Supporting Information

H₂-Free Re-Based Catalytic Dehydroxylation of Aldaric Acid to Muconic and Adipic Acid Esters

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experimental

dehydroxylation process

Experiments were performed in a six parallel batch high-pressure autoclave system (Amar Equipment Pvt. Ltd., Mumbai, India). Each batch system consists of a 250 mL vessel (inner diameter 67 mm and height 80 mm), with a magnetically driven Rushton turbine impeller (diameter of 30 mm, placed 14 mm above the autoclave bottom), a gaseous phase condenser where gaseous products cool down prior the analysis by gas chromatography, and a liquid phase sampling line, which enables collecting the liquid samples along the reaction time. The autoclave system is equipped with a separate internal and external cooling system that ensures proper temperature regulation inside of the each autoclave and for outer parts (sampling lines, head of the impeller). Each autoclave can operate under different operating conditions (reaction mixture composition, reaction temperature, time and pressure), each of them in a batch regime. Separately, each autoclave is directly connected to the micro GC through a gaseous phase condenser. Initial reaction mixture consisted of 120 mL (or 95 g) of solvent (MeOH, 99.9 wt%, Sigma Aldrich, St. Louis, MO, USA), 0.2 g of reactant, which was aldric acid (Mucic acid, 97 wt%, Sigma Aldrich, St. Louis, MO, USA or Glucaric (D-saccharic) acid monopotassium salt, >98 wt%, Sigma Aldrich, St. Louis, MO, USA), appropriate amount (5 – 15 wt% regarding to the reactant) of homogeneous Re catalyst (MeReO$_3$ (71.0-76.0 wt% of Re), KReO$_4$ (trace metal basis) or HReO$_4$ (75-80 wt% in H$_2$O)), all of them purchased at Sigma Aldrich, St. Louis, MO, USA) or heterogeneous catalyst(s) (Re/C, Re/SiO$_2$, Re/Al$_2$O$_3$; 5 wt% Re loading, powder; Riogen, NJ, USA). Hydrogenation heterogeneous catalysts were used in few experiments; Pt/C (5 wt% Pt loading, powder; Sigma Aldrich, St. Louis, MO, USA) and Pd/C (5 wt% Pd loading, powder; Sigma Aldrich, St. Louis, MO, USA). Reactant, solvent and catalyst(s) were in appropriate amounts weighted in an autoclave vessel, placed to the housing with a heating belt and sealed. Firstly, each autoclave was flushed with inert atmosphere (N$_2$; 5.0, Messer, Bad Soden am Taunus, Germany), then pressurized with hydrogen (H$_2$; 5.0, Messer, Bad Soden am Taunus, Germany). Agitation of 600 min$^{-1}$ ensured sufficient mixing for complete dispersion of the catalyst particles and gaseous phase aspiration. The influence of reaction temperature was tested in the range between 100 to 140 °C, started at the room temperature, heated up to the set temperature with a heating ramp 5 K min$^{-1}$. Dehydroxylation reactions were performed normally for 72 h at the plateau temperature than autoclave was rapidly cooled down. When the temperature decreased below 30 °C the pressure was released from autoclave, and before opening the headspace was purged with inert atmosphere (N$_2$). During the reaction time liquid samples were collected. All tested experimental conditions are summarized in Table S11, S12 and S13.

Additional dehydroxylation reaction was performed in a Parr reactor system (Parr 5000), where firstly catalyst was reduced under hydrogen atmosphere (H$_2$ flow of 100 mL h$^{-1}$) at 400 °C for 3 h. After catalyst reduction, closed autoclave was transferred to glove box, where appropriate amount of catalyst and mucic acid (in same mass ratio as in previous experiments)
were weighted. Weighting in inert atmosphere (argon) in glove box prevents contacting the reduced catalyst with air. Autoclave was closed and transferred back to reaction set-up, where appropriate amount of methanol was firstly vacuumed and purged with nitrogen to remove any traces of air or oxygen and added into the autoclave. Reaction mixture was heated up to 120 °C under 0.5 MPa of nitrogen and kept it for next 72 hours at the plateau temperature. During the reaction time liquid samples were collected and were analyzed by GCMS. After reaction finished and cooled down, gaseous phase was removed from headspace and 3 MPa of hydrogen was added to hydrogenate the obtained product. Hydrogenation was performed at 200 °C for additional 9 hours.

