Electronic Supplementary Material (ESI) for Energy & Environmental Science.

SUPPORTING INFORMATION

Catalytic limitations on alkane dehydrogenation under H_2 deficient conditions relevant to membrane reactors

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Catalysis Studies – Recirculating Batch Reactor

Catalytic reactions were carried out in a packed-bed in a 3/8" O.D. quartz tube, in which the reactor effluent was recycled, such that the reactor behaves as a well-mixed batch reactor (Loop Reactor, Figure S1). The reactor is equipped with an on-line GC-MS/FID (Agilent 7890-5977A MSD) with two 320 μm GS-GASPro columns, and gas aliquots are taken at selected time-points by using a gas-switching valve. The sample-loop in the gas-sampling valve is 50 μL, and the reactor volume is ~200 mL, such that each GC aliquot is 0.025% of the total reactor volume. The quartz tube is positioned within a three-zone heated furnace, and bed temperature was held constant and measured and controlled with type K thermocouples. The reactor is equipped with several gas-feeds, including: H_2, He, ethane, and ethylene. Each gas is purified through a drying column to remove trace H_2O and an oxygen column to remove O_2. The catalysts were held between quartz chips, and quartz wool. The catalyst was initially treated with an ex-situ pre-reduction in 100% H_2 for 12 hr at 600 °C on a Micromeritics chemisorption unit. Catalysts were re-reduced in the batch reactor in H_2 (100 sccm) at 600 °C (10 °C/min), and held there for 30 mins prior to catalytic reactions.

For each catalytic ethane dehydrogenation run or simulated feed run, the following procedure was followed. The reactor, at a selected reaction temperature, was evacuated (< 50 mTorr) and then charged with H_2 (800 Torr). The H_2 was recirculated over the catalyst bed for 2 minutes. The reactor was then evacuated again, and charged with He (900 Torr). The reactor bed was then isolated, and held under He, while the rest of the reactor was evacuated. The reactor, excluding the reactor bed which is under He, was then charged with selected pressures of ethane, ethylene, H_2 and He. The gases were then recirculated and mixed, GC-MS/FID aliquot(s) were taken (time-point 0) to assess the reaction mixture prior to catalysis, and then the reactor bed was opened, and the bypass (3 mL) was closed. After switching from bypass to reactor, the partial pressure of the dosed gases decreases to ~75% its initial (dose) value. The gases are recirculated over the catalyst bed typically for 1 hr, and GC aliquots were taken at selected time-points and analyzed by the GC-FID to assess peak areas and hydrocarbon partial pressures. The GC-MS were collected under 70 eV EI, which were used to confirm product identification.

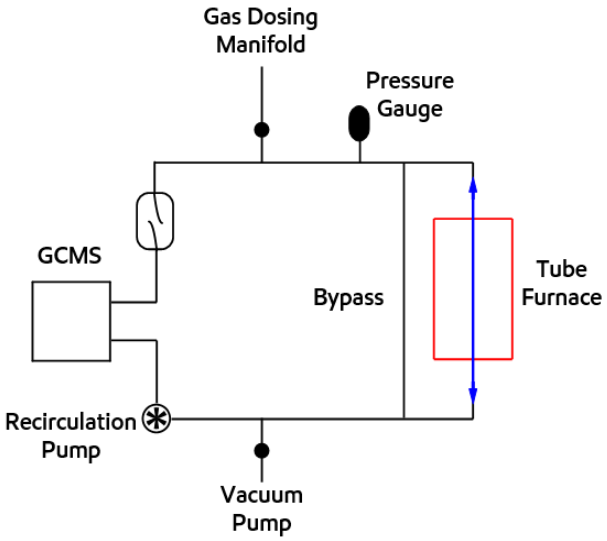

Figure S1. Schematic of recirculation reactor used in this study.

Catalysis Studies – Low Pressure Fixed-Bed Reactor

Reactions were carried out in a quartz 3/8" OD plug-flow reactor heated by an electrical furnace (Applied Test Systems). Typically, 100 mg of catalyst was physically mixed with 1.00 g of quartz chips (mesh size 35-60) and loaded into the reactor. When checking thermal reactivity, 1.10 g of quartz chips was loaded instead. The catalyst was initially treated with an ex-situ pre-reduction in 100% H_2 for 12 hr at 600 °C on a Micromeritics chemisorption unit. The catalyst underwent an in-situ re-reduction for 2 hr at 600 °C after a 10 °C/min ramp from ambient temperature under 100% H_2 at 100 sccm. After reduction, the reactor was prepared for EDH by purging for 1 h at 600 °C with 100% N_2 at 100 sccm.

