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# Supporting Information

# Trimerization and tetramerization of ethylene in continuous gas-phase reaction using a Cr-based supported liquid phase catalyst

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## Semi-batch autoclave setup

5 mmol of Cr(acac3) and an equimolar amount of the respective ligand was taken from a prepared stock solution and transferred into a Schlenk tube inside a glove box. This solution was made up with cyclohexane to a total volume of 5 mL. The solution was activated under an inert argon atmosphere with 270 equivalents MMAO-3A (7wt % solution in heptane) with respect to the chromium. This activated solution was transferred immediately into the autoclave containing 195 mL of cyclohexane at the desired reaction temperature. The reaction was initiated by pressurization with ethylene which was fed on demand throughout the duration of the experiment. The temperature was monitored via an internal thermocouple and maintained by cooling the autoclave with ice water. After 20 min, the reaction was terminated by closing the ethylene supply, switching off the gas entrainment stirrer and cooling the autoclave to 0 °C.

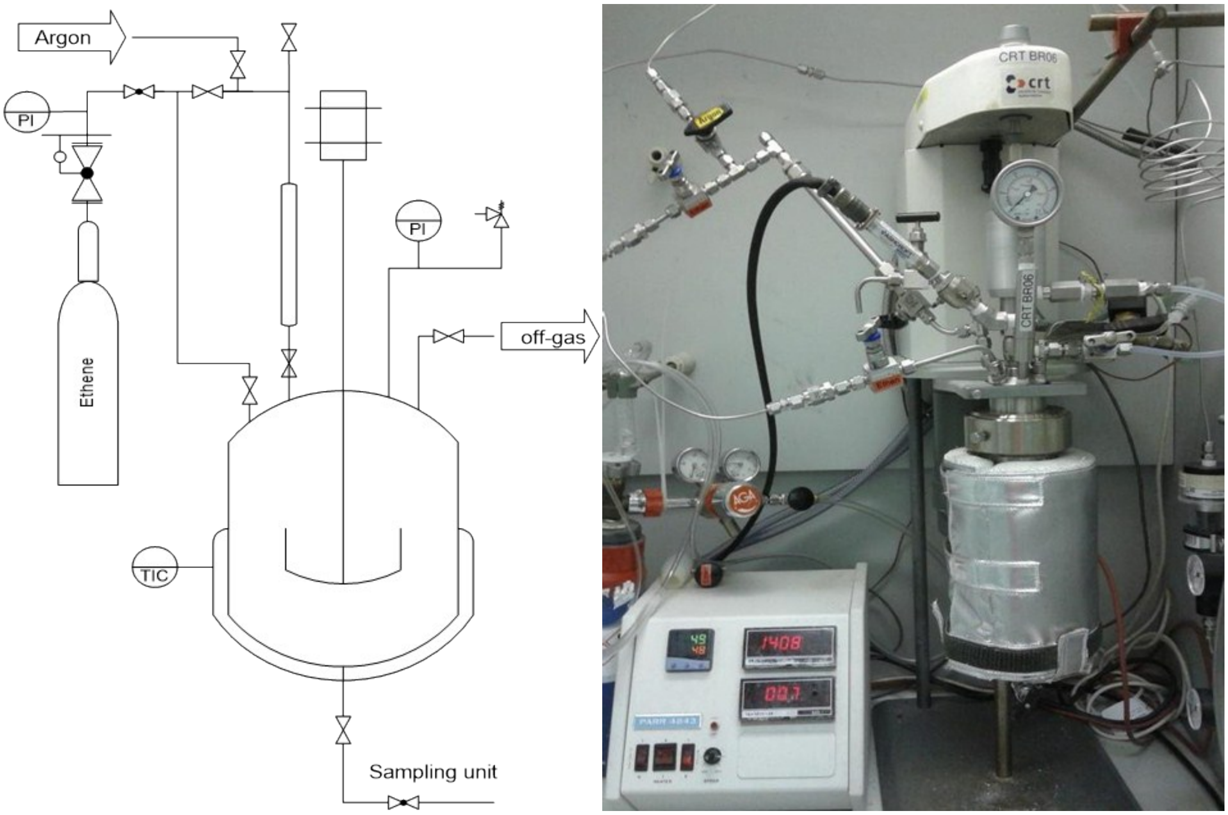

Figure S1. Experimental setup for the semi-batch trimerization experiments.

