Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

# Supplementary Information for

# Ethylene oligomerization into linear olefins over cobalt oxide on carbon catalyst

**Authors:**

Alvin Jonathan[1], Nathaniel M. Eagan[1], David L. Bruns[2], Shannon S. Stahl[2], Michael P. Lanci[3], James A. Dumesic[1], and George W. Huber*[1]

[1]Department of Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI, 53706, USA.

[2]Department of Chemistry, University of Wisconsin-Madison, Madison, WI, 53706, USA.

[3]ExxonMobil Research and Engineering, Annandale, NJ, 08801, USA.

*Corresponding author: gwhuber@wisc.edu

**Table of contents:**

## Supplementary Method: Calculating calibration constants for $C_2$ up to $C_{10}$ 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 $C_2$ up to $C_6$ olefins from the Scotty gas standard (a mixture of 0.1 mol% of each $C_2$-$C_6$ LAO and 99.5 mol% of He). From the linear extrapolation of $1/k_i$ as a function of $i$, the calibration constants for $C_8$ and $C_{10}$ 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:

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

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:

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

$$\log_{10}\left(\frac{W_n}{n}\right) = n\log_{10}(\alpha) + \left[2\log_{10}(1-\alpha) - log_{10}(\alpha)\right] \tag{3}$$

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:

$$\frac{da}{dt} = -k_d a \tag{4}$$

$$a = \frac{rate\ (t)}{rate\ (t_0)} \tag{5}$$

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:

$$\ln(rate(t)) = -k_d t + \ln(rate(t_0)) \tag{6}$$

A plot of $\ln(rate(t))$ 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.

| **Sample** | **BET surface area ($m^2$ $g^{-1}$)** |
|---|---|
| Fresh[a] | 418 |
| Spent 80 °C[b] | 70 |
| Spent 200 °C[b] | 105 |

[a]Fresh catalyst after pretreatment at 230 °C in argon. [b]Spent catalysts after 24 h reactions and Soxhlet extractions.

