to 353-453 K and vigorously stirred at that temperature for certain time. During the reaction, hydrogen was added from time to time to keep the system pressure at 3 MPa. After the test, the reactor was quenched to room temperature with cool water. The unreacted hydrogen was released. The liquid product was separated with catalyst by filtration, diluted and analyzed by an Agilent 7890A GC. The bisphenol conversions and yields of specific products during the HDO tests were calculated according following equations.

**Conversion of bisphenol (%)**

\[
\text{Conversion of bisphenol} \% = \left( \frac{\text{Initial mole of bisphenol in the feedstock} - \text{mole of}
\]
unreacted bisphenol in the product)/(Initial mole of bisphenol in the feedstock) × 100%

Yield of specific product (%) = (Mole of carbon atoms in the specific HDO product/Mole of carbon atoms in the bisphenol feedstock) × 100%

**General experimental details for NMR and GC-MS analysis**

$^1$H NMR and $^{13}$C NMR spectra were recorded at room temperature in CDCl$_3$ on Bruker AVANCE III 400 MHz instrument. The chemical shifts for $^1$H NMR were recorded in ppm downfield using the peak of CDCl$_3$ (7.26 ppm) as the internal standard. The chemical shifts for $^{13}$C NMR were recorded in ppm downfield using the central peak of CDCl$_3$ (77.16 ppm) as the internal standard. GC-MS analysis of the samples was carried out by Varian Corp 450GC/320MS which was equipped with a HP-5 capillary column.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.75–1.58 (m, 10H), 1.39–1.08 (m, 8H), 1.02 (t, $J = 7.0$ Hz, 2H), 0.91–0.74 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 45.8, 34.5, 33.9, 27.0, 26.6.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.81–1.65 (m, 10H), 1.30–1.13 (m, 8H), 1.00–0.89 (m, 4H), 0.70 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 44.0, 27.6, 27.3, 27.2, 20.6.
Table S1. Specific BET surface areas ($S_{\text{BET}}$), actual metal contents, average metal particle sizes and metal dispersions of activated carbon loaded noble metal catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$S_{\text{BET}}$ ($\text{m}^2 \text{ g}^{-1}$)$^a$</th>
<th>Actual metal content (wt.%)$^b$</th>
<th>Metal dispersion (%)$^c$</th>
<th>Average metal particle size (nm)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>882</td>
<td>3.7</td>
<td>7.7</td>
<td>0.9</td>
</tr>
<tr>
<td>Pd/C</td>
<td>1108</td>
<td>4.0</td>
<td>14.0</td>
<td>4.9</td>
</tr>
<tr>
<td>Ru/C</td>
<td>659</td>
<td>4.6</td>
<td>0.2</td>
<td>2.7</td>
</tr>
</tbody>
</table>

$^a$ Measured by $\text{N}_2$-physisorption. $^b$ Measured by ICP analysis. $^c$ Calculated based on the CO-chemisorption results. $^d$ Estimated from the XRD results by Debye-Scherrer equation.
Figure S1. GC chromatograms of the products from the reaction of PC waste with methanol (a), ethanol (b), 1,2-propylene glycol (c) and ethylene glycol (d). Reaction conditions: 453 K, 3 h; 1 g PC waste and 40 mL alcohol (or polyol) were used in the tests.
Figure S2. GC chromatograms of the products from the HDO of 1A over the Pt/C catalyst.

Reaction conditions: 453 K, 3 MPa H$_2$, 1 h; 5 mmol 1A, 40 mL cyclohexane and 0.04 g Pt/C catalyst were used for the test.
Figure S3. Mass spectrogram of the 1B from the HDO of 1A over the Pt/C catalyst. Reaction conditions: 453 K, 3 MPa H$_2$, 1 h; 5 mmol 1A, 40 mL cyclohexane and 0.04 g Pt/C catalyst were used for the test.
**Figure S4.** Mass spectrogram of the 1C from the HDO of 1A over the Pt/C catalyst. Reaction conditions: 453 K, 3 MPa H₂, 1 h; 5 mmol 1A, 40 mL cyclohexane and 0.04 g Pt/C catalyst were used for the test.
Figure S5. GC chromatograms of the products from the HDO of 1A over the Pt/C + H-MOR (a), Pt/C + H-ZSM-5 (b) and Pt/C + H-β (c) catalysts. Reaction conditions: 453 K, 3 MPa H₂, 1 h; 5 mmol 1A, 40 mL cyclohexane, 0.04 g Pt/C catalyst and 0.5 g zeolite were used for the tests.
Figure S6. Mass spectrogram of the 1D from the HDO of 1A over the Pt/C + H-β catalyst. 

