Supplementary Information for

Ethylene oligomerization into linear olefins over cobalt oxide on carbon catalyst

Authors:
Alvin Jonathan¹, Nathaniel M. Eagan¹, David L. Bruns², Shannon S. Stahl², Michael P. Lanci³, James A. Dumesic¹, and George W. Huber*¹

¹Department of Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI, 53706, USA.
²Department of Chemistry, University of Wisconsin-Madison, Madison, WI, 53706, USA.
³ExxonMobil Research and Engineering, Annandale, NJ, 08801, USA.
*Corresponding author: gwhuber@wisc.edu

Table of contents:
Supplementary Method
Supplementary Discussion
Table S1
Figures S1-12
Supplementary Method: Calculating calibration constants for C₂ up to C₁₀ olefins in GC-FID

A calibration constant \( k_i \) with \( i \) carbon atoms is defined as the ratio of the olefin concentration (mol\%) with \( i \) carbon atoms and the corresponding GC area (a.u.). A linear correlation of \( 1/k_i \) as a function of \( i \) was observed for C₂ up to C₆ olefins from the Scotty gas standard (a mixture of 0.1 mol\% of each C₂-C₆ LAO and 99.5 mol\% of He). From the linear extrapolation of \( 1/k_i \) as a function of \( i \), the calibration constants for C₈ and C₁₀ olefins were calculated.
Supplementary Discussion: Obtaining the $\alpha$ parameter of a Schulz-Flory distribution

The equation defining the Schulz-Flory distribution is given as follows:

$$W_n = \frac{\alpha^{n-1}(1 - \alpha)^2}{n}$$

(1)

Where $W_n$ is the product weight fraction (which in this case is the same as the carbon selectivity), $n$ is the number of repeat units, and $\alpha$ is the chain growth probability. From rearrangement of the equation and taking the $\log_{10}$, the equation becomes:

$$\log_{10} \left( \frac{W_n}{n} \right) = (n - 1)\log_{10} (\alpha) + 2\log_{10} (1 - \alpha)$$

(2)

$$\log_{10} \left( \frac{W_n}{n} \right) = n\log_{10} (\alpha) + [2\log_{10} (1 - \alpha) - \log_{10}(\alpha)]$$

(3)

By making a plot of $\log_{10} \left( \frac{W_n}{n} \right)$ as a function of $n$, the chain growth probability ($\alpha$) could be calculated from $10^{\text{slope}}$.

First order deactivation rate constant

The equation for first order deactivation is defined as:

$$\frac{da}{dt} = -k_d a$$

(4)

$$a = \frac{\text{rate}(t)}{\text{rate}(t_0)}$$

(5)

Here $k_d$ is the first order deactivation rate constant and $a$ is the relative ethylene consumption rate at time $t$ with respect to the initial ethylene consumption rate at $t_0$. From rearrangement of the equation and integration from $t = t_0$ to $t = t$, the following equation is obtained:

$$\ln(\text{rate}(t)) = -k_d t + \ln(\text{rate}(t_0))$$

(6)

A plot of $\ln(\text{rate}(t))$ versus $t$ (which in this case is time on stream) therefore has a slope equal to $-k_d$. 
Table S1 BET surface area of fresh and spent catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh&lt;sup&gt;a&lt;/sup&gt;</td>
<td>418</td>
</tr>
<tr>
<td>Spent 80 °C&lt;sup&gt;b&lt;/sup&gt;</td>
<td>70</td>
</tr>
<tr>
<td>Spent 200 °C&lt;sup&gt;b&lt;/sup&gt;</td>
<td>105</td>
</tr>
</tbody>
</table>

