

Supplementary information

Supported Rhenium catalysts for the hydrogenation of levulinic acid derivatives: limits and potential

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Experimental

The reactions were conducted in 50 ml batch autoclave equipped with a stirring bar. After the addition of the reaction components (i.e. 5-6 g of substrate and 5%wt of catalyst) the system was flushed three times with H₂ and finally set to the desired H₂ pressure. Afterwards the autoclave was placed in a heating mantle. The reaction time started once the respective temperature was reached. Because it has been decided to operate at the same pressure initially set, the system need hydrogen refilling in order to keep constant hydrogen pressure. The reactions were quenched by external cooling with ice water. After a cool-down period of 25 min, 1 mL of gas phase was sampled and injected to GC-MS. The reaction solution was stored in 50 mL flask adding acetonitrile. A sample 0,5 mL of the as-obtained reaction solution was added in 25 mL flask with acetonitrile adding 20 µL of external standard (i.e. *n*-octane). Last, final solution was filtered to remove the catalyst particles before transferring it in a glass vial to carried out quantification by GC.

The compounds of interest were analyzed and quantified using a Shimadzu Gas Chromatograph 2010 Pro equipped with a non-polar capillary column Agilent HP-5 (5% phenyl–95% methylsiloxane) having these dimensions: 25m x 320µm x 1.05µm. The injector was maintained at a temperature of 280°C in the split mode (30:1), the carrier gas was nitrogen (1.2 mL/min in column). The volume of solution injected for each analysis was 0.5 µL. The standard programmed temperature was as follow: 2 min isotherm at 50°C, then a 10°C/min temperature increase up to 110°C (the latter maintained for 2 min), and then 20°C/min up to 280°C (the latter for 2 min). Each compound was calibrated with respect to *n*-octane in order to find the corresponding response factor in the appropriate range of concentrations (5×10^{-5} to 5×10^{-3} M for each LA derivatives and for methanol)

The GC-MS was an Agilent Technologies 6890 GC coupled with a mass spectrometer Agilent Technologies 5973 equipped with a non-polar column (5% phenyl - 95% methylsiloxane), 30 m x 250 µm x 1.05 µm. Helium was used as carrier gas and flow rate in the column equal to 1ml/min; in the split mode (50:1); total flow was 23.9 mL/min. For gas phase analysis the injector was maintained at a temperature of 250 ° C The standard temperature program was: 10 min isotherm at 40°C, then a 10°C/min temperature increase up to 220°C, final isothermal step for 5 min. Product liquid phase identification was performed by means of a GC-MS spectroscopy. The injector was maintained at a temperature of 280 ° C. The volume of solution injected was 0.5 µL and the standard temperature program was the same as that used for GC: 2 min isotherm at 50°C, then a 10°C/min temperature

increase up to 110°C (the latter maintained for 2 min), and then 20°C/min up to 280°C, final isothermal step for 5 minutes.

The reagent conversion (eq 1) and product yield (eq 2) were calculated using the following equations:

$$Conv. R = \frac{mol R_{in} - mol R_{out}}{mol R_{in}} * 100 \quad (1)$$

$$Yield P = \frac{mol P_{out}}{mol R_{in}} * n_s * 100 \quad (2)$$

n_s = ratio of stoichiometric coefficients of R and product P{i.e. usually 1, but also 2 or 1/2}

Molar balance based on starting reagent was considered as follow (eq 3):

$$Molar\ balance\ (\%) = \frac{mol R_{out} + \sum n_s * mol P_{out}}{mol R_{in}} = 100 - Conv. R + \sum Yield P \quad (3)$$

The molar coefficients “ n_s ” taken in consideration for the main products are the following:

γ -valerolactone (GVL), methyl valerate (MV), valeric acid (VA), 1-pentanol (1-PAO), methyl-pentyl ether = 1; pentyl valerate (PV) and di-pentyl ether = 2

VA/VE productivity is calculated based on the equation as below:

$$Productivity_{VA+VE} = \frac{mmol_{VA+VE}}{metal\ weight(g) * Reaction\ time(h)} \quad (4)$$

Catalyst's characterization

The powder X-ray diffraction (XRD) patterns were obtained with Ni-filtered Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) on a Philips X'Pert vertical diffractometer equipped with a pulse height analyzer and a secondary curved graphite-crystal monochromator.