Table S1: List of experiments using mucic acid as a reactant. Homogeneous Re species were used as catalysts with or without Pt/C or Pd/C as hydrogenation catalysts. Experiments were performed under elevated hydrogen or nitrogen pressure.

| Exp. number | Catalyst | Catalyst hom. (wt%)¹ | Active metal amount (mmol) | Mucic acid amount (mmol) | Solvent | t (h) | T (°C) | $P_{H_2}$ (MPa) | $P_{N_2}$ (MPa) |
|-------------|----------|----------------------|-----------------------------|------------------------|---------|------|-------|--------------|---------------|
| 1₂ M        | MeReO₃   | 12.0                 | 0.096                       | 0.95                   | MeOH    | 4    | 120   | 0.5          | 0             |
| 2₂ M        | MeReO₃   | 12.0                 | 0.096                       | 0.95                   | EtOH    | 4    | 120   | 0.5          | 0             |
| 3₂ M        | MeReO₃   | 12.0                 | 0.096                       | 0.95                   | PrOH    | 4    | 120   | 0.5          | 0             |
| 4₂ M        | MeReO₃   | 12.0                 | 0.096                       | 0.95                   | EtOH    | 4    | 120   | 0.5          | 0             |
| 5₂ M        | MeReO₃   | 12.0                 | 0.096                       | 0.95                   | MeOH    | 72   | 100   | 0.5          | 0             |
| 6₂ M        | MeReO₃   | 12.0                 | 0.096                       | 0.95                   | MeOH    | 72   | 120   | 0.5          | 0             |
| 7₂ M        | MeReO₃   | 12.0                 | 0.096                       | 0.95                   | MeOH    | 72   | 140   | 0.5          | 0             |
| 8₂ M        | MeReO₃   | 12.0                 | 0.096                       | 0.95                   | MeOH    | 72   | 100   | 0.5          | 0             |
| 9₂ M        | MeReO₃   | 12.0                 | 0.096                       | 0.95                   | MeOH    | 72   | 120   | 1.0          | 0             |
| 10₂ M       | MeReO₃   | 6.0                  | 0.048                       | 0.95                   | MeOH    | 72   | 120   | 0.5          | 0             |
| 11₂ M       | MeReO₃   | 18.0                 | 0.145                       | 0.95                   | MeOH    | 72   | 120   | 0.5          | 0             |
| 12₂ M       | MeReO₃   | 12.0                 | 0.096                       | 0.95                   | MeOH    | 72   | 120   | 0.5          | 0             |
| 13₂ M       | MeReO₃   | 12.0                 | 0.096                       | 0.95                   | MeOH    | 72   | 120   | 0.5          | 0             |
| 14₂ M       | MeReO₃   | 12.0                 | 0.096                       | 0.95                   | MeOH    | 72   | 120   | 0.5          | 0             |
| 15₂ M       | MeReO₃   | 12.0                 | 0.096                       | 0.95                   | MeOH    | 72   | 120   | 0.5          | 0             |
| 16₂ M       | MeReO₃   | 12.0                 | 0.096                       | 0.95                   | MeOH    | 72   | 120   | 0.5          | 0             |
| 17₂ M       | KReO₄     | 12.0                 | 0.083                       | 0.95                   | MeOH    | 72   | 120   | 0.5          | 0             |
| 18₂ M       | KReO₄     | 12.0                 | 0.083                       | 0.95                   | MeOH    | 72   | 140   | 0.5          | 0             |
| 19₂ M       | HReO₄     | 12.0                 | 0.076                       | 0.95                   | MeOH    | 72   | 120   | 0.5          | 0             |
| 20₂ M       | HReO₄     | 12.0                 | 0.076                       | 0.95                   | MeOH    | 72   | 140   | 0.5          | 0             |
| 21₂ M       | KReO₄     | 12.0                 | 0.083                       | 0.95                   | MeOH    | 72   | 120   | 0.5          | 0             |
| 22₂ M       | KReO₄     | 12.0                 | 0.083                       | 0.95                   | MeOH    | 72   | 140   | 0.5          | 0             |
| 23₂ M       | KReO₄     | 12.0                 | 0.083                       | 0.95                   | MeOH    | 72   | 120   | 0.5          | 0             |
| 24₂ M       | KReO₄     | 12.0                 | 0.083                       | 0.95                   | MeOH    | 72   | 140   | 0.5          | 0             |

