Supplementary material for:

Setting up In_2O_3-ZrO_2/SAPO-34 Catalyst for Improving Olefin Production via Hydrogenation of CO_2/CO Mixtures

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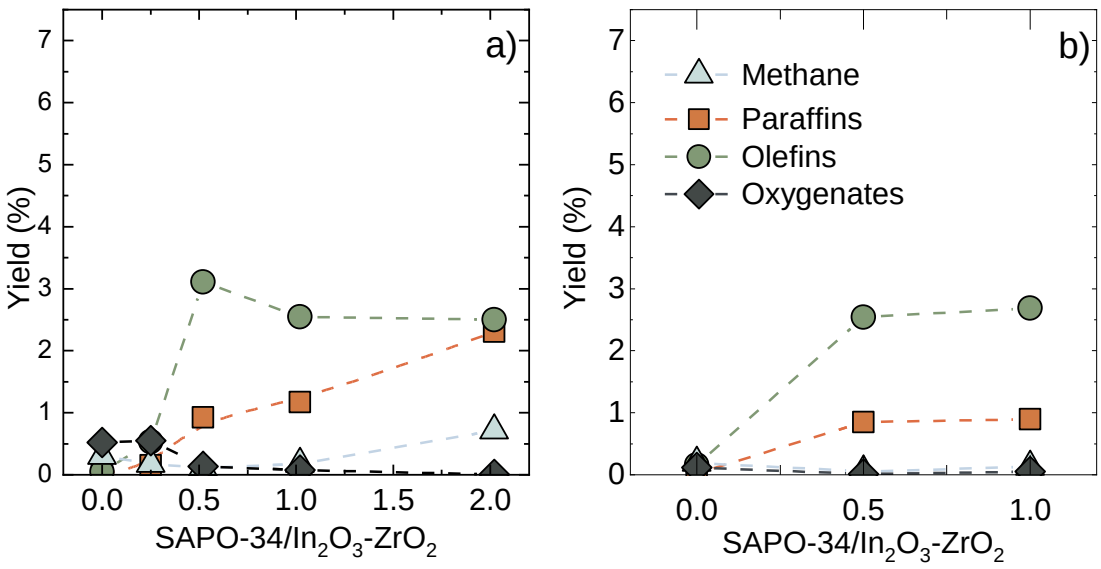

Figure S1 Effect of SAPO-34/In_2O_3-ZrO_2 mass ratio in the tandem catalyst on products yields. Feed: a) $H_2/CO/CO_2$, b) H_2/CO_2.Reaction conditions: 400 ºC; 30 bar; H_2/CO_x, 3; space time, 3.35 g_{InZr} h mol_C^{-1}; time on stream, 16 h.