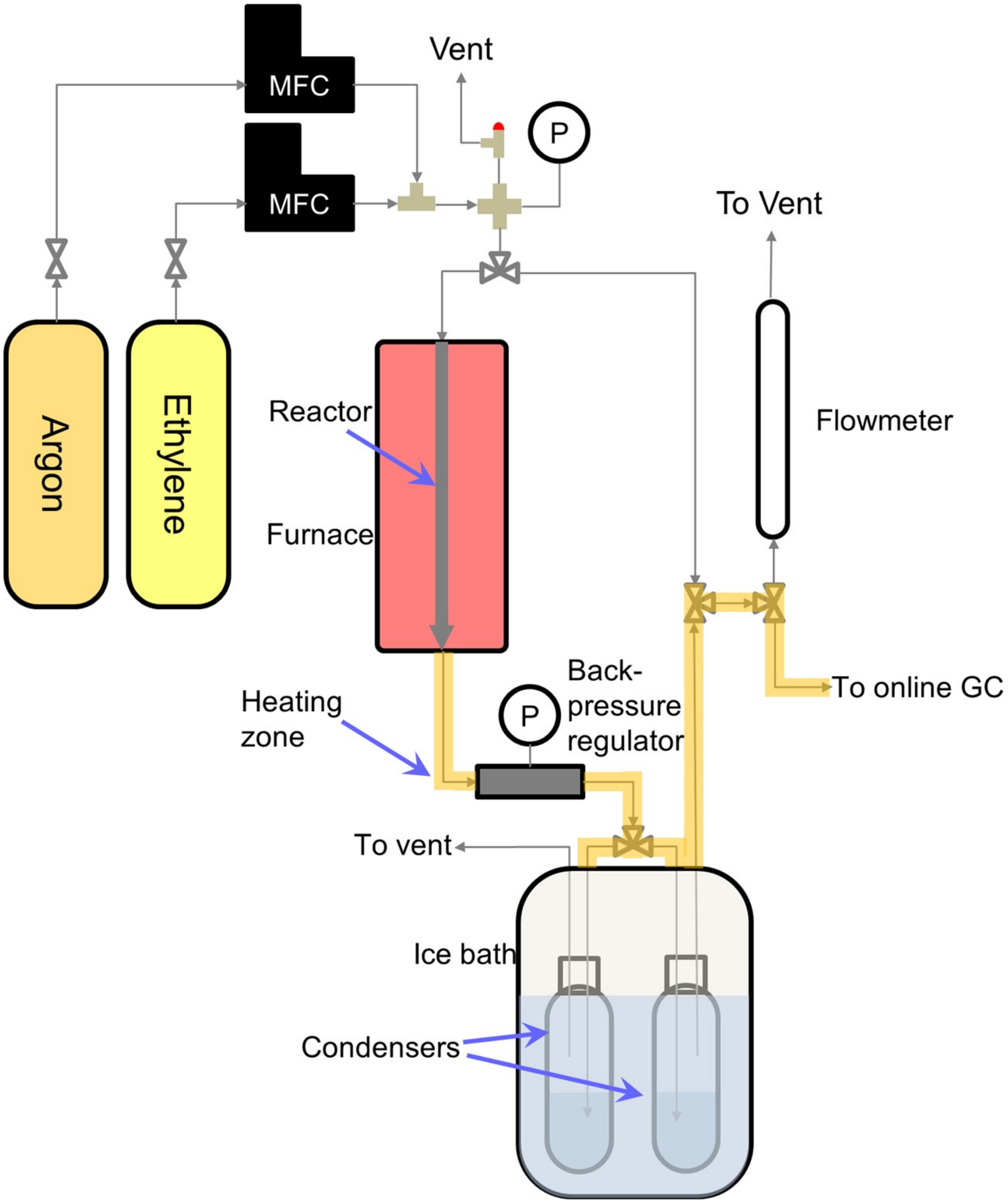

**Fig. S1** Process flow diagram of ethylene oligomerization reaction.

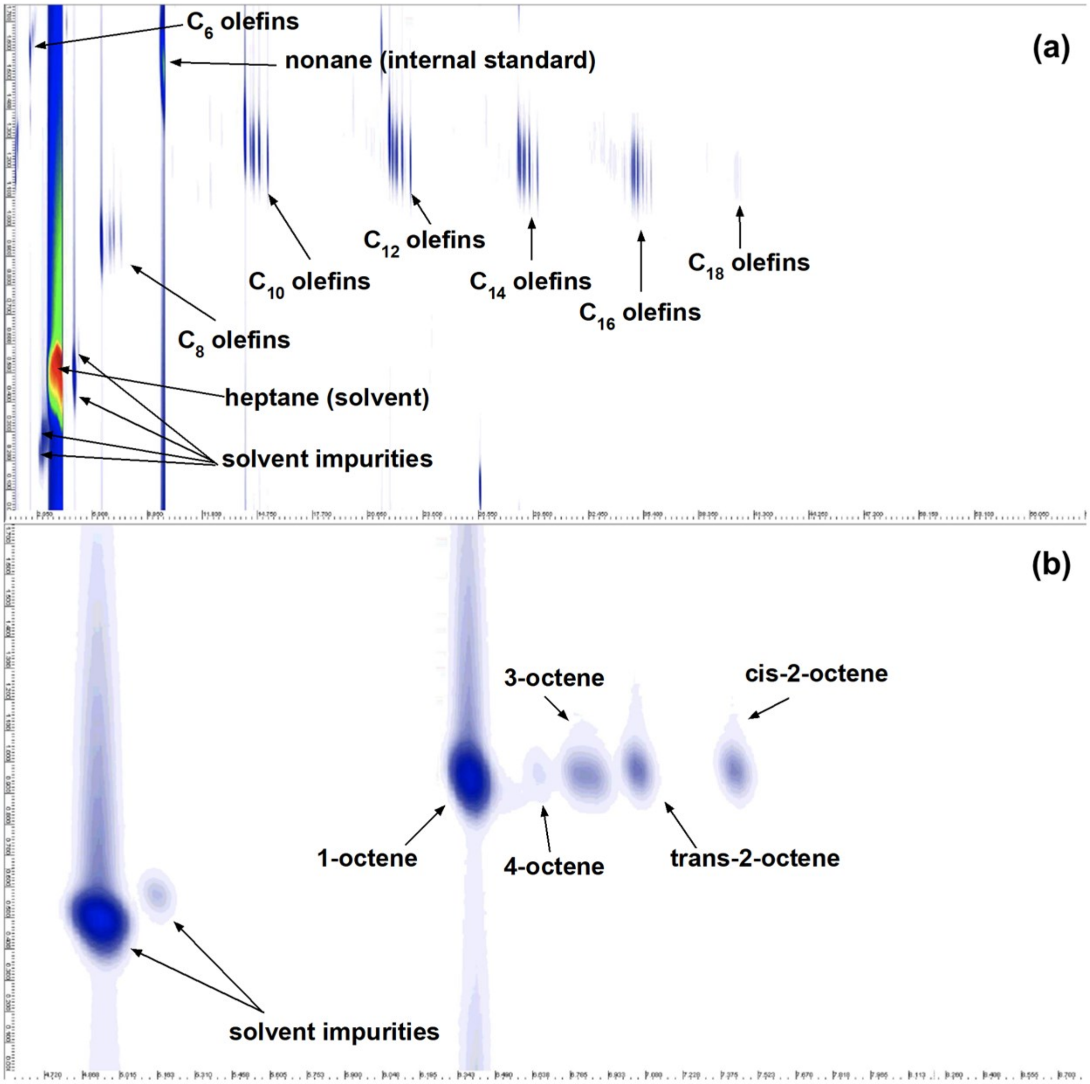

**Fig. S2** Representative 2D-GC-FID chromatograms from an ethylene oligomerization reaction at 200 °C, 16 bar ethylene, 16 bar argon, 12 wt% $CoO_x$/HTTC, and 0.72 h contact time. (a) Overall products. (b) $C_8$ olefin products.