¹ Regarding to the mass of mucic acid in the autoclave
Table SI2: List of experiments using mucic acid as a reactant. Heterogeneous Re species were used as catalysts with or without Pd/C as a hydrogenation catalyst. Experiments were performed under elevated hydrogen or nitrogen pressure.

| Exp. No | Catalyst | Catalyst (wt%)$^1$ | Active metal amount (mmol) | Mucic acid amount (mmol) | Solvent | t (h) | T (°C) | $P_{H2}$ (MPa) | $P_{N2}$ (MPa) |
|---------|-----------|---------------------|-----------------------------|--------------------------|---------|-------|-------|-------------|-------------|
| 25      | Re/SiO$_2$ | 0.42                | 0.107                       | 0.95                     | MeOH    | 72    | 120   | 0.5         | 0           |
| 26      | Re/SiO$_2$ | 0.42                | 0.107                       | 0.95                     | MeOH    | 72    | 140   | 0.5         | 0           |
| 27      | Re/Al$_2$O$_3$ | 0.42            | 0.107                       | 0.95                     | MeOH    | 72    | 120   | 0.5         | 0           |
| 28      | Re/Al$_2$O$_3$ | 0.42            | 0.107                       | 0.95                     | MeOH    | 72    | 140   | 0.5         | 0           |
| 29      | Re/C      | 0.42                | 0.107                       | 0.95                     | MeOH    | 72    | **120**| **0.5**     | 0           |
| 30      | Re/C      | 0.42                | 0.107                       | 0.95                     | MeOH    | 72    | 140   | 0.5         | 0           |
| 31      | Re/C      | 0.42                | 0.107                       | 0.95                     | MeOH    | 72    | 140   | 1           | 0           |
| 32      | Re/C dried | 0.42               | 0.096                       | 0.95                     | MeOH    | 72    | 120   | 0.5         | 0           |
| 33      | Re/C reduced | 0.42             | 0.094                       | 0.95                     | MeOH    | 72    | 120   | 0.5         | 0           |
| 34      | Re/C      | 0.42                | 0.103                       | 0.95                     | MeOH    | 72    | 120   | 0.5         | 0           |
| 35      | Re/C      | 0.42                | 0.103                       | 0.95                     | MeOH    | 72    | 140   | 0.5         | 0           |
| 36      | Re/C      | 0.42                | 0.096                       | 0.95                     | MeOH    | 72    | 120   | 0.5         | 0           |
| 37      | Re/C reduced | 0.42             | 0.094                       | 0.95                     | MeOH    | 72    | 120   | 0.5         | 0           |
| 38      | Re/C      | 0.42                | 0.094                       | 0.95                     | MeOH    | 72    | 120   | 0.5         | 0           |
| 39      | Re/C      | 0.42                | 0.103                       | 0.95                     | MeOH    | 72    | 120   | 0           | **0.5**   |
| 40      | Re/C dried | 0.42               | 0.096                       | 0.95                     | MeOH    | 72    | 120   | 0           | 0.5        |
| 41      | Re/C reduced | 0.42             | 0.094                       | 0.95                     | MeOH    | 72    | 120   | 0           | 0.5        |
| 42      | Re/C reduced | 0.42             | 0.094                       | 0.95                     | MeOH    | 72    | 120   | 0           | 0.5        |
| 43      | Re/C      | 0.42                | 0.103                       | 0.95                     | MeOH    | 72    | 150   | 0           | 0.5        |
| 44      | Re/C      | 0.42                | 0.103                       | 0.95                     | MeOH    | 72    | 175   | 0           | 0.5        |
| 45      | Re/C reduced | 0.42             | 0.094                       | 0.95                     | MeOH    | 72    | 175   | 0           | 0.5        |
| 46      | Re/C reduced | 0.42             | 0.094                       | 0.95                     | i-PrOH  | 72    | 120   | 0           | 0.5        |
| 47      | Re/C reduced | 0.42             | 0.094                       | 0.95                     | BuOH    | 72    | 120   | 0           | 0.5        |
| 48      | Re/C      | 0.42                | 0.094                       | 0.95                     | MeOH    | 336   | 120   | 0           | 0.5        |
| 49      | Re/C      | 0.42$^2$            | 0.103$^3$                   | 0.95$^3$                  | MeOH    | 72    | 120   | 0           | 0.5        |
| 50      | Re/C first red. | 0.42$^2$        | 0.094$^3$                   | 0.95$^3$                  | MeOH    | 72    | 120   | 0           | 0.5        |
| 51      | Re/C each red. | 0.42$^2$        | 0.094$^3$                   | 0.95$^3$                  | MeOH    | 72    | 120   | 0           | 0.5        |
| 52      | Pt/C      | 0.052               | 0.013                       | 0.95                     | MeOH    | 72    | 120   | 0           | 0.5        |
| 53      | Pd/C      | 0.052               | 0.024                       | 0.95                     | MeOH    | 72    | 120   | 0           | 0.5        |
| 54      | C         | 0.40                | n.a.                        | 0.95                     | MeOH    | 72    | 120   | 0           | 0.5        |
| 55      | Re/C reduced$^3$ | 0.42             | 0.094                       | 0.95                     | MeOH    | 24+24 | 120   | 0           | 0.5        |