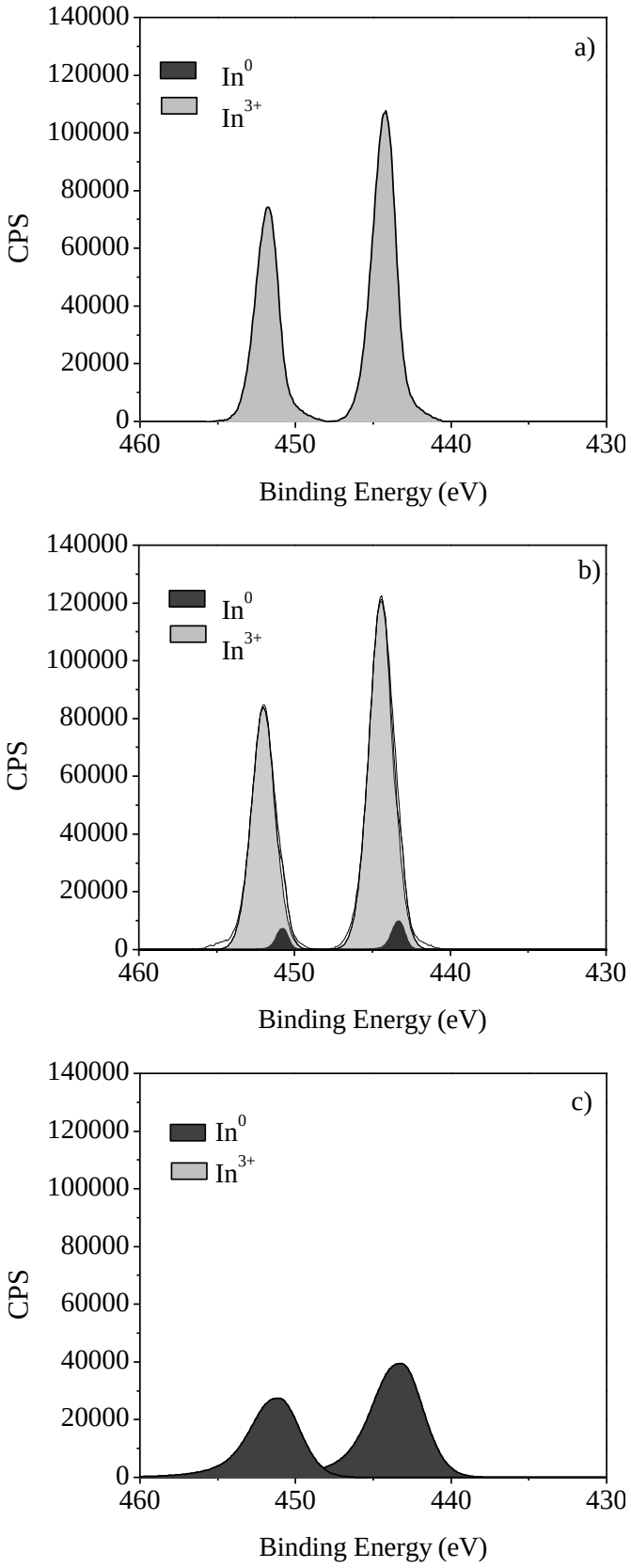

Figure S2 XPS profiles of In_2O_3-ZrO_2 catalyst subjected to different reduction treatments: a) without treatment, b) partial reduction, c) complete reduction.

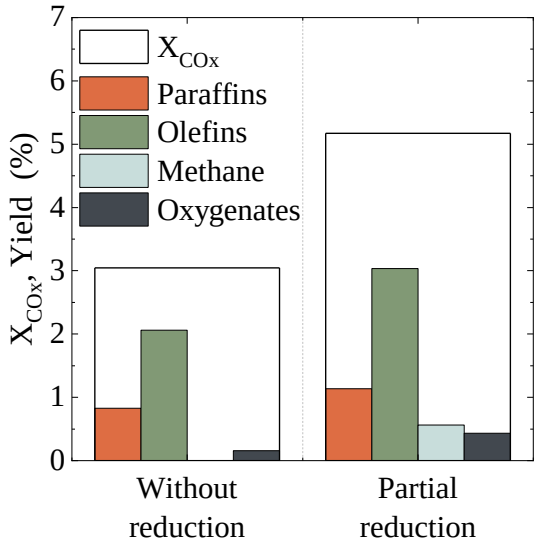

Figure S3. Effect of catalyst reduction on products yields and on CO_x conversion. Reaction conditions: feed, H_2/CO; 400 ºC; 30 bar; H_2/CO_x ratio, 3; CO_2/CO_x, 0; space time, 3.35 g_{InZr} h mol_C^{-1}; time on stream, 16 h.