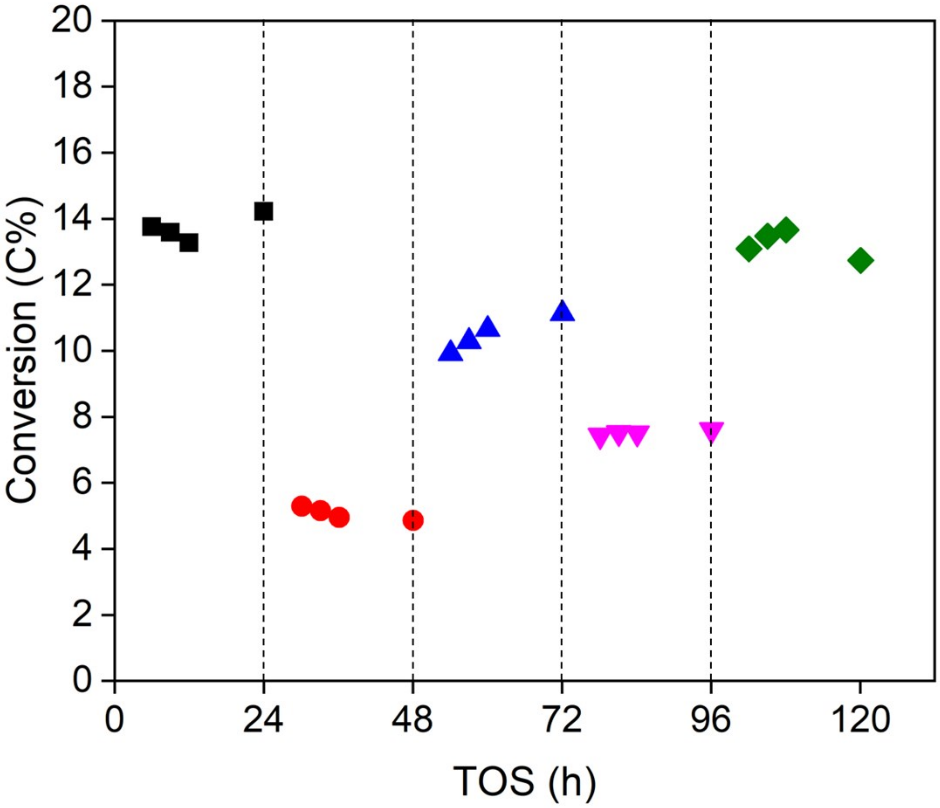

**Fig. S3** Ethylene conversion as a function of time on stream (TOS) at first 200 °C (black square), 140 °C (red circle), 180 °C (blue triangle), 160 °C (magenta upside-down triangle), and last 200 °C (green diamond). Reaction conditions: 16 bar ethylene, 16 bar argon, 12 wt% $CoO_x$/HTTC, and 1.45 h contact time.

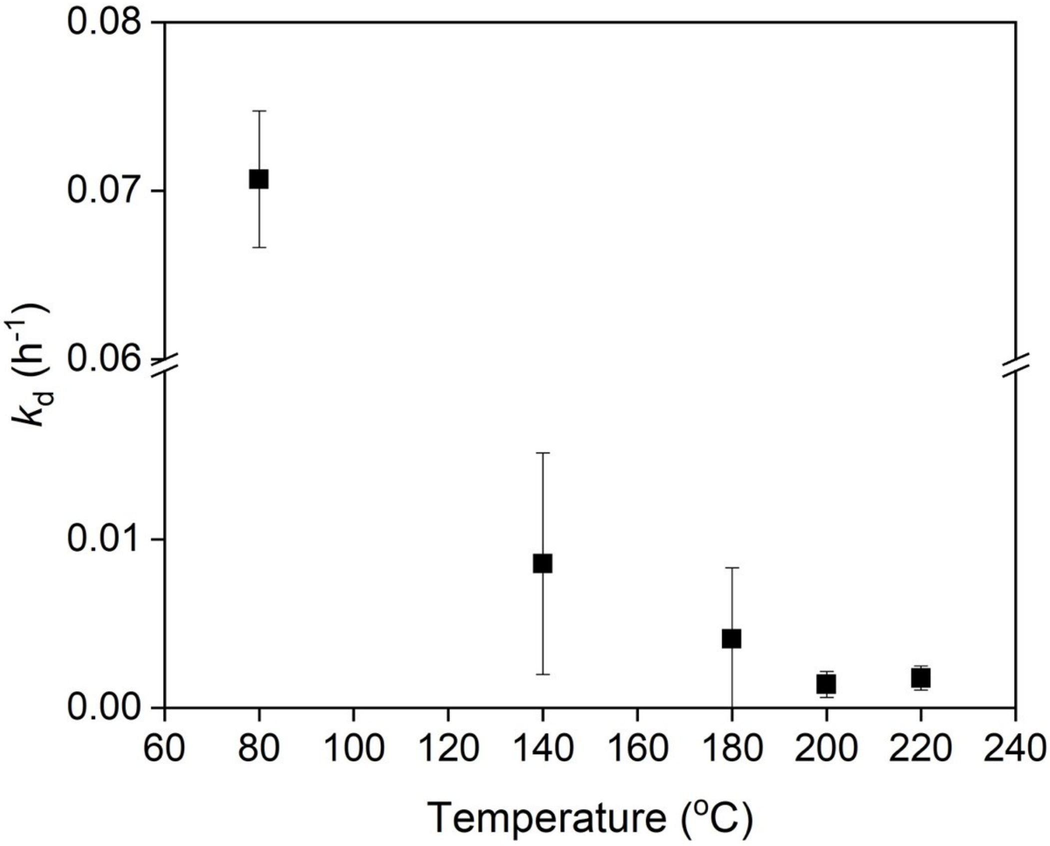

**Fig. S4** First order deactivation rate constant at different reaction temperatures during 24 h reactions. Reaction conditions: 16 bar ethylene, 16 bar argon, 12 wt% $CoO_x$/HTTC, and 0.18 -1.45 h contact time. Bounds represent standard errors from the slopes of ln(rate) versus time on stream (TOS) from the LINEST function in Excel. All conversions were below 20%.