Reaction conditions: 453 K, 3 MPa H₂, 1 h; 5 mmol 1A, 40 mL cyclohexane, 0.04 g Pt/C catalyst and 0.5 g H-β zeolite were used for the test.
Figure S7. $^{13}$C and $^1$H NMR spectra of the 1D from the HDO of 1A over the Pt/C + H-β catalyst. Reaction conditions: 413 K, 3 MPa H$_2$, 4 h; 5 mmol 1A, 40 mL cyclohexane, 0.04 g Pt/C and 0.5 g H-β zeolite were used for the test.
Figure S8. Mass spectrogram of the methylcyclohexane from the HDO of 1A over the Pt/C + H-β catalyst. Reaction conditions: 453 K, 3 MPa H$_2$, 1 h; 5 mmol 1A, 40 mL cyclohexane, 0.04 g Pt/C catalyst and 0.5 g H-β zeolite were used for the test.
Figure S9. Mass spectrogram of the ethylcyclohexane from the HDO of 1A over the Pt/C + H-β catalyst. Reaction conditions: 453 K, 3 MPa H₂, 1 h; 5 mmol 1A, 40 mL cyclohexane, 0.04 g Pt/C catalyst and 0.5 g H-β zeolite were used for the test.
**Figure S10.** The pore diameters of H-ZSM-5, H-Beta (H-β) and H-MOR zeolites according to reference.¹
Figure S11. GC chromatograms of the products from the HDO of 2A (a) and 3A (b) over the Pt/C + H-β catalyst. Reaction conditions: 413 K, 3 MPa H₂, 4 h; 5 mmol 2A or 3A, 40 mL cyclohexane, 0.04 g Pt/C catalyst and 0.5 g H-β zeolite were used for each test.
Figure S12. Mass spectrogram of the 2D from the HDO of 2A over the Pt/C + H-β catalyst.

Reaction conditions: 413 K, 3 MPa H\textsubscript{2}, 4 h; 5 mmol 2A, 40 mL cyclohexane, 0.04 g Pt/C catalyst and 0.5 g H-β zeolite were used for the test.

In this work, we could not selectively produce 2D and 2E under the investigated conditions. 2D and 2E always produced at the same time. It is difficult to separate them. That is the reason why we did not give the \textsuperscript{13}C and \textsuperscript{1}H NMR spectra of the 2D and 2E.
**Figure S13.** Mass spectrogram of the 2E from the HDO of 2A over the Pt/C + H-β catalyst.

Reaction conditions: 413 K, 3 MPa H₂, 4 h; 5 mmol 2A, 40 mL cyclohexane, 0.04 g Pt/C catalyst and 0.5 g H-β zeolite were used for the test.
**Figure S14.** Mass spectrogram of the **3D** from the HDO of **3A** over the Pt/C + H-β catalyst.

Reaction conditions: 413 K, 3 MPa H₂, 4 h; 5 mmol **3A**, 40 mL cyclohexane, 0.04 g Pt/C catalyst and 0.5 g zeolite were used for the test.
Figure S15. $^{13}$C and $^1$H NMR spectra of the 3D from the HDO of 3A over the Pt/C + H-β catalyst. Reaction conditions: 413 K, 3 MPa H$_2$, 4 h; 5 mmol 3A, 40 mL cyclohexane, 0.04 g Pt/C and 0.6 g H-β zeolite were used for each test.
Figure S16. Mass spectrogram of the 3E from the HDO of 3A over the Pt/C + H-β catalyst. Reaction conditions: 413 K, 3 MPa H₂, 4 h; 5 mmol 3A, 40 mL cyclohexane, 0.04 g Pt/C catalyst and 0.5 g H-β zeolite were used for the test.

In this work, we could not selectively produce 3E under the investigated conditions. 3D and 3E always produced at the same time. It is difficult to separate them. That is the reason why we did not give the $^{13}$C and $^1$H NMR spectra of the 3E.
Figure S17. GC chromatogram of the products from the HDO of 3A over the Pt/C catalyst.

Reaction conditions: 413 K, 3 MPa H₂, 4 h; 5 mmol 3A, 40 mL cyclohexane, 0.04 g Pt/C catalyst were used for the test.
Figure S18. Mass spectrogram of the 3F from the HDO of 3A over the Pt/C catalyst.

Reaction conditions: 413 K, 3 MPa H₂, 4 h; 5 mmol 3A, 40 mL cyclohexane, 0.04 g Pt/C catalyst were used for the test.
Reference