Next, the autoclave was depressurized slowly. The liquid product was filtered and submitted for GC-FID analysis (Shimadzu GC2010, column CP Sil Pona CB 50 m x 0.21 mm).

## GC analysis of liquid- and gas-phase reaction mixture

The response factors for the individual fractions were calculated based on calibrated GC data for both the liquid-phase and the gas-phase. In Figure S2 an artificial product mixture is shown (top) together with the typical chromatogram of the semi-batch (middle) and gas-phase (bottom) runs.

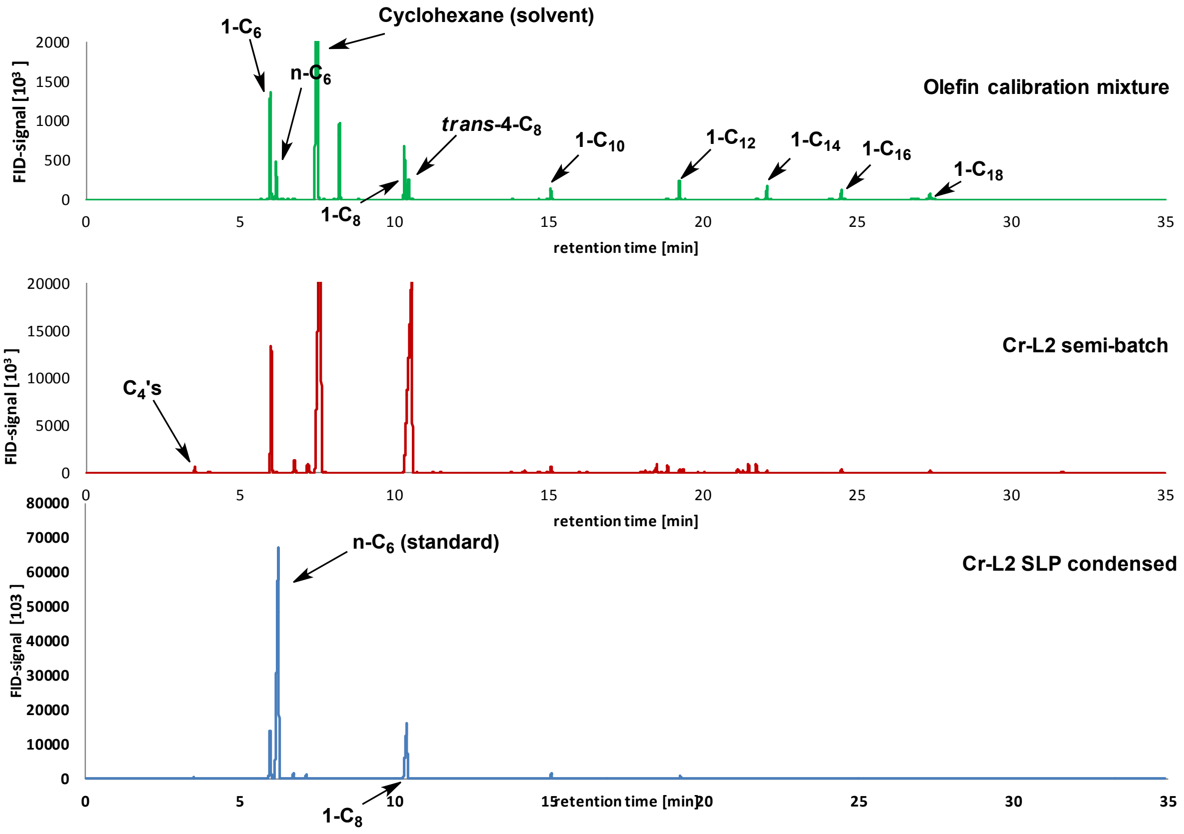

Figure S2. Offline GC data for olefin mixture (top), semi-batch trimerization run (middle) and condensed liquid from SLP run (bottom).