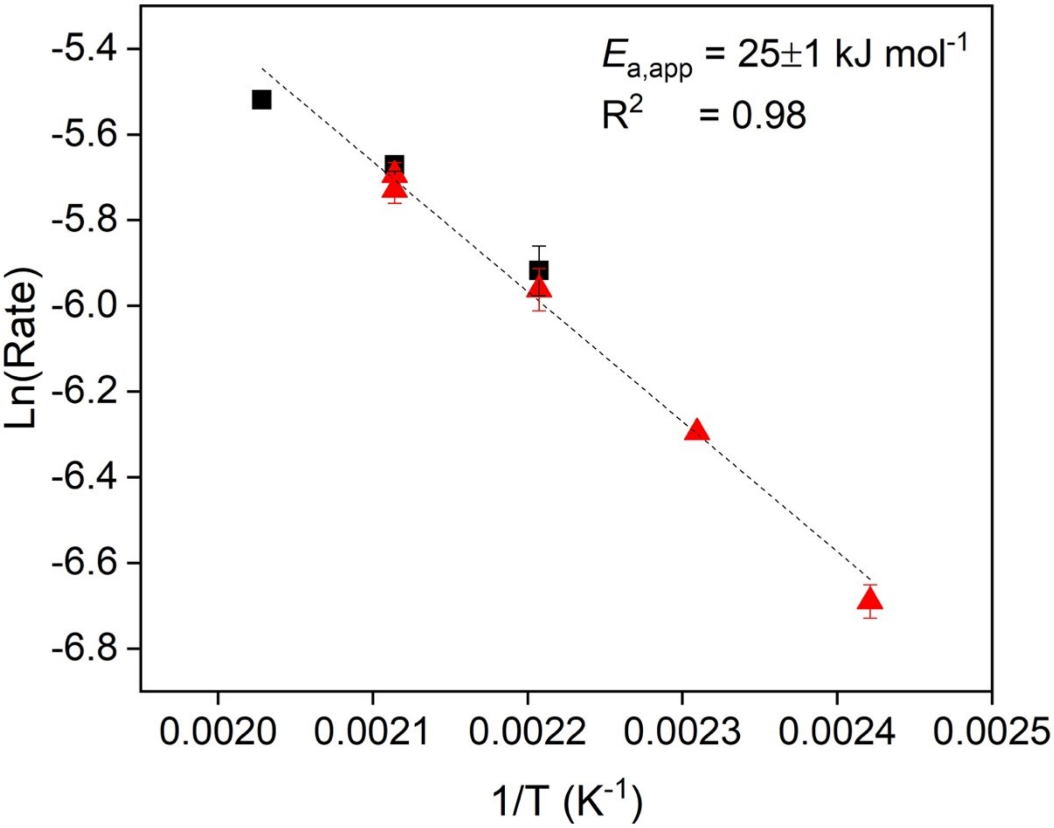

**Fig. S5** Ln(Rate) versus 1/T. Reactions with fresh catalysts at 180, 200, and 220 °C (black square) and sequential reactions at 200-140-180-160-200 °C (red triangle) with 24 h for each reaction temperature. Reaction conditions: 16 bar ethylene, 16 bar argon, 12 wt% $CoO_x$/HTTC, and 1.45 h contact time. Bounds represent standard deviations.

