Supporting information

Direct Conversion of Syngas to Aromatics

Junhao Yang\textsuperscript{[a] \ [b]}, Xiulian Pan\textsuperscript{* \ [a]}, Feng Jiao\textsuperscript{[a] \ [b]}, Jian Li\textsuperscript{[a] \ [b]}, Xinhe Bao\textsuperscript{* \ [a]}

\textsuperscript{[a]} State Key Laboratory of Catalysis, National Laboratory for Clean Energy, 2011-Collaboative Innovation Center of Chemistry for Energy Materials, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, China
\textsuperscript{[b]} University of Chinese Academy of Sciences, 19 A Yuquan Road, Shijingshan District, Beijing 100049, China

Email: panxl@dicp.ac.cn, xhbao@dicp.ac.cn

Experimental Details

Catalyst preparation

The mixed metal oxide was prepared by co-precipitation method, similar to our previous report.\textsuperscript{[1]} Briefly, 12.48 g Zn(NO$_3$)$_2$·6H$_2$O, 5.61 g Cr(NO$_3$)$_3$·9H$_2$O, 5.27 g Al(NO$_3$)$_3$·9H$_2$O were dissolved in 100 ml distilled water and (NH$_4$)$_2$CO$_3$ aqueous solution was used as the precipitant. After precipitation, it was aged for 3 h at the same temperature, followed by filtration and washing by distilled water. The resulting product was dried overnight at 383 K and then calcined at 773 K for 4 h.

ZSM-5 was synthesized hydrothermally. Typically, NaAlO$_2$, 25\% tetrapropylammonium hydroxide (TPAOH), tetraethyl orthosilicate (TEOS) and urea were dissolved in 26.7 ml distilled water with a molar ratio of SiO$_2$ : Al$_2$O$_3$ : TPAOH : H$_2$O : urea = 1 : 0.0025 : 0.4 : 45 : 2.8 unless otherwise stated.\textsuperscript{[2]} Then the mixture was transferred into a Teflon-lined autoclave, and kept for 4 days at 453 K. After filtering and washing by distilled water, the resulting product was dried overnight at
383 K, and then it was calcined for 4 h at 773 K.

The composite catalyst is prepared by mixing and grinding of the two components in an agate mortar with the mass ratio of \( \text{ZnCrO}_x / \text{ZSM-5} = 3/1 \) unless otherwise stated.

**Catalytic reaction tests**

Catalytic reactions were performed with fixed-bed stainless steel reactor furnished with a quartz tube (outside diameter = 7 mm) lining in a continuous flow. Typically 280 mg composite catalyst (20 – 40 mesh) with \( \text{ZnCrO}_x / \text{ZSM-5} = 3/1 \) (mass ratio) was used. The catalyst was subjected to in situ reduction in \( \text{H}_2 \) for 4 h at 623 K. A premixed syngas was used as the feed with \( \text{CO}/\text{H}_2 = 1/1 \) (molar) containing 5% Ar as the internal standard for online gas chromatography (GC) analysis. Reaction was carried out at 4.0 MPa, 623 K and 1500 ml h\(^{-1}\)·g\(_{\text{cat}}^{-1}\) unless otherwise stated. Data were collected after at least 4 hours on stream.

MTA was performed on the same ZSM-5 for comparison at atmospheric pressure. Methanol was introduced into the catalyst bed with He as the carrier gas. The weight hourly space velocity of methanol was 0.3 h\(^{-1}\), equivalent to the CO converted in the OX-ZEO process assuming 100% methanol conversion.

Products were analyzed by an online GC (Agilent 7890B) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Porapak Q and 5 Å molecular sieves packed columns were connected to TCD while HP-FFAP and HP-AL/S capillary columns were connected to FID. Oxygen-containing compounds and hydrocarbons up to \( \text{C}_{17} \) were analyzed by FID, while CO, \( \text{CO}_2 \), \( \text{C}_2\text{H}_4 \), and \( \text{C}_2\text{H}_6 \) were analyzed by TCD. \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_6 \) were taken as a reference bridge between FID and TCD. CO conversion was calculated on a carbon atom basis, i.e.

\[
\text{Con}_{\text{co}} = \frac{\text{CO}_{\text{inlet}} - \text{CO}_{\text{outlet}}}{\text{CO}_{\text{inlet}}} \times 100\%
\]

Where \( \text{CO}_{\text{inlet}} \) and \( \text{CO}_{\text{outlet}} \) represent moles of CO at the inlet and outlet, respectively. \( \text{CO}_2 \) selectivity (\( \text{Sel}_{\text{CO}_2} \)) was calculated according to:
\[ \text{Sel}_{CO_2} = \frac{CO_{2\text{outlet}}}{CO_{inlet} - CO_{outlet}} \times 100\% \]

Where \( CO_{2\text{outlet}} \) denotes moles of \( CO_2 \) at the outlet.