# Post-run thermogravimetric analysis of Cr-L1 SLP catalyst

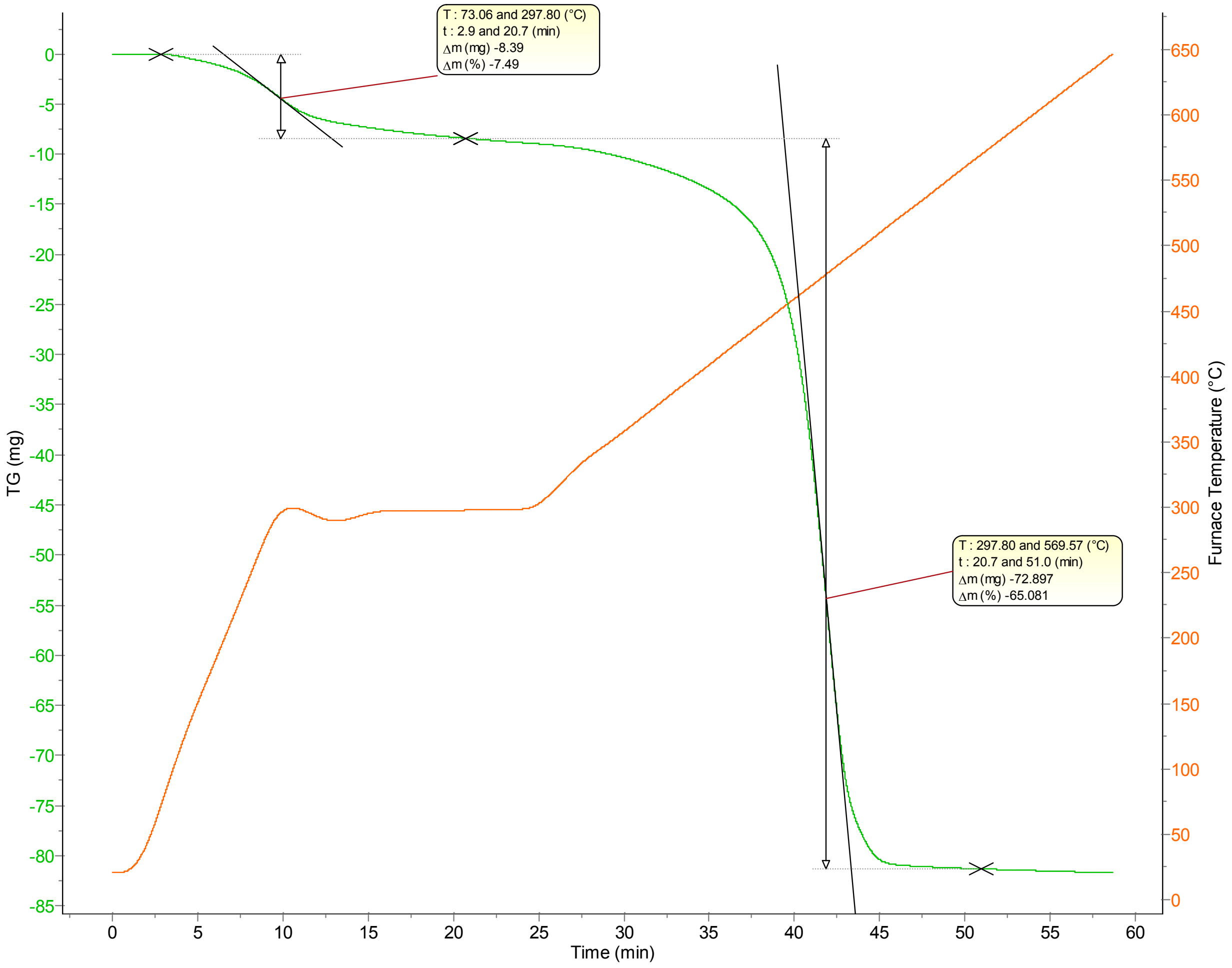

Figure S3. TGA graph for spent Cr-L1 SLP catalyst.