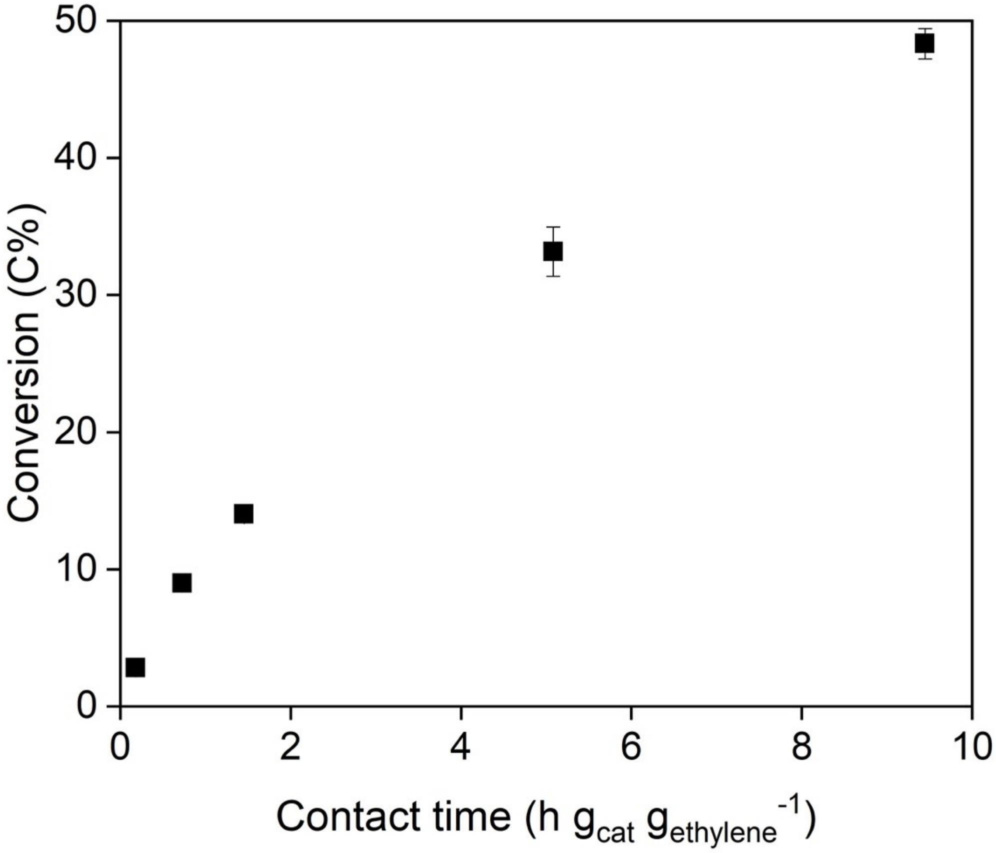

**Fig. S6** Conversion versus contact time. Reaction conditions: 200 °C, 16 bar ethylene, 16 bar argon, 12 wt% $CoO_x$/HTTC. Bounds represent standard deviations.

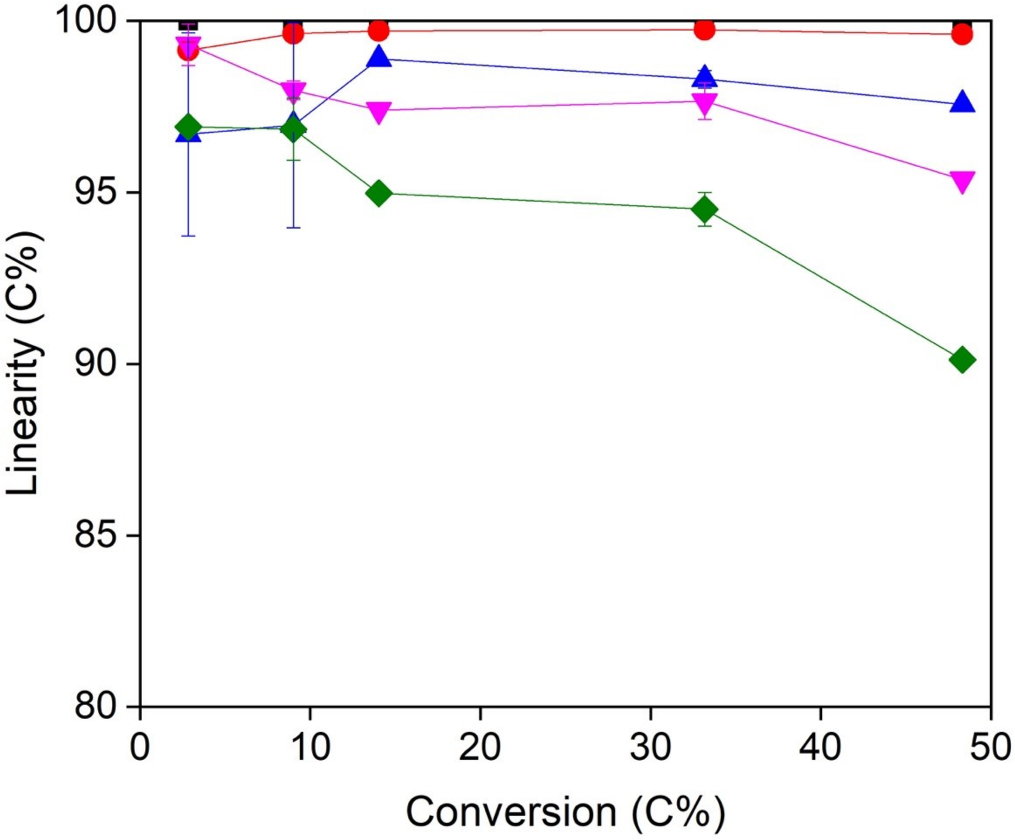

**Fig. S7** Product linearities versus conversion of $C_4$ (black square), $C_6$ (red circle), $C_8$ (blue triangle), $C_{10}$ (magenta upside-down triangle), and $C_{12}$ (green diamond) olefins. Reaction conditions: 200 °C, 16 bar ethylene, 16 bar argon, 12 wt% $CoO_x$/HTTC, and 0.18 - 9.45 h contact time. Bounds represent standard deviations.