During a catalytic EDH run, 95% ethane/5% He was fed to the reactor. All analytical was conducted using an on-line 4 channel MicroGC (Agilent, Model 490) with CP-molesieve (Agilent J&W) and PoraPLOT-U (Agilent J&W) columns, and TCD detectors. WHSV (weight hourly space velocity) was calculated as grams of ethane fed per hour per gram of catalyst, and is reported in units of hr^{-1}. To change WHSV, both catalyst loading and/or ethane flow rate were changed. Ethane flow varied from 15 – 100 sccm.

Catalysis Studies – Simulated Feed Fixed-Bed Reactor

Ethane dehydrogenation and simulated feed experiments were collected at 600 °C and 5 atm pressure utilizing a ½"OD 316H stainless steel reactor. Gas feeds included ethane, ethylene, H_2, and N_2, as independent feeds controlled with Brooks 5850 mass flow controllers (MFCs). The furnace set point was controlled by the reactor bed K-type thermocouple. Pressure was controlled using a back-pressure regulator located below the reactor outlet. Catalyst beds contained an inter-dilution of catalyst (≤ 295 mg of 100 mesh powder) with acid-washed quartz (800+ mg of 20 mesh grains) and occupied a volume of 3 mL within the isothermal zone of the furnace. The catalyst was initially treated with an ex-situ pre-reduction in 100% H_2 for 12 hr at 600 °C on a Micromeritics chemisorption unit. Before reaction, the pre-reduced catalyst were re-reduced in-situ with 50 sccm of pure H_2 at 600 °C for 40 min at atmospheric pressure. Following reduction, the bed was placed under N_2 while the bypass line stabilized reaction gases for 10 min. Reaction gasses were then passed over the catalyst bed at temperature. GC injections began after 2 min of exposure. In space velocity experiments, the WHSV was lowered incrementally to approach equilibrium conversion. A higher WHSV was typically revisited as the last reaction condition to assess the extent of deactivation away from equilibrium. WHSV for simulated feeds was defined by ethane equivalents fed and was calculated as (grams of ethane + grams of ethylene fed) per hour per gram of catalyst, and is reported in units of hr^{-1}. Reactor effluent was analyzed using an on-line GC (Agilent 7890B) equipped with a 320 μm GS-GASPro column, FID, and TCD under argon carrier gas.

Supporting Data

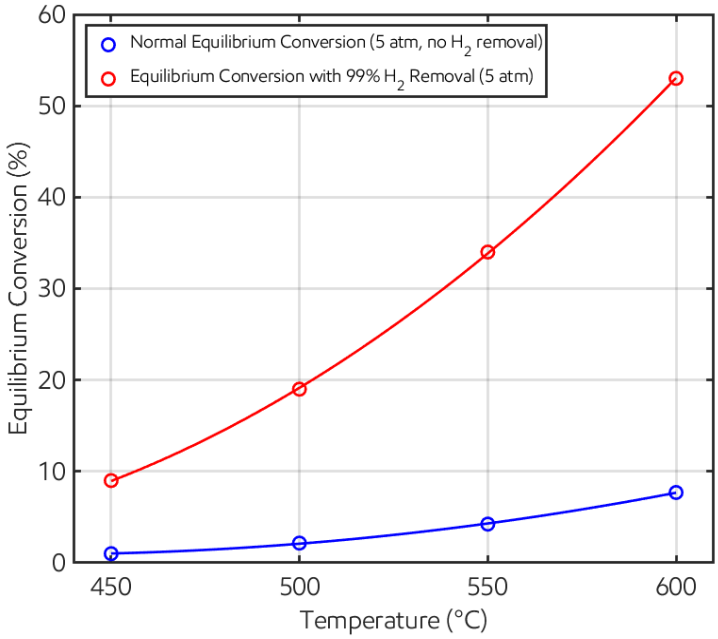

Figure S2. Calculated equilibrium conversions for ethane dehydrogenation at selected temperatures. Process conditions: (blue) 5 atm, 0% H_2 removal; (red) 5 atm, 99% H_2 removal.