The specific surface area (SSA) was estimated by single point Brunauer-Emmett-Teller (BET) method through nitrogen adsorption-desorption isotherms of the catalysts by measurement at 77 K on a Sorptly 1750 Fison instrument. Sample (usually 100 mg) was outgassed at 150 °C before N₂ absorption the analysis.

For Temperature Programmed Reduction (TPR) analysis, 100 mg of dry sample were placed into a quartz U-tube, which functions as a fixed bed reactor. The instrument employed was a Autochem 2920 - Micromeritics. In order to ensure a completely dry sample, the U-tube was heated to 120 °C and kept there for 30 minutes under He flow. For the TPR measurement a flow of 5 % H₂ in Argon was applied and the U-tube was heated from room temperature to 500 °C at a rate of 5 °C/min. Hydrogen consumption was detected with a thermal conductivity detector (TCD).

Attenuated Total Reflectance FTIR spectra were recorded on a Bruker Alpha Platinum-ATR spectrophotometer equipped with Diamond window (4000-400 cm⁻¹ spectral window, 4 cm⁻¹ resolution, 32 scans).

Re content was measured by microwave plasma-atomic emission spectroscopy (MP-AES) analyses using an Agilent Technologies 4210 MP-AES instrument. In particular, post reaction solutions were filtered with a 0.2 micron TEFLON syringe filter to completely and effectively remove the heterogeneous catalyst from the solution. Then the obtained solution was diluted in H₂O to fall within the range of the calibration curve (0-300 ppm). The emissions at 346.046 nm, 346.473 nm and 488.914 nm for rhenium were evaluated. The mol% of leached Rhenium was calculated taking into account the actual amount of Rhenium present over the catalysts evaluated by analogous MP-AES analyses performed via the complete acid mineralization of a precise amount of catalyst and proper dilution in water.

Materials

Reagents and standards used during the experiments were analytical grade: acetonitrile ≥99.9%, octane 98%, methyl levulinate ≥98%, γ-valerolactone 99%, 2-methyltetrahydrofuran 99%, 1,4-pentadiol 99%, valeric acid 99%, methyl valerate 99%, 1-pentanol 99%, valeraldehyde 97%, methanol ≥99.9%, ruthenium(III) chloride hydrate 99%, ammonium perrhenate(VII) ≥99%, zirconium(IV) oxynitrate hydrate 99%, ammonium hydroxide solution 28–30% (NH₃ basis), obtained from Sigma-Aldrich, while pentyl valerate 97% and di pentyl ether 98%, obtained from TCI. All used as received.

Commercial supports NH₄ZSM-5 (Zeolyst, CBV 8014) SiO₂ (GRACE)

Catalyst's characterization - N₂-Physisorption, MP-AES, XRD and TPR Results

Table S1 Catalyst characterization *via* N₂-physisorption and MP-AES

Catalyst	SSA m ² /g	Re loading %wt
Re-O/SiO ₂	420	4,63
Re-O/HZSM-5	414	4,43
Re-Ru-O/SiO ₂	238	4,57
Re-Ru-O/HZSM-5	403	4,69