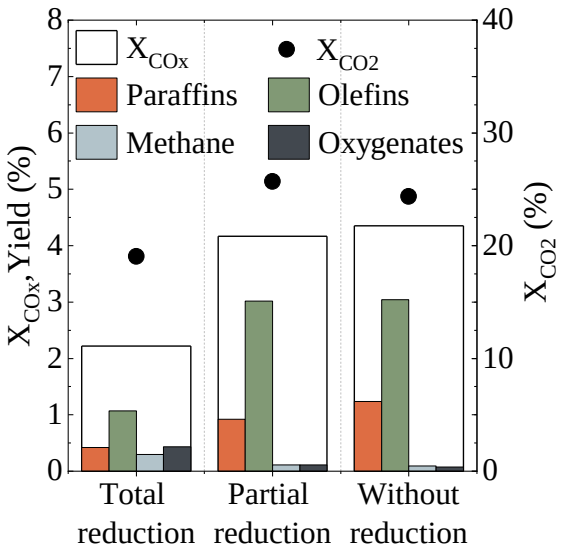

Figure S4. Effect of catalyst treatment on product yields and CO_x and CO_2 conversion. Reaction conditions: feed, $H_2/CO_2/CO$; 400 ºC; 30 bar; H_2/CO_x, 3; CO_2/CO_x, 0.5; space time, 3.35 g_{InZr} h mol_C^{-1}; time on stream, 16 h.

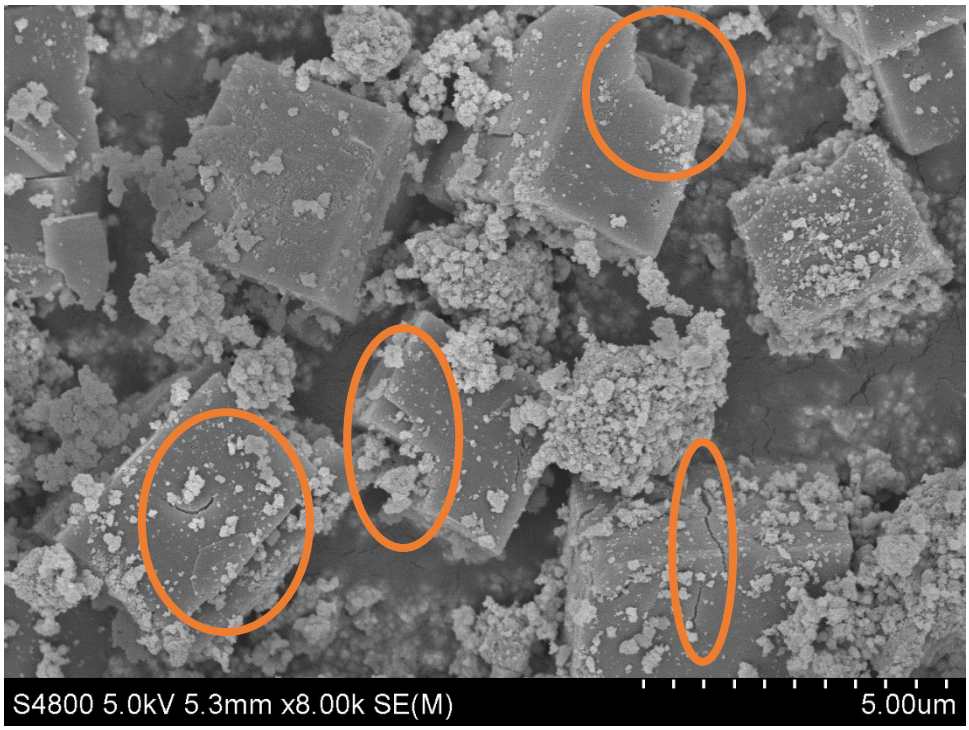

Figure S5 SEM image of the hybrid In_2O_3-ZrO_2/SAPO-34 catalyst.

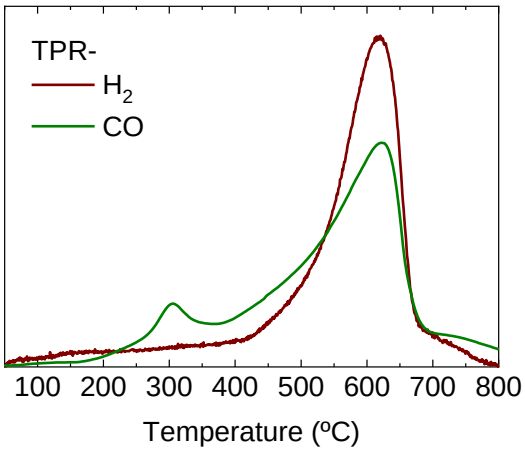

Figure S6 H_2-TPR and CO-TPR profiles for In_2O_3-ZrO_2 catalyst.