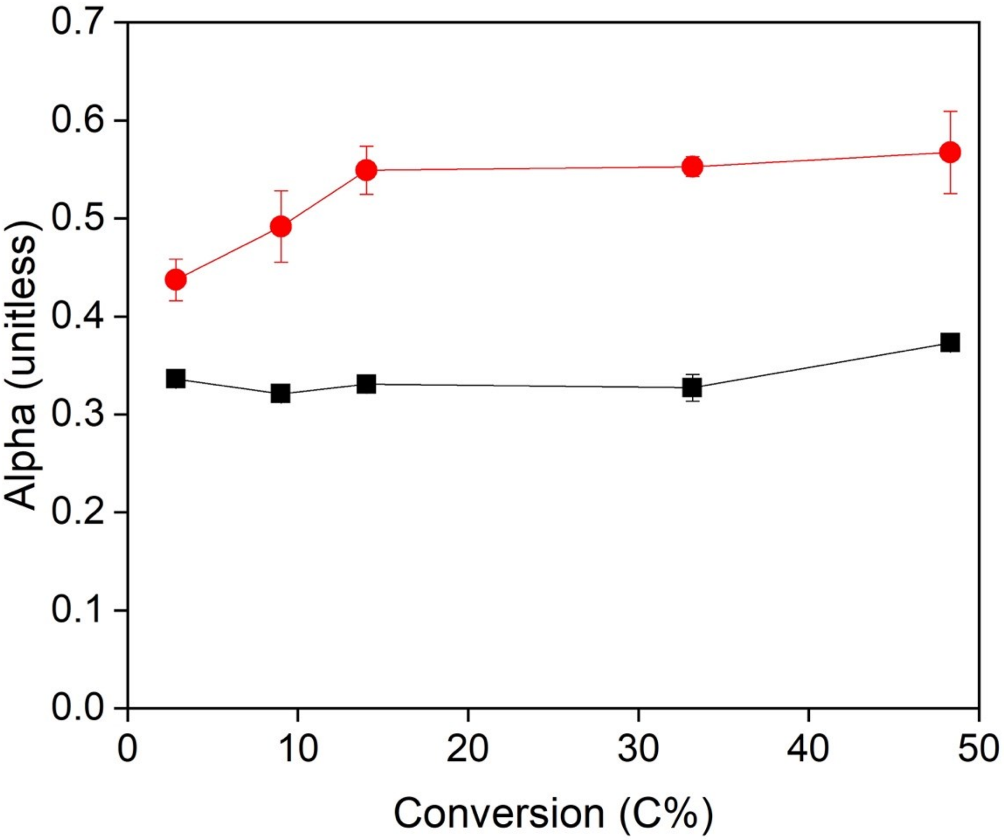

**Fig. S8** Chain growth probabilities from $C_4$ – $C_{10}$ olefins (black square) and $C_{10+}$ olefins (red circle) versus conversion. Reaction conditions: 200 °C, 16 bar ethylene, 16 bar argon, 12 wt% $CoO_x$/HTTC, and 0.18 - 9.45 h contact time. Bounds represent standard errors from the slopes of ln(Carbon selectivity / *n*) versus *n* from the LINEST function in Excel.

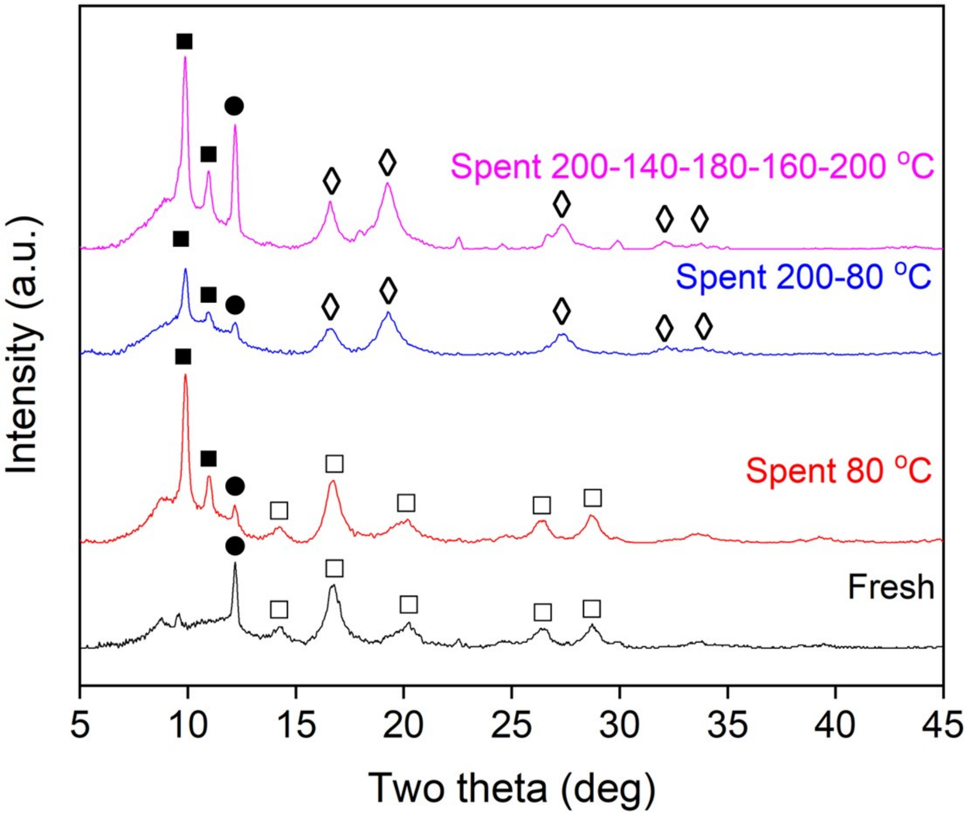

**Fig. S9** Mo-XRD patterns of fresh and spent catalysts with exposure to air. Characteristic peaks are carbon (graphite) - filled circle, polyethylene - filled square, $Co_3O_4$ - unfilled square, and CoO - unfilled diamond.