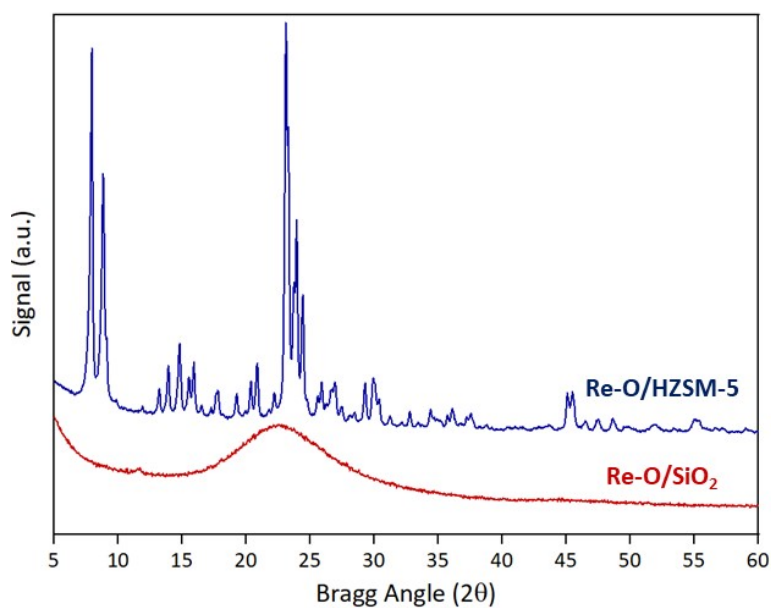


Figure S1. XRD pattern of the Re oxide supported on SiO₂ (red) and HZSM-5 (blue) catalysts.

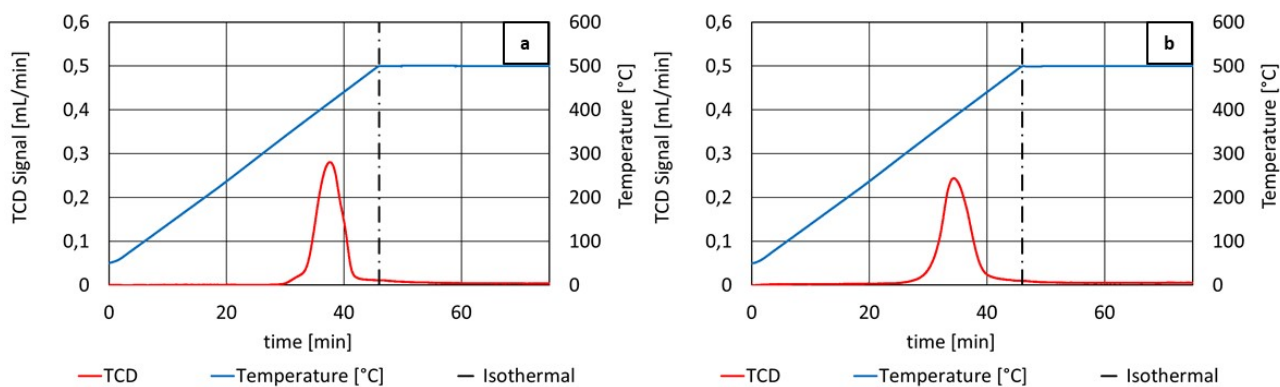


Figure S2. TPR profiles of the Re oxide supported on a) SiO₂ and b) HZSM-5 catalysts, isotherm 500 °C.