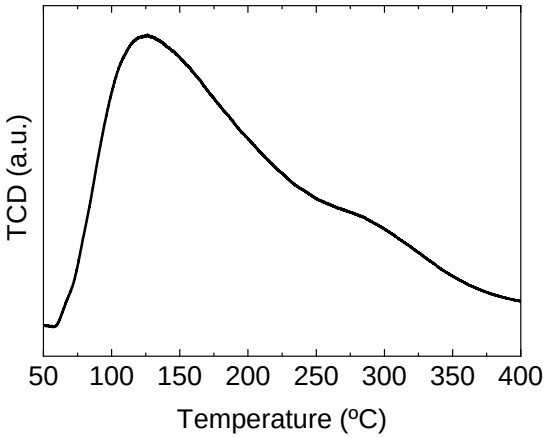

Figure S7 CO_2-TPD profile for In_2O_3-ZrO_2 catalyst.

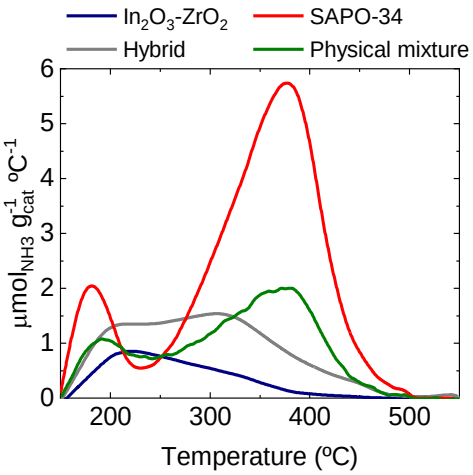

Figure S8 NH_3-TPD profiles for the In_2O_3-ZrO_2, SAPO-34, hybrid In_2O_3-ZrO_2/SAPO-34 catalyst and In_2O_3-ZrO_2/SAPO-34 prepared by physical mixture of both.

Description of the reaction equipment

An automated *PID En. & Tech. Microactivity Reference* equipment, provided with an isothermal packed-bed reactor connected to a gas (micro)-chromatograph *Varian CP-4900* was used for the kinetic runs. The reaction equipment is designed to operate up to 700 ºC and 100 bar for heterogeneous catalytic studies, and it allows operating with liquid and gaseous feeds.

The gaseous reactants are fed to the reactor through a set of *Bronkhorst High Tech B. V.Series* mass controllers, which are independent to pressure and temperature changes and protected by check valves. Shut off valves and a lecture system to measure and control the flowrates (10-100 cm^3 min^{-1}) complement the system. The equipment allows to feed up to six gaseous streams and one liquid stream simultaneously, classified as follows:

- Reactive gases: H_2, CO and CO_2
- Inert gases: N_2, used for conditioning the system, or He, utilized for dragging the sample into the chromatograph.
- Oxidant gas for catalyst regeneration: air.

When the operating pressure requires the CO_2 to be fed in liquid form, a *Gilson 307* piston pump, connected to a *Huber Minichiller* refrigeration system to keep the CO_2 at -10 ºC, was used. This equipment allowed feeding a liquid flowrate comprised between 0.010 mL min^{-1} and 5 mL min^{-1}, up to 200 bar. For other liquid feeds, *an Analytical Scientific Instruments 521 HPLC* pump designed to operate up to a maximum flow of 10 mL min^{-1} and 400 bar.

Both streams, liquid and gaseous, mix in a tee connector inside a hot box, where they homogenize and preheat, avoiding condensations, before going to a six-port valve. Depending on the position of the valve, the gases are sent to the reactor inlet or bypass the reactor and are sent to analysis in the micro-GC. Thus, this configuration allows to analyze reactant gases or products stream.

The reactor is made of 316 stainless steel, with an inner diameter of 9 mm and 30.5 cm long, of which 10 cm are used as effective length. With the aim of avoiding possible interactions of the reactor walls (Fe oxides, giving way to side reactions) the inside was coated with a ceramic layer to avoid the direct contact of the reaction components with the steel, ensuring that the walls are inert. The reactor is inside a cylindrical stainless steel covered ceramic oven. The catalytic bed is formed by the corresponding mixture of catalyst/catalysts and an inert solid (SiC, carborundum) added to ensure isothermal conditions along the bed, avoid preferential flow paths and achieve a sufficient bed height when operating with low space time values.

