# Supporting Information

# High Selectivity Production of Propylene from 2-Butene: Non-Degenerate Pathways to Convert Symmetric Olefins via Olefin Metathesis

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## Experimental Section

All experiments were carried out under controlled atmosphere, using Schlenk and glove box techniques for preparation or handling of organometallic compounds. The alumina supported tungsten hydride was prepared as already reported.

**Representative procedure for the grafting of $W(\equiv CC(CH_3)_3)(CH_2C(CH_3)_3)_3$, on γ-alumina$_{(500)}$:** An excess of $W(\equiv CC(CH_3)_3)(CH_2C(CH_3)_3)_3$ (311 mg, 0.66 mmol) and γ-alumina$_{(500)}$ (2 g) were stirred at 66 °C for 4 h. All volatile compounds were condensed into another reactor (of known volume) in order to quantify 2,2-dimethylpropane evolved during grafting. Analysis by gas chromatography indicated the formation of 0.654±0.05 mmol of 2,2-dimethylpropane (0.9±0.1 $CH_3tBu/W$). Pentane (10 mL) was introduced into the reactor by distillation, and the solid was washed three times. After evaporation of the solvent, the resulting light brown powder was dried under vacuum. Elemental analysis W: 5,5%$_{wt}$, C: 5,2%$_{wt}$

**Preparation of the tungsten hydride on γ-alumina$_{(500)}$:** 2g of the grafted tungsten complex was heated at 150 °C in the presence of a large excess of anhydrous $H_2$ (77 kPa). After 15 h, the gaseous products were quantified by GC, and the resulting catalyst was obtained after evacuating the gas phase for 15 min under vacuum.

**Catalytic test:** Conversion of butenes to propylene was performed in a continuous flow reactor. The tungsten hydride $WH_3/Al_2O_{3-(500)}$, 1 (135 mg; 5.5 wt% W) was charged, by using a glove box, into a stainless steel ½' cylindrical reactor which can be isolated from atmosphere. After connection to the gas lines and purging with Ar, a flow of 1 bar 1-butene controlled by a "Brooks" mass flow controller was sent onto the catalyst bed heated at 150 °C, with flow rates 20 $mL{\cdot}min^{-1}$ (VHSV = 5200 h-1). Hydrocarbon products were analyzed on line by GC (HP 8890 chromatograph fitted with an $Al_2O_3/KCl$ 50 m x 0.32 mm capillary column, FID detector for hydrocarbons). The high pressure experiment was carried out in a PID Microactivity Reactor equipped with a hot box (preheated at 150 °C) where the inlet and outlet tubes from the reactor were heated. 1-butene was charged in a high pressure syringe (model PMHP50-500 purchased from TOP Industrie). 0.076 ml/min liquid 1-butene was continuously injected to the reactor (corresponds to 20 ml/min in gas phase). The products were determined by an online Varian GC3800 ($KCl/Al_2O_3$ capillary column, FID).

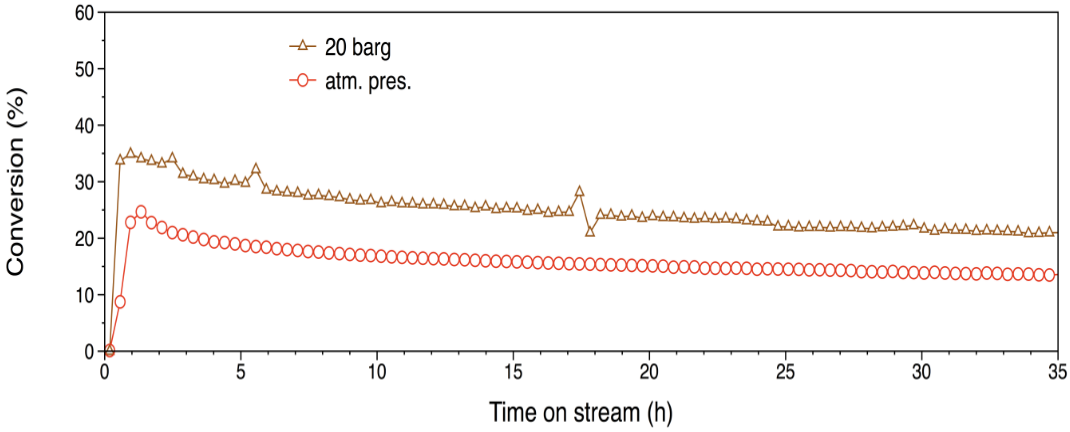


Figure S1. *Conversion of trans-2-butene vs. time on stream* on **WH/$Al_2O_{3-(500)}$** at 150°C at 1 bar and 20 bar.