Gas phase chromatograms by GC-MS analysis

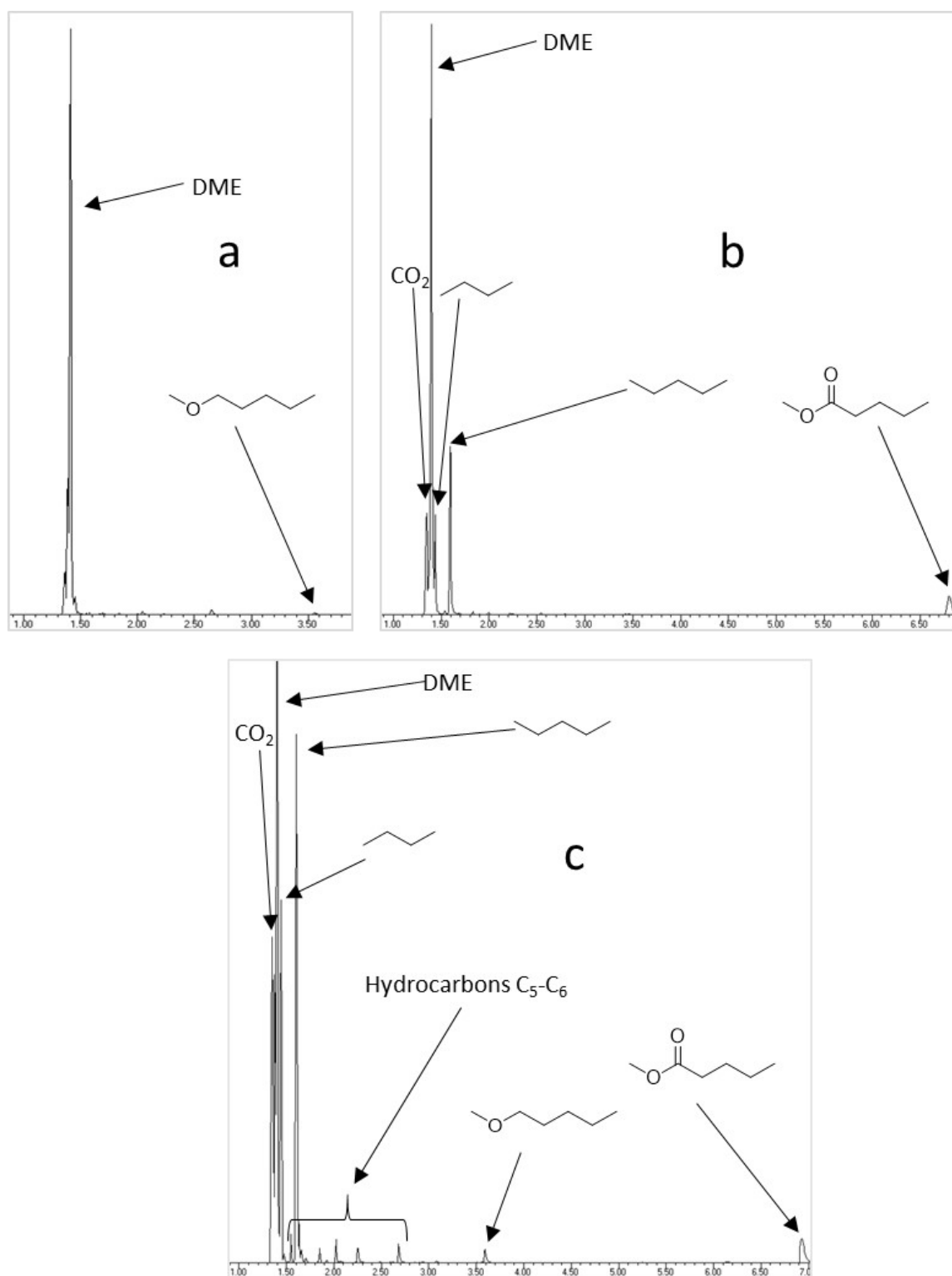


Figure S3. Chromatograms of GC-MS analysis of the headspace after: a) 4 h over Re-O/HZSM-5; b) 4 h over Re-Ru-O/HZSM-5; c) 24 h over Re-Ru-O/HZSM-5. Reaction conditions: *Solvent free*, T = 230°C, P_{H₂} = 40 bar, catalyst loading = 5 %wt [m_{cat}/m_{ML}].

Reaction trends of hydrogen conversion and methanol balance

“Apparent H₂ Conv.” means the molar conversion of hydrogen considering the initial pressure (and possible refilling) and assuming the final pressure composed only by H₂. MeOH balance is the molar ratio of MeOH and its derivatives (i.e. MV, ML, ecc...) respect to the starting amount of ML. Meanwhile, assuming that most of the methanol is converted to DME is possible to estimate its pressure contribution on the headspace. Hence, it has been calculated “Estimated H₂ Conv.”, the latter is the molar conversion of hydrogen subtracting the contribution of DME to the pressure after reaction.