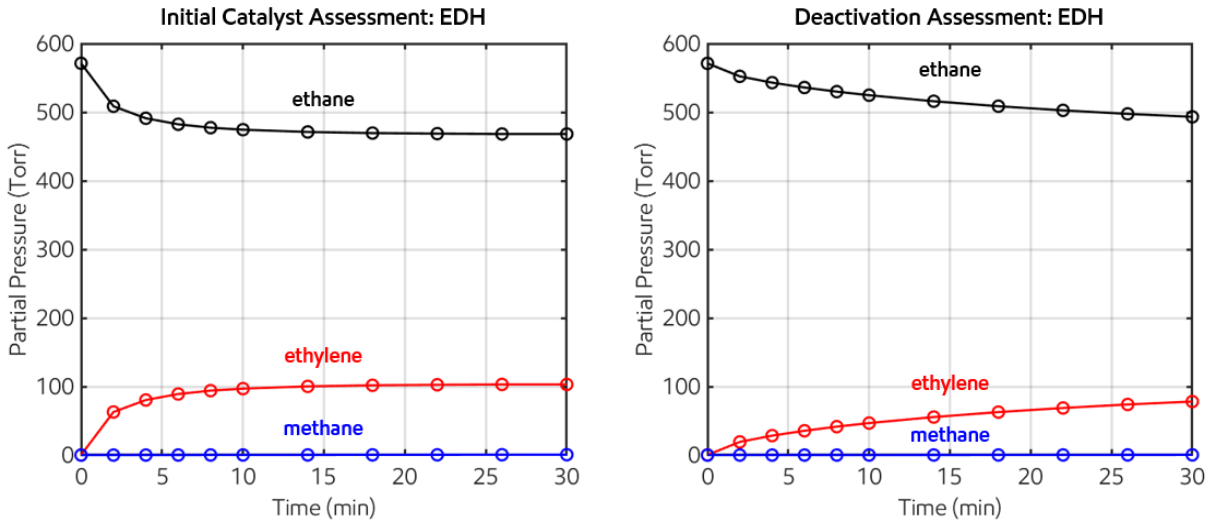

Figure S3. Assessment of catalyst deactivation before and after simulated feed experiments. Left: Experiment #1, 570 Torr ethane only at 600 °C (same experiment in Figure 6). Right: Experiment #3A, which is a replicate of Experiment #1 (570 Torr ethane only at 600 °C) after Experiments #1, #2 and #3 (main text, Figure 6) have been run on the same catalyst load. Catalyst deactivation can be seen by the large decrease in the rate of ethylene production (~10× based on initial rates), but is not completely deactivation, still allowing for catalytic ethane dehydrogenation to ethylene.

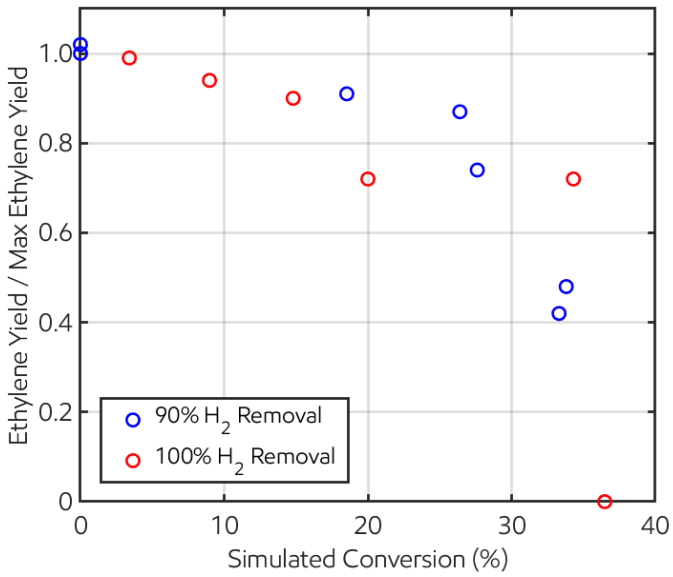

Figure S4. Summary of batch reactor EDH and simulated feed experiments, demonstrating at higher simulated conversions, the ethylene yield achieved is farther away from the maximum thermodynamic ethylene yield.