$^1$ Regarding to the total mass in the autoclave, metal loading slightly varied based on the pre-treatment method.

$^2$ The catalyst (Re/C) to mucic acid mass ratio was kept constant for three consecutive tests, while their total mass was subsequently lower.

$^3$ Hot filtration test (24h at 120 °C and 24 h rkc with supernatante).
Table SI3: List of experiments using glucaric (saccharic) acid monopotassium salt as a reactant, MeOH as solvent and homogeneous and heterogeneous Re species as a dehydroxylation catalysts with or without Pd/C as a hydrogenation catalyst. Experiments were performed under elevated hydrogen pressure.

| Exp. number | Catalyst 1 Dehydroxylati on cat. | Catalyst 2 Hydrogenation cat. | Catalyst hom. (wt%) | Active metal amount (mmol) | Glucaric acid amount (mmol) | t (h) | T (°C) | P \( \text{H}_2 \) (MPa) |
|-------------|---------------------------------|------------------------------|--------------------|---------------------------|---------------------------|-------|--------|---------------------|
| 1\(_G\)     | G MeReO\(_3\)                  |                              | 12.0               | 0.096                     | 0.80                      | 72    | 120    | 1.0                 |
| 2\(_G\)     | G MeReO\(_3\)                  |                              | 12.0               | 0.096                     | 0.80                      | 72    | 140    | 0.5                 |
| 3\(_G\)     | G MeReO\(_3\)                  | Pd/C                         | 0.038              | 0.017                     |                           |       |        |                     |
| 4\(_G\)     | G MeReO\(_3\)                  | Pd/C                         | 0.038              | 0.017                     |                           |       |        |                     |
| 5\(_G\)     | KReO\(_3\)                     | Pd/C                         | 0.038              | 0.017                     |                           |       |        |                     |
| 6\(_G\)     | KReO\(_3\)                     | Pd/C                         | 0.038              | 0.017                     |                           |       |        |                     |
| 7\(_G\)     | HReO\(_3\)                     | Pd/C                         | 0.038              | 0.017                     |                           |       |        |                     |
| 8\(_G\)     | HReO\(_3\)                     | Pd/C                         | 0.038              | 0.017                     |                           |       |        |                     |
| 9\(_G\)     | Re/C reduced                   |                              | 0.42               | 0.094                     | 0.80                      | 72    | 140    | 1.0                 |
| 10\(_G\)    | Re/C reduced                   | Pd/C                         | 0.038              | 0.017                     |                           |       |        |                     |

\(^{1}\) Regarding to the mass of mucic acid in the autoclave  
\(^{2}\) Regarding to the total mass in the autoclave, metal loading slightly varied based on the pre-tretment method.

**Product analysis**

Liquid samples (volume of 1 mL) were collected from the reaction vessel during the reaction time within different time intervals. In the case, when reaction time was 72 h, first sample was taken at the beginning as an initial sample (Sample 0, time 0, \( T_{\text{RT}}, P_{\text{initial}} \)). Next 10 samples were collected within different time intervals, from 4-12 hours in-between. The last sample was taken directly from the cooled final reaction mixture. The collected samples were prior analysis filtered if heterogeneous catalyst participated in the experimental set-up.