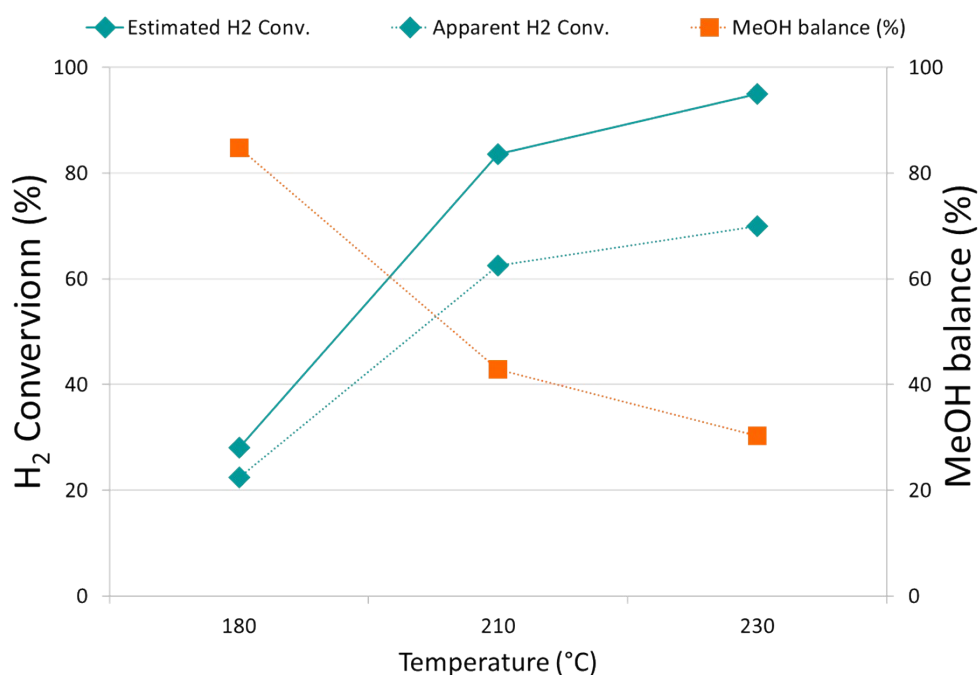


Figure S4. Reaction trends of H₂ conversion and MeOH balance in ML hydrogenation over Re-O/HZSM-5. Reaction conditions: Solvent free, T = variable, P_{H₂} = 40 bar, t = 4 h, catalyst loading = 5 %wt [m_{cat}/m_{ML}].

$$H_2 \text{ Conversion (\%)} = \left(1 - \frac{\text{mol } H_{2,f}}{\text{mol } H_{2,in} + \text{mol } H_{2,refill}}\right) * 100 \quad (5)$$

$$MeOH \text{ balance (\%)} = \frac{\Sigma \text{mol } MeOH_{derivatives}}{\text{mol } ML_{in}} * 100 \quad (6)$$

Effect of hydrogen pressure on catalytic activity

The role of hydrogen pressure was evidenced by means of experiments at different pressure in the range from 10 to 40 bar (**Figure S5**). During tests at 10 and 25 bar, which correspond to a H₂/ML molar ratio of 0.4 and 1 respectively, ML conversion ranged from 64% to 90% respectively, demonstrating the role of the pressure for increasing hydrogen solubility in the organic phase. Meanwhile, GVL and Others yields are similar to each other and close to 15% at 10 bar decreasing down to ca. 5% at higher pressure with the concomitant increase of MV+VA yield. Interestingly, also the molar balance is affected by hydrogen pressure and is below 67% in the milder conditions. During the reaction time, initial H₂/ML molar ratio did not change for the test at 10 bar because no hydrogen refilling was done. For the 25 bar test, H₂/ML molar ratio increased from 1 to 1.2 to keep constant pressure, meanwhile in the 40 bar test H₂/ML molar ratio showed the maximum increasing, from 1.4 to 2. This suggest that lower hydrogen pressure tests are significantly affected to light product generation as DME, which may interfere with hydrogen refilling in order to face pressure decreasing. Thus, in the presence of a limited amount of dissolved hydrogen, which means limited amount of activated hydrogen over the catalyst surface, ML mixtures may undergo several acid-catalyzed parasite reactions, promoting heavy product generation not detected in liquid phase, the latter may also promote fouling effect on catalyst.