<sup>a</sup>Fresh catalyst after pretreatment at 230 °C in argon.<br><sup>b</sup>Spent catalysts after 24 h reactions and Soxhlet extractions.
Fig. S1 Process flow diagram of ethylene oligomerization reaction.
Fig. S2 Representative 2D-GC-FID chromatograms from an ethylene oligomerization reaction at 200 °C, 16 bar ethylene, 16 bar argon, 12 wt% CoO\textsubscript{x}/HTTC, and 0.72 h contact time. (a) Overall products. (b) C\textsubscript{8} olefin products.
**Fig. S3** Ethylene conversion as a function of time on stream (TOS) at first 200 °C (black square), 140 °C (red circle), 180 °C (blue triangle), 160 °C (magenta upside-down triangle), and last 200 °C (green diamond). Reaction conditions: 16 bar ethylene, 16 bar argon, 12 wt% CoOₓ/HTTC, and 1.45 h contact time.
**Fig. S4** First order deactivation rate constant at different reaction temperatures during 24 h reactions. Reaction conditions: 16 bar ethylene, 16 bar argon, 12 wt% CoOₓ/HTTC, and 0.18 - 1.45 h contact time. Bounds represent standard errors from the slopes of ln(rate) versus time on stream (TOS) from the LINEST function in Excel. All conversions were below 20%.
**Fig. S5** Ln(Rate) versus 1/T. Reactions with fresh catalysts at 180, 200, and 220 °C (black square) and sequential reactions at 200-140-180-160-200 °C (red triangle) with 24 h for each reaction temperature. Reaction conditions: 16 bar ethylene, 16 bar argon, 12 wt% CoOₓ/HTTC, and 1.45 h contact time. Bounds represent standard deviations.

$E_{a,\text{app}} = 25\pm1 \text{ kJ mol}^{-1}$

$R^2 = 0.98$
**Fig. S6** Conversion versus contact time. Reaction conditions: 200 °C, 16 bar ethylene, 16 bar argon, 12 wt% CoOₓ/HTTC. Bounds represent standard deviations.
**Fig. S7** Product linearities versus conversion of C\textsubscript{4} (black square), C\textsubscript{6} (red circle), C\textsubscript{8} (blue triangle), C\textsubscript{10} (magenta upside-down triangle), and C\textsubscript{12} (green diamond) olefins. Reaction conditions: 200 °C, 16 bar ethylene, 16 bar argon, 12 wt% CoO\textsubscript{x}/HTTC, and 0.18 - 9.45 h contact time. Bounds represent standard deviations.
Fig. S8 Chain growth probabilities from \( \text{C}_4 - \text{C}_{10} \) olefins (black square) and \( \text{C}_{10+} \) olefins (red circle) versus conversion. Reaction conditions: 200 °C, 16 bar ethylene, 16 bar argon, 12 wt% CoO\(_x\)/HTTC, and 0.18 - 9.45 h contact time. Bounds represent standard errors from the slopes of \( \ln(\text{Carbon selectivity} / n) \) versus \( n \) from the LINEST function in Excel.
**Fig. S9** Mo-XRD patterns of fresh and spent catalysts with exposure to air. Characteristic peaks are carbon (graphite) - filled circle, polyethylene - filled square, $\text{Co}_3\text{O}_4$ - unfilled square, and CoO - unfilled diamond.
Fig. S10  N 1s XPS region of fresh catalyst after pretreatment in argon at 230 °C.
Fig. S11 TGA of spent catalysts in N₂ before and after Soxhlet extractions. (a) Spent catalyst after a 24 h reaction at 80 °C before the Soxhlet extraction. (b) Spent catalyst after a 24 h reaction at 200 °C before the Soxhlet extraction. (c) Spent catalyst after a 24 h reaction at 80 °C after the Soxhlet extraction. (d) Spent catalyst after a 24 h reaction at 200 °C after the Soxhlet extraction. TGA conditions: 50 cm³ (STP) min⁻¹ of N₂, 10 °C min⁻¹ ramp rate, and ~10 mg sample.
Fig. S12 BJH pore size distributions of fresh catalyst after pretreatment in argon at 230 °C and spent catalysts after Soxhlet extractions.