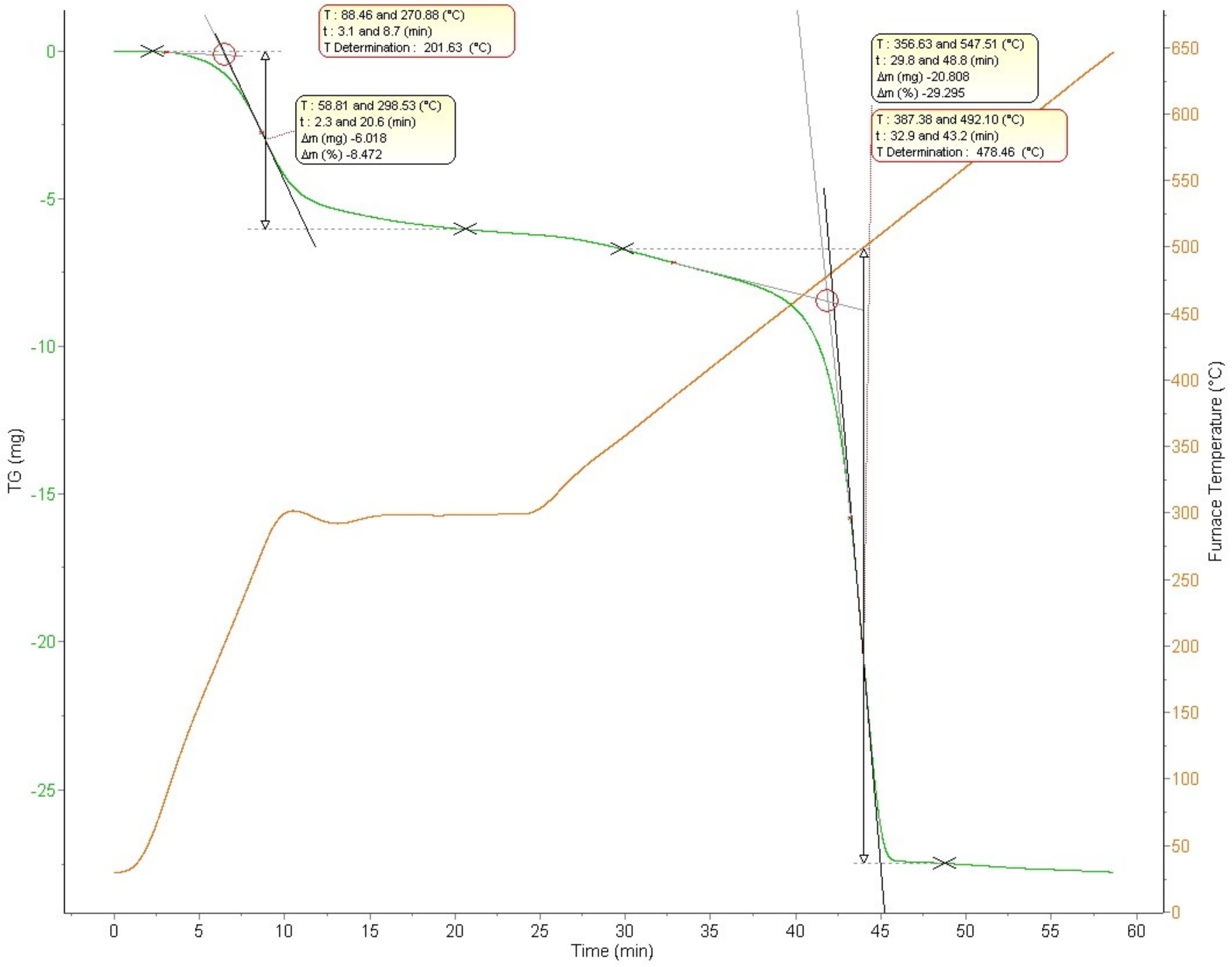

Figure S4. TGA graph for spent Cr-L2 SLP catalyst.