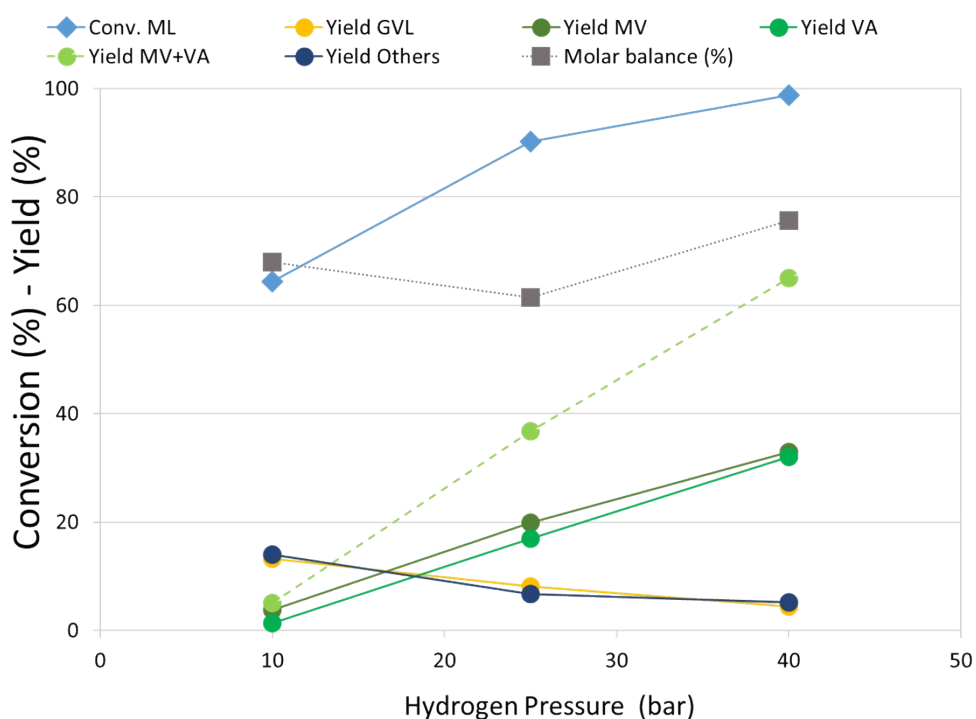


Figure S5. Effect of hydrogen pressure in ML hydrogenation over Re-Ru-O/HZSM-5. Reaction conditions: *Solvent free (Neat ML)*, $T = 230^{\circ}\text{C}$, $P_{\text{H}_2} = \text{variable}$, $t = 4 \text{ h}$, catalyst loading = 5%wt [$m_{\text{cat}}/m_{\text{ML}}$]. Others = 2-MTHF, 4-HPA/E and unidentified products.

Post reaction catalyst's characterization

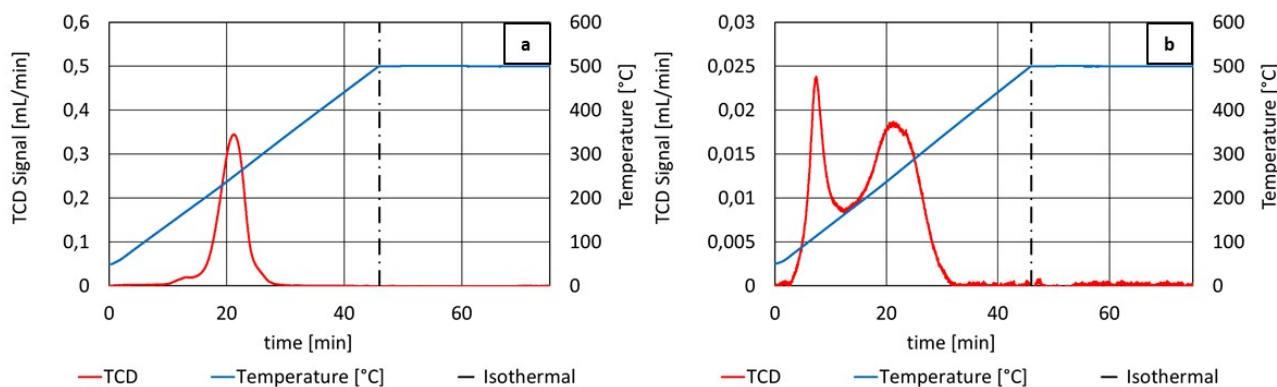


Figure S6. TPR profiles of the Re-Ru-O/HZSM-5 a) pre and b) post reaction, isotherm 500°C . Reaction conditions: *Solvent free (Neat ML)*, $T = 230^{\circ}\text{C}$, $P_{\text{H}_2} = 40 \text{ bar}$, $t = 4 \text{ h}$, catalyst loading = 5 %wt [$m_{\text{cat}}/m_{\text{ML}}$].