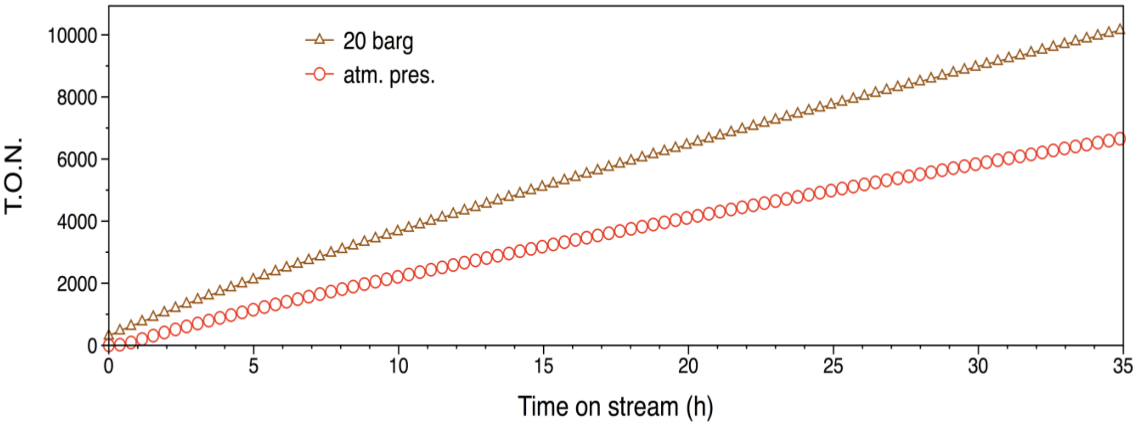
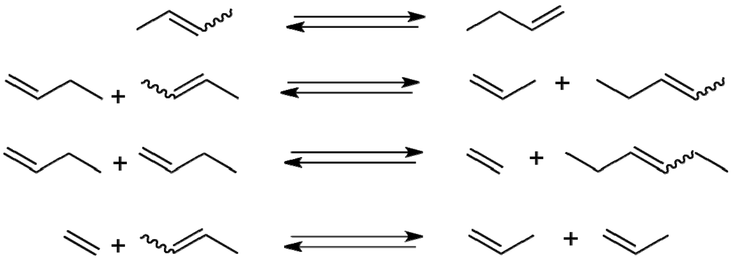


Figure S2. *T.ON vs. time on stream for /trans-2-butene conversion* on **WH/$Al_2O_{3-(500)}$** at 150°C at 1 bar and 20 bar.



Scheme S1. Reaction occurring during the conversion of 2-trans-butene.

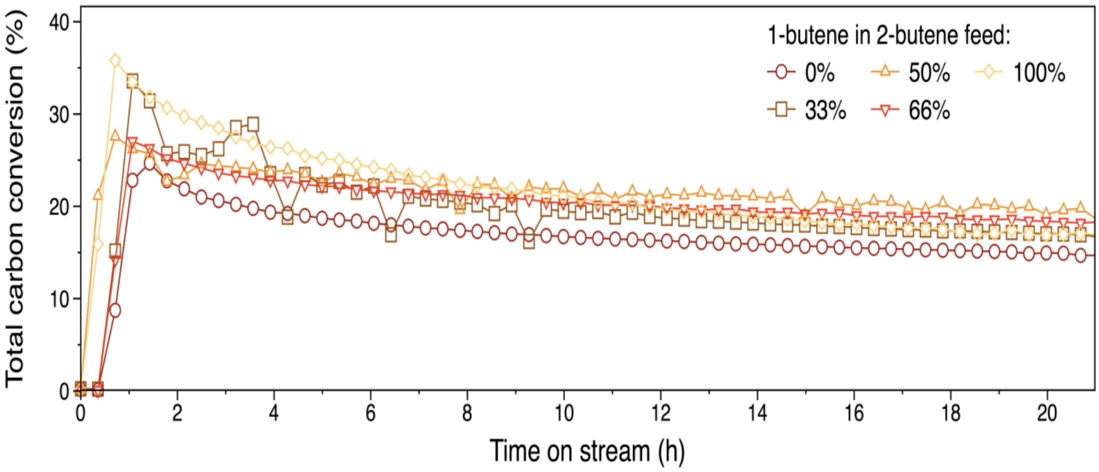


Figure S3. *Conversion vs. time on stream for 1-butene/trans-2-butene metathesis* on **WH/Al$_2$O$_{3\text{-(500)}}$** at 150°C for different feed compositions.