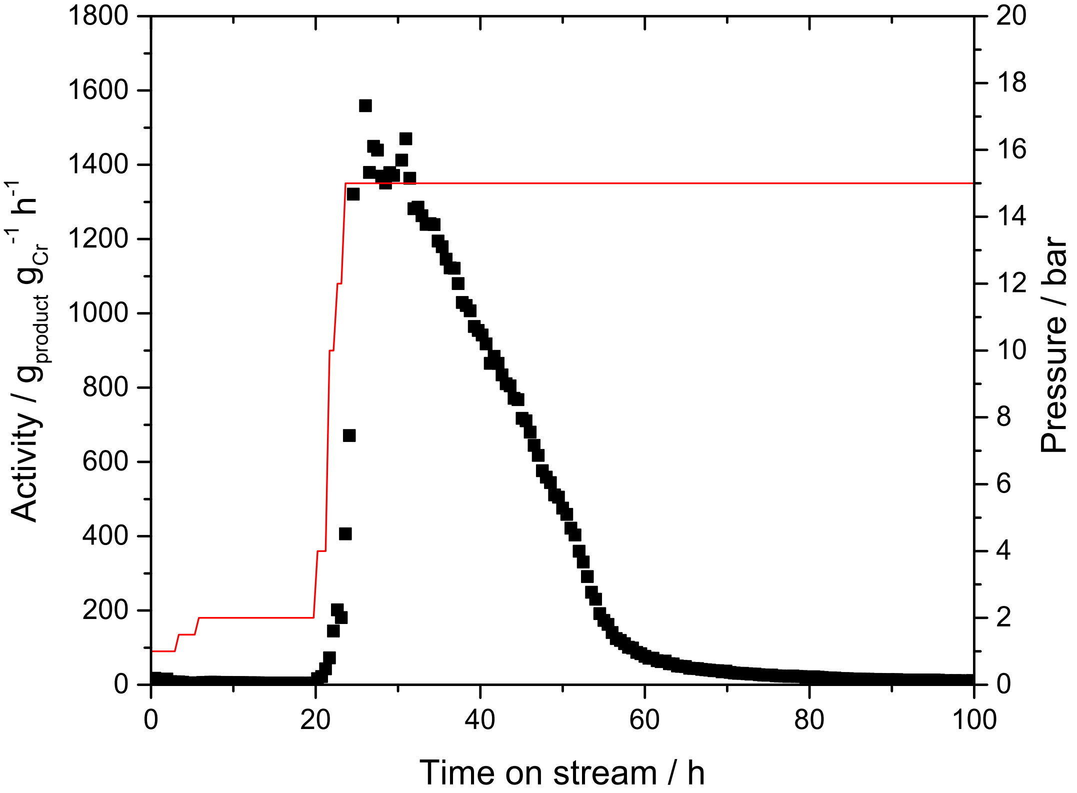

Figure S5. Gas-phase ethylene trimerization using a Cr-L1 SLP catalyst supported in H18-DBT onto AC. SiC was used as inert material to dilute the SLP catalyst in the fixed bed. T = 43 °C, p as indicated, Cr-loading = 0.013 %, 2000 eq MAO, $\alpha = 0.25$, 1 g of AC, solvent = H18-DBT.

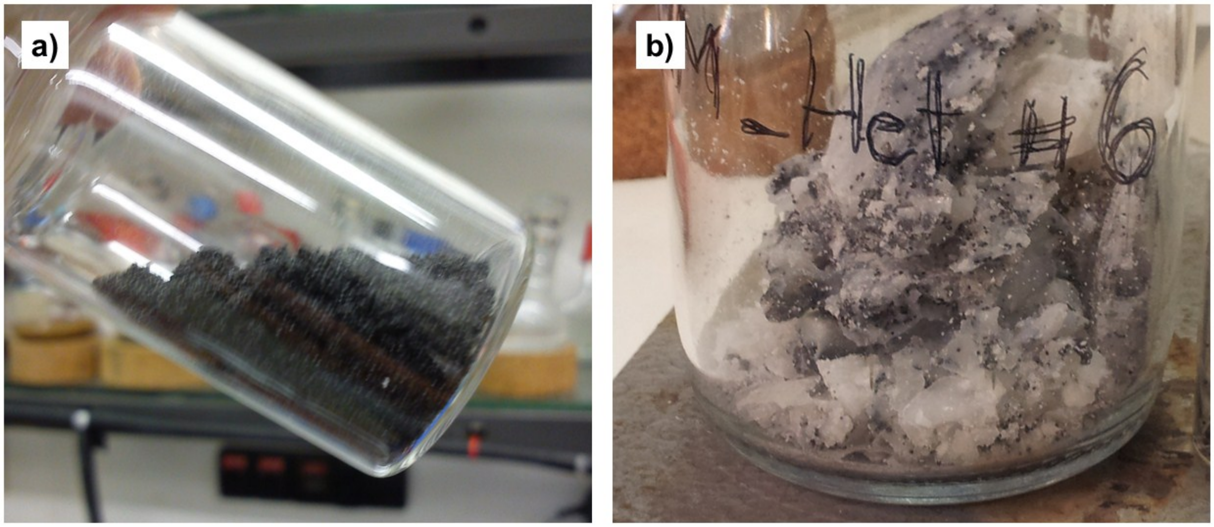

Figure S6. SLP catalysts supported in H18-DBT onto AC for the gas-phase ethylene trimerization. The fresh catalyst is shown in a), while the spent and PE coated catalyst is depicted in b).