Effect of pre-reduction treatment over bimetallic system

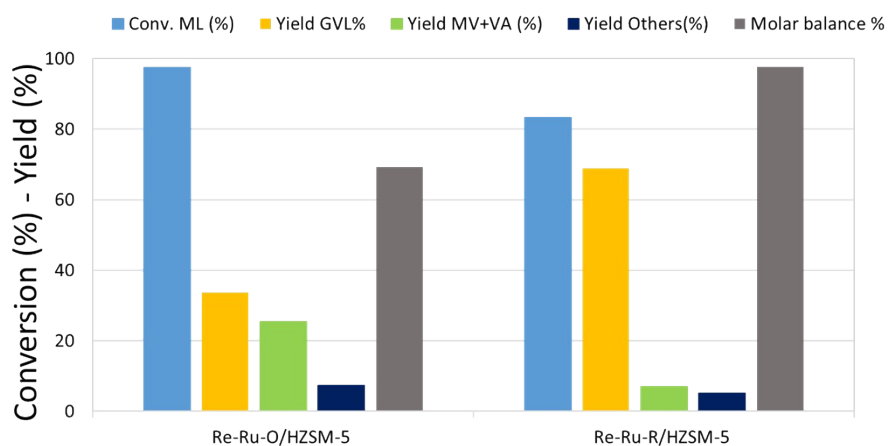


Figure S7. ML hydrogenation over Re-Ru-R/HZSM-5. Reaction conditions: *Solvent free (Neat ML)*, $T = 210^{\circ}\text{C}$, $P_{\text{H}_2} = 40 \text{ bar}$, $t = 4 \text{ h}$, catalyst loading = 5 %wt [$m_{\text{cat}}/m_{\text{ML}}$]. Others = 2-MTHF, 4-HPA/E and unidentified products.

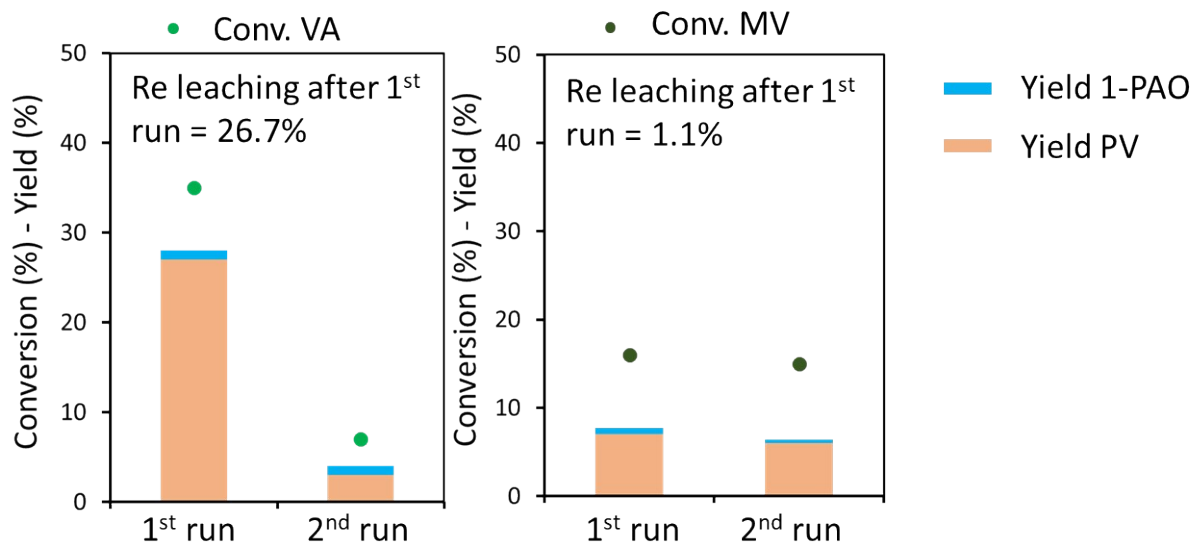


Figure S8. VA (left) and ML (right) hydrogenation over Re-O/SiO₂. Reaction conditions: *Solvent free (Neat reactant)*, T = 210 °C, P_{H₂} = 40 bar, t = 4 h, catalyst loading = 5 %wt [m_{cat}/m_{ML}]. Others = 2-MTHF, 4-HPA/E and unidentified products.