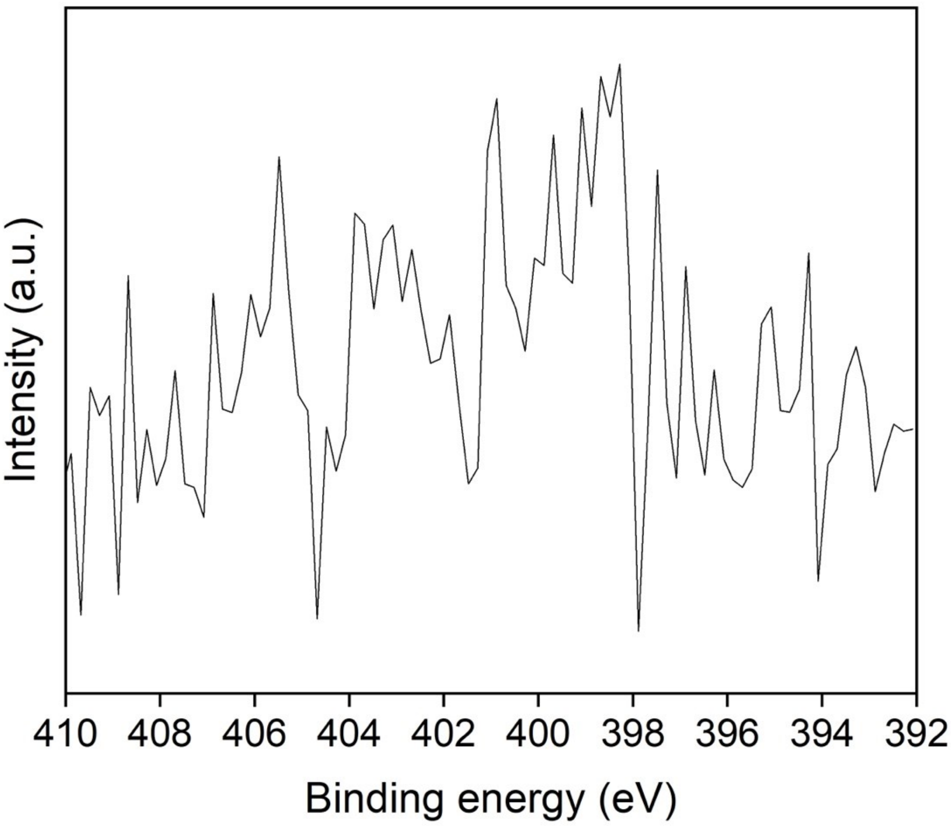

**Fig. S10** N 1s XPS region of fresh catalyst after pretreatment in argon at 230 °C.

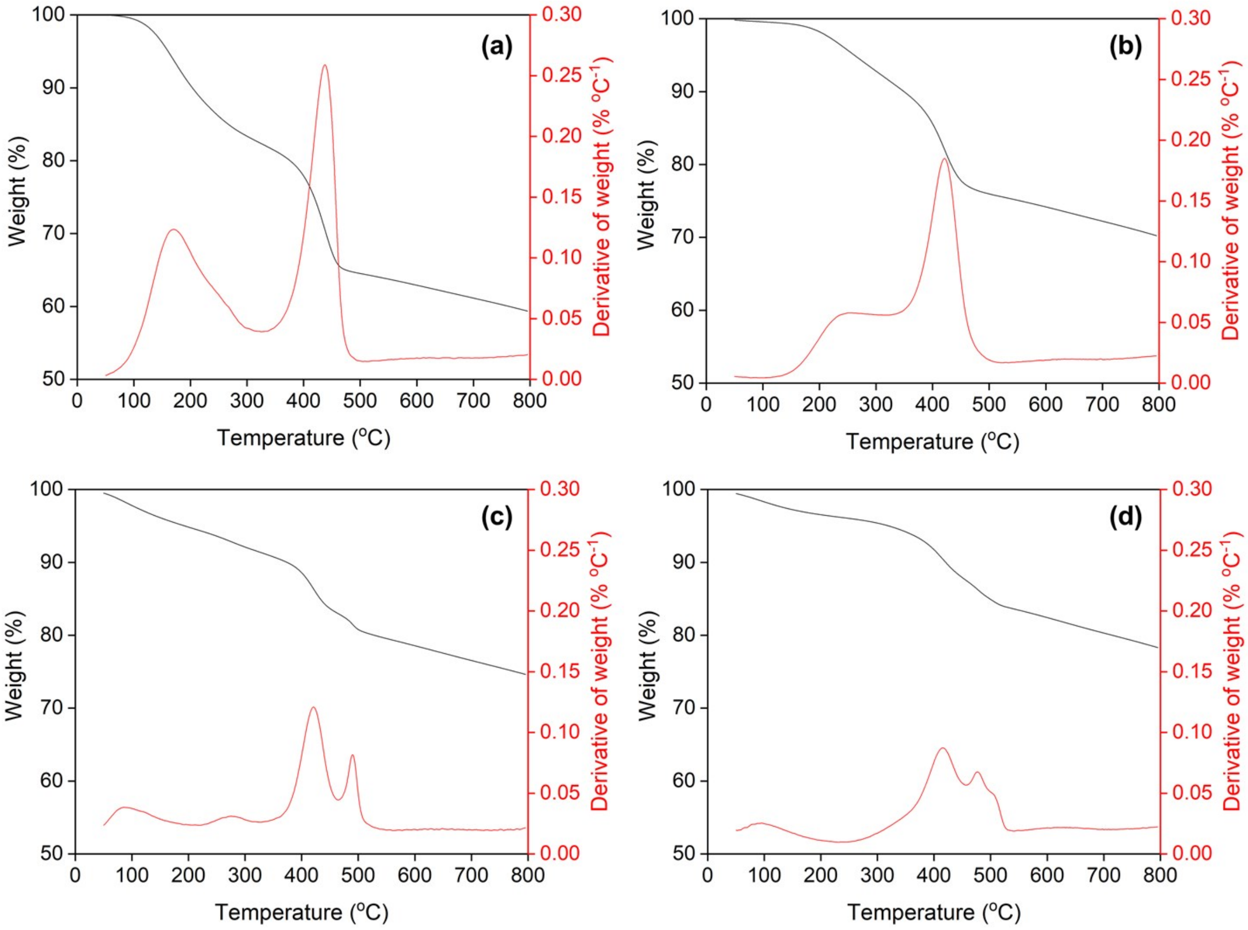

**Fig. S11** TGA of spent catalysts in $N_2$ before and after Soxhlet extractions. (a) Spent catalyst after a 24 h reaction at 80 °C before the Soxhlet extraction. (b) Spent catalyst after a 24 h reaction at 200 °C before the Soxhlet extraction. (c) Spent catalyst