Title: Production of $p$-xylene from bio-based 2,5-dimethylfuran over high performance catalyst WO$_3$/SBA-15

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Supporting information

1. Material synthesis

Preparation of WO$_3$. WO$_3$ was synthesized according to the literature.$^1$ Solution A was prepared by dissolving 3.33 g of CaCl$_2$ (Aladdin) and 0.20 g of PVP (Sigma) in 25 mL of water and solution B was prepared by dissolving 1.65 g of Na$_2$WO$_4$·2H$_2$O (Sinopharm) and 0.20 g of PVP in 25 mL of water. Then solution B was added dropwise into solution A and the mixture was stirred for another 30 min. And then 16 mL of 6 N HCl was added. Finally the mixture was transferred into 150 mL round-bottom flask and reacted at 80 °C for 3 h to get the yellow precipitate. The precipitate was collected by filtration, dried, and calcined at 550 °C for 2 h to get WO$_3$.

Preparation of WO$_3$/ZrO$_2$. WO$_3$/ZrO$_2$ was synthesized according to the literature.$^2, 3$ 1.0 g of P123 (EO$_{20}$PO$_{70}$EO$_{20}$, average Mn=5800, Aldrich) and 3.222 g of ZrOCl$_2$·8H$_2$O (Sinopharm) were added in 25 mL of water under stirring at 60 °C. After P123 was absolutely dissolved, NH$_3$·H$_2$O was added dropwise until the pH of the resulting synthesis gel reached 9.0. After further stirring for another 20 h, the synthesis gel was transferred into a Teflon-lined stainless steel autoclave and kept at 100 °C for 24 h. The solid product was washed with a large amount of water and ethanol to wipe off P123 and dried at 80 °C to obtain Zr(OH)$_4$. The as-synthesized Zr(OH)$_4$ was added to the (NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$·xH$_2$O aqueous solution by the impregnation method. The mixture was treated with an ultrasonic cleaner for 0.5 h to sufficiently disperse WO$_3$. It was afterwards stirred for another 4 h and dried at 120 °C overnight. Finally, it was calcined in air at 700 °C for 3 h with a rate of 2 °C/min and 0.20-WO$_3$/ZrO$_2$-700 was obtained.

Preparation of Sn-Beta. Sn-Beta was prepared by a post-synthetic insertion of Sn atoms into framework vacancy defects of dealuminated Beta zeolites via isopropanol flux.$^4$ Dealumination
treatment of Al-Beta (SiO$_2$/Al$_2$O$_3$=25, Nankai University Catalyst Co., Ltd) was performed using HNO$_3$ (Beijing Chemical Plant). 5.0 g of Al-Beta was treated by 100 mL of concentrated HNO$_3$ (65 wt%) at 80 ºC for 20 h. Then the dealuminated zeolite Beta was collected by centrifugation, washed by water until the supernatant approached a neutral pH and dried at 80 ºC overnight. Then 2.0 g of the dealuminated zeolite Beta was added to 54 mmol of SnCl$_4$·5H$_2$O (Sigma) in 200 mL of dried isopropanol (anhydrous grade, Aladdin) and placed in a reflux setup under inert atmosphere. After 7 h, the product was filtered, washed with dry isopropanol, dried, and calcined at air (3 ºC/min to 200 ºC, dwell 6 h, 3 ºC/min to 550 ºC, dwell 6 h).

2. Figures and Tables

![Figure S1 The reactor and sampling system](image)

The reactor and sampling system were designed as described in Figure S1. The inlet gas valve was connected with the gas cylinder by a one-way valve to ensure safety and realize the constant supply of ethylene. There was also a sampling system which can be operated under the reaction conditions by turning off the inlet valve and opening the sampling valve. The sample (2~3 mL) was temporarily stored in a sampling tube and cooled to ambient temperature. When the sample was taken, about 50~80 psi pressure was lost. The inlet valve was opened to restore the initial
pressure.

Figure S2 EDS images of 0.05-WO$_3$/SBA-15-700

Figure S3 EDS images of 0.20-WO$_3$/SBA-15-700
Figure S4 EDS images of 0.35-WO₃/SBA-15-700

Figure S5 (a) N₂ adsorption/desorption isotherms and (b) pore size distributions of SBA-15 and WO₃/SBA-15 with different loading

Figure S6 NH₃-TPD profiles of 0.20-WO₃/SBA-15-700.
Figure S7 (a) Pore size distribution (corresponds to the desorption branch) of WO$_3$/ZrO$_2$ and (b) NH$_3$-TPD profiles of WO$_3$/ZrO$_2$.

Figure S8 Carbon balance versus X with different concentrations of acid sites (catalyst: 0.20-WO$_3$/SBA-15-700)
Table S1 Catalytic results of 0.20-WO$_3$/SBA-15-y with varying calcined temperature

(Reaction conditions: catalyst amount, 1.0 g; reaction time, 24 h)

<table>
<thead>
<tr>
<th>Calcined temperature ($^\circ$C)</th>
<th>X of DMF (%)</th>
<th>Carbon balance (%)</th>
<th>PX (%)</th>
<th>HDO (%)</th>
<th>MPB (%)</th>
<th>Cycloadduct (%)</th>
<th>MCP (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>93.5</td>
<td>71.6</td>
<td>88.8</td>
<td>5.0</td>
<td>4.7</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>500</td>
<td>71.9</td>
<td>75.7</td>
<td>80.2</td>
<td>7.9</td>
<td>9.5</td>
<td>0.9</td>
<td>1.5</td>
</tr>
<tr>
<td>600</td>
<td>73.7</td>
<td>79.4</td>
<td>82.9</td>
<td>6.7</td>
<td>8.5</td>
<td>0.8</td>
<td>1.1</td>
</tr>
<tr>
<td>700</td>
<td>88.7</td>
<td>80.0</td>
<td>88.0</td>
<td>3.0</td>
<td>7.8</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>800</td>
<td>73.2</td>
<td>83.8</td>
<td>85.2</td>
<td>5.0</td>
<td>8.0</td>
<td>0.9</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Figure S9 Carbon balance versus X with catalysts calcined at different temperatures

(catalyst amount: 1.0 g)
Figure S10 (a) TEM image of 0.20-WO$_3$/SBA-15-700 after reaction; (b) TEM image of fresh Sn-Beta; (c) TEM image of Sn-Beta after reaction

Figure S11 TG curves of the fresh and spent catalysts
Table S2 Selectivity for other products after 24 h of reaction

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$X$ (%)</th>
<th>Carbon balance (%)</th>
<th>Product distribution (%)</th>
<th>PX</th>
<th>HDO</th>
<th>MPB</th>
<th>Cycloadduct</th>
<th>MCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20-WO$_3$/SBA-15-700</td>
<td>92.7</td>
<td>81.0</td>
<td>88.1, 3.3, 7.7, 0.9, 0</td>
<td></td>
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</tr>
<tr>
<td>Sn-Beta</td>
<td>58.8</td>
<td>78.1</td>
<td>83.8, 5.4, 4.5, 1.7, 4.6</td>
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</tr>
</tbody>
</table>

Figure S12 (a) XRD patterns of fresh and reused (after five runs) 0.20-WO$_3$/SBA-15-700; (b) TEM image of regenerated 0.20-WO$_3$/SBA-15-700 after five runs

References