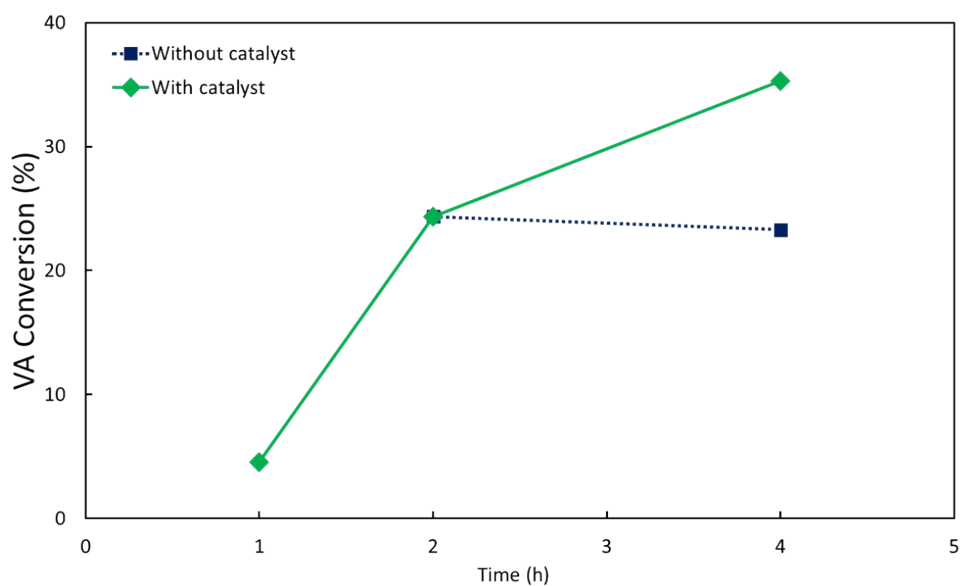


Figure S9. Sheldon test over Re-O/SiO₂. Reaction conditions: *Solvent free (Neat VA)*, T = 210 °C, P_{H₂} = 40 bar, t = variable, catalyst loading = 5 %wt [m_{cat}/m_{ML}]. Others = 2-MTHF, 4-HPA/E and unidentified products.

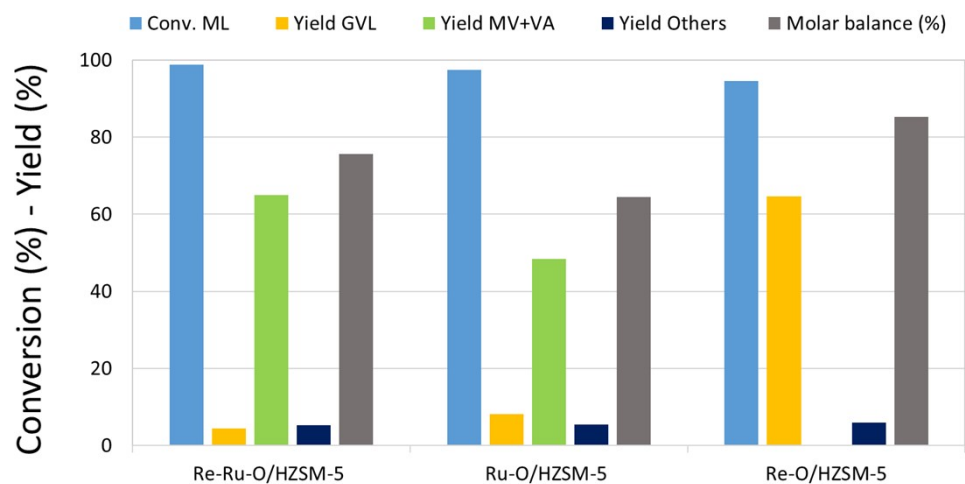


Figure S10. Comparison of the catalytic activity of 5-1 wt% Re-Ru-O/HZSM-5, 5 wt% Ru-O/HZSM-5 and 5 wt% Re-O/HZSM-5. Reaction conditions: Solvent free (Neat ML), T = 230 °C, P_{H₂} = 40 bar, t = 4 h, catalyst loading = 5 %wt [mcat/mML].