after a 24 h reaction at 80 °C after the Soxhlet extraction. (d) Spent catalyst after a 24 h reaction at 200 °C after the Soxhlet extraction. TGA conditions: 50 $cm^3$ (STP) $min^{-1}$ of $N_2$, 10 °C $min^{-1}$ ramp rate, and ~10 mg sample.

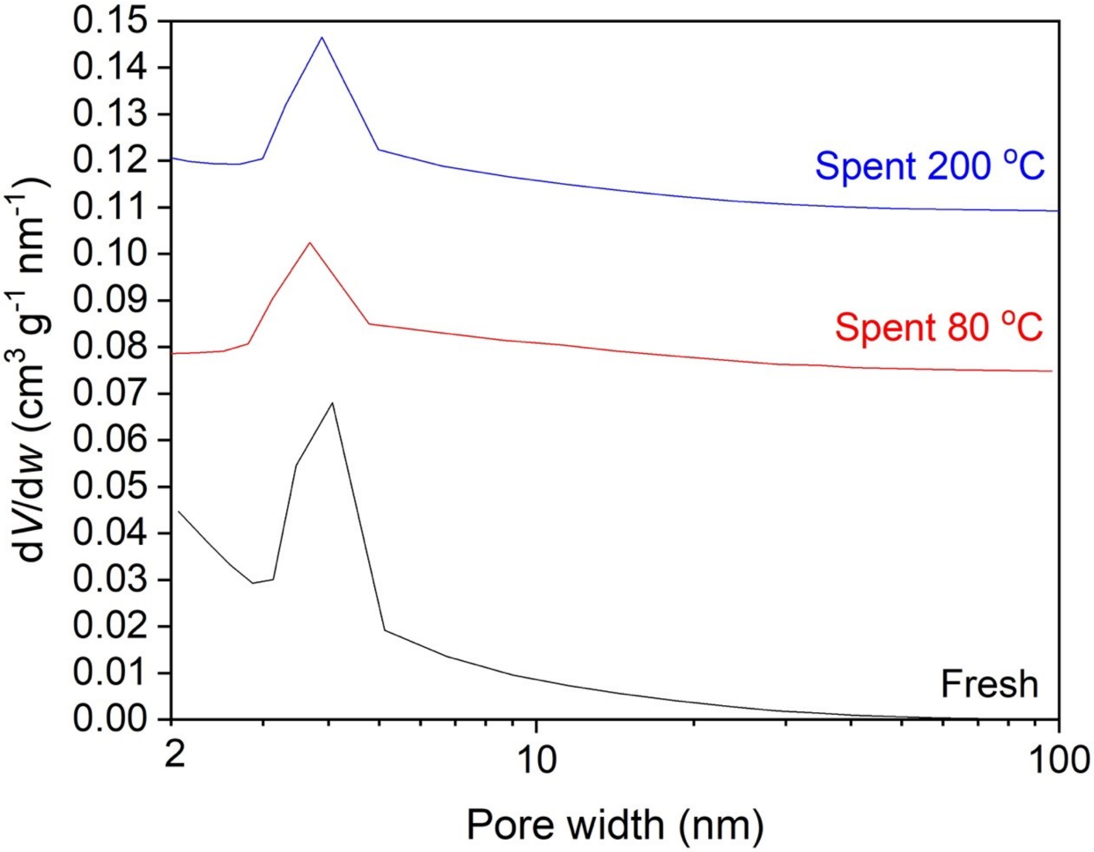

**Fig. S12** BJH pore size distributions of fresh catalyst after pretreatment in argon at 230 °C and spent catalysts after Soxhlet extractions.