Temperature is measured by K type thermocouples and controlled by a digital *TOHO TTM 005*. Additionally, *Sensor-Technik-Wiedemann* type transducers are used to measure reactors pressure. These transducers can operate in a wide pressure range (from 100 mbar up to 100 bar). A *P-600* series pressure controller acts on a needle valve.

For the products analysis, a sample of the reactor outlet stream is diluted in a He flow and sent to the micro-GC every 4 minutes through a heat-insulated line ensuring that no liquid enters to the micro chromatograph, the remaining stream exits the system through a vent outlet. The system is also equipped with a peltier to cool down the outlet stream to 0 ºC in order to condensate the heaviest compounds. If needed, the liquid level can be controlled by its own controller, that acts on a needle valve for the extraction of condensed liquids.

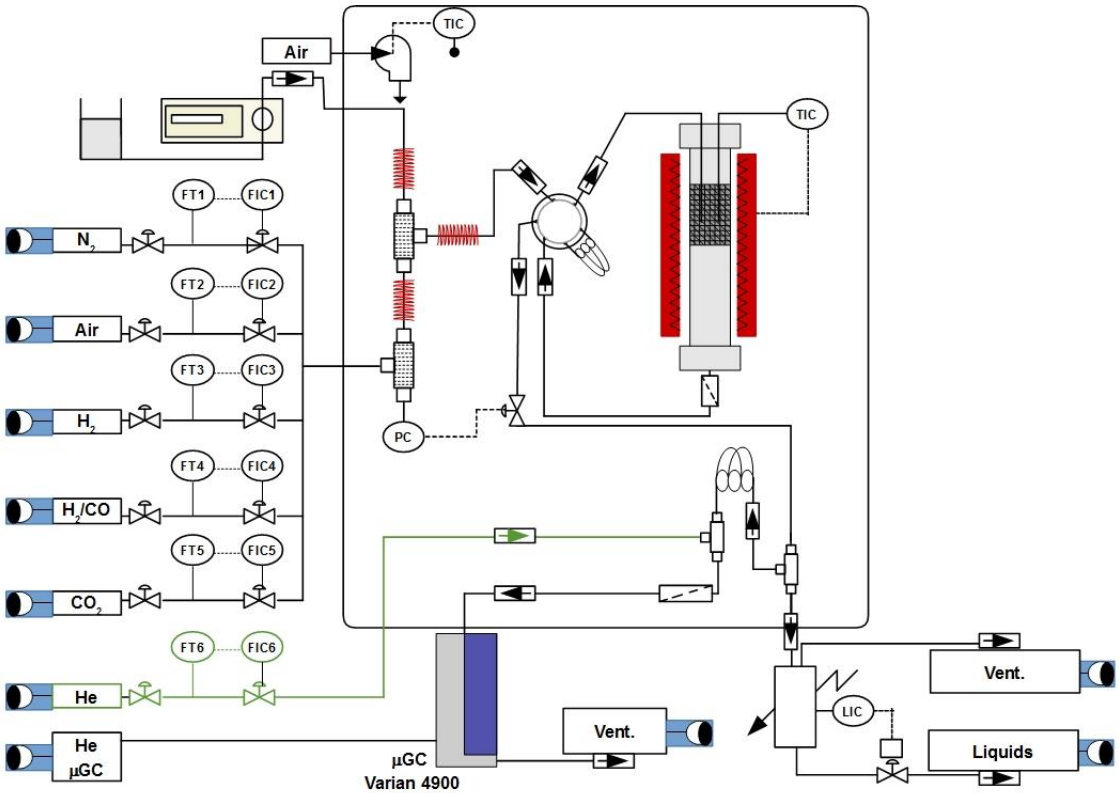

Figure S9 Flow diagram of the reaction equipment.