All collected samples were analyzed by liquid and gas chromatography in order to follow the dehydroxylation/hydrogenation reaction pathway. The analysis by liquid chromatography followed the same method as in our previous study \(^{[1]}\), analyzed by UHPLC (Thermo Scientific Ultimate 3000, equipped with a DAD-RI detector and fraction collector; ThermoFisher, Waltham, MA, USA) using AcclaimTM Organic Acid LC Column (OA, 5 μm, 12nm, 4.0 x 250 mm, ThermoFisher, Waltham, MA, USA). The same gradient method (with a combination of aqueous and organic mobile phase) was applied as in our previous study \(^{[1]}\) with an injection volume of 20 μL. Acetonitrile (anhydrous, 99.8 %, Sigma Aldrich, St. Luis, MO, USA) was used as organic mobile phase and 2.5 mM H\( \text{SO}_4 \) (98.0 % H\( \text{SO}_4 \), Sigma Aldrich, St. Luis, MO, USA) as water phase. Column temperature was kept at the 30 °C during analysis and column flow at 1 mL min\(^{-1}\). Reactants, intermediates, and products were identified and quantified at the reference wavelength of 210 nm by a UV detector.
Additionally, the collected samples were analyzed by gas chromatography (GCMS–QP 2010 Ultra, Shimadzu, Kyoto, Japan) equipped with a nonpolar column (ZebronTM ZB–5MSi, length 60m, diameter 0.25 mm, film thickness 0.25 μm). Compounds were identified by MS (mass spectrometry; fragments were scanned in the range from 35 to 500 m/z and compared to the NIST 17 (National Institute of Standards and Technology) library) and quantified by FID (flame ionization detector). Analysis method followed temperature programmed method, initially kept at 333 K for 5.5 min, than increased to 563 K with a heating rate of 20 K min⁻¹, where the temperature was kept constant for additional 8 min. Injection volume was 0.5 μL and the split ratio was set to 5. The injector and FID detector temperature were maintained at 563 K. For quantification, the standards were used (dimethyl adipate and dimethyl ester of t,t-muconic acid) and 5-point calibration curves were made, presented in Figure SI1. For the dehydroxylated products with one double bond, the average of both calibration curves was used (note that there is no significant difference between them).

The yields of products were calculated as:

\[ Y (\%) = \frac{c_{product}}{c_{muconic acid initial}} \times 100 \text{ (Eq. 1)} \]

![Figure SI1](image1.png): 5 point calibration curves for quantification of dehydroxylated products by GCMS.

Final cooled gaseous mixture in each autoclave was analyzed by micro GC (490 Micro GC System, Agilent, Santa Clara, CA, USA). Micro GC is equipped with a multi-loop sampling valve enabling fast analysis of gaseous phase from each autoclave in a few minute intervals. Gaseous compounds were detected by TCD (thermal conductivity) detector and separated on different columns (MS5A – Molecular Sieve Packed Column, length of 10 m – and PPU – ParaPLOT column; length of 10 m). The injector temperature was maintained at 363 K and column at 373 K during analysis.

NMR Spectroscopy

Qualitative 1H NMR, spectra were recorded using a Spinsolve 60 Carbon ULTRA spectrometer operating at 60 MHz. The measurements were conducted in DMSO-d6 at 25°C and tetramethylsilane (TMS) was used as an internal standard. The free induction decay (FID) was multiplied by an exponential factor corresponding to the 4 Hz line broadening prior to
performing a Fourier transformation. For each spectrum, typically about 64 scans were accumulated.

Catalyst characterization

H₂ temperature programed reduction (TPR) analyses of the fresh, reduced and Re/C red-ox samples were performed on Micromeritics Autochem II 2920 with 100 mg of the catalyst sample. The catalysts were first purged with Ar at low temperature to avoid ReOx sublimation (110 °C/3h) for 1 h proceeding with H₂ TPR starting at 60°C with the heating rate of 10°C/min to 700 °C at the flow rate of 50 mL/min 5% H₂ in Ar