The selectivity of individual hydrocarbon \( C_nH_m \) \( (\text{Sel}_{C_nH_m}) \) was obtained according to:

\[ \text{Sel}_{C_nH_m} = \frac{nC_nH_m\text{outlet}}{\sum nC_nH_m\text{outlet}} \times 100\% \]

The selectivity to oxygenates were below 1\% C and therefore were not reported in the product selectivity. The carbon balance was over 95%.

**Catalyst characterization**

Temperature-programmed-desorption of \( NH_3 \) \( (NH_3-\text{TPD}) \) was performed on a Micromeritics AutoChem 2910 equipped with a thermal conductivity detector (TCD). The catalyst was first pretreated in a flowing He at 723 K for 1.5 h. After cooling down to 373 K under flowing He, the sample was exposed to 15\% \( NH_3/He \) at 373 K. Then the sample was swept by He at 373 K till a stable baseline was obtained. Subsequently, signal was recorded while the temperature was increased from 373 to 1073 K at a heating rate of 10 K/min.

X-ray diffraction (XRD) was measured on a PANalytical X'pert PPR diffractometer equipped with CuK\( \alpha \) radiation source \( (\lambda = 1.5418 \text{ Å}) \), operated at 40 mA and 40 kV. XRD patterns were recorded in the range of \( 2\theta = 5 \text{ – } 40^\circ \).

Scanning electron microscope (SEM) was performed on an FEI QUANTA 200FEG microscope at 20 kV.

X-ray fluorescence (XRF) was measured on PANalytical ZETIUM operated at 3 kW.
Figure S1. XRD patterns of ZSM-5 with different SiO$_2$/Al$_2$O$_3$ ratios.

Table S1. The specific production selectivity of syngas conversion over ZnCrO$_x$–ZSM-5-533.[a]

<table>
<thead>
<tr>
<th>CO Conversion [%]</th>
<th>16.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ Selectivity [%]</td>
<td>46.9</td>
</tr>
</tbody>
</table>

Selectivity in hydrocarbons [%]

<table>
<thead>
<tr>
<th>Hydrocarbons</th>
<th>Selectivity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>1.7</td>
</tr>
<tr>
<td>C$_2$−C$_4$</td>
<td>7.1</td>
</tr>
<tr>
<td>C$_2$−C$_4$</td>
<td>8.0</td>
</tr>
<tr>
<td>Total C$_5$+</td>
<td>83.2</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.7</td>
</tr>
<tr>
<td>Xylenes</td>
<td>13.0</td>
</tr>
<tr>
<td>Trimethylbenzenes</td>
<td>34.2</td>
</tr>
<tr>
<td>Tetramethylbenzenes</td>
<td>10.2</td>
</tr>
<tr>
<td>Other aromatics (C$<em>8$–C$</em>{10}$)</td>
<td>14.8</td>
</tr>
<tr>
<td>Total aromatics</td>
<td>73.9</td>
</tr>
<tr>
<td>Non-aromatic C$_{5+}$</td>
<td>9.3</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: ZnCrO$_x$–ZSM-5-533 (containing 50 wt% ZnCrO$_x$), 623 K, 4.0 MPa, GHSV = 1500 ml h$^{-1}$ g$_{cat}^{-1}$, H$_2$/CO = 1/1. There are no C$_{11+}$ hydrocarbons detected.
Figure S2. Reproducibility test of catalysts, which have been prepared and evaluated in different batches under the same reaction conditions. Reaction conditions: 623 K, 4.0 MPa and GHSV 1500 ml h\(^{-1}\)·g\(_{\text{cat}}\)^{-1}.

References