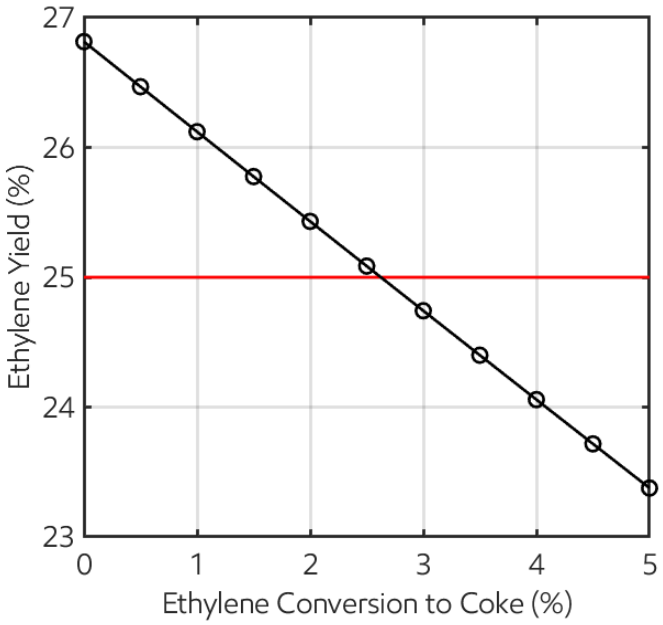

Figure S5. Calculated thermodynamic ethylene yield at 25% simulated conversions, 100% H_2 removal, 600 °C, 5 atm and 90% hydrocarbon feed with 10% inert. The calculation demonstrates the effect on ethylene yield if a given percent of ethylene converts to coke (i.e. $C_2H_4 \rightarrow 2C + 2H_2$), resulting in the production of H_2 and re-equilibration of the gas-phase species. If more than ~2.5% of ethylene is converted to coke, the excess H_2 produced causes ethylene hydrogenation to occur, due to re-equilibration of the gas-phases species, only considering the EDH equilibrium.

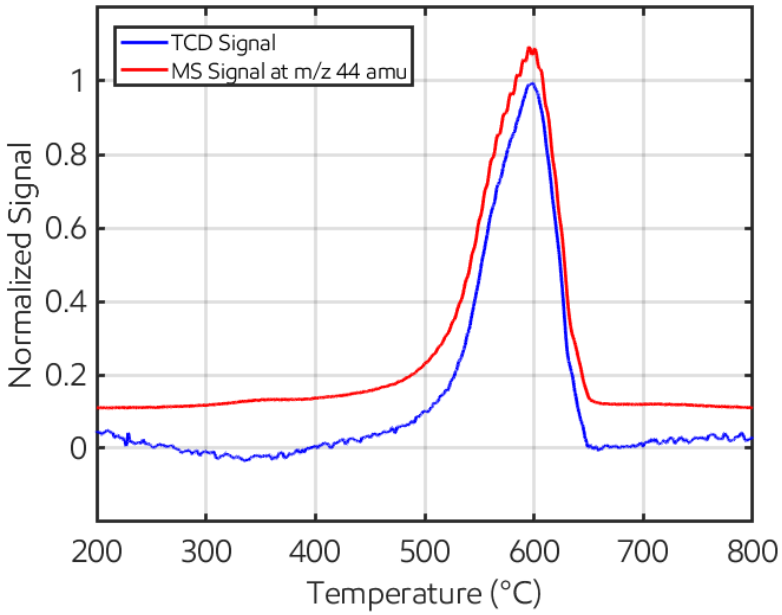

Figure S6. Temperature Programmed Oxidation (TPO) of the spent catalyst used for the simulated ethane dehydrogenation testing in Figure 9. The TPO experiment was run with 5% O_2/He, with a temperature ramp rate of 5 °C/min. Analysis was done with two detectors: TCD and mass spectrometry (signals vertically offset for clarity). CO_2 production, in which the carbon source is coke, was confirmed by monitoring the mass spectra at m/z of 44 amu, which is the molecular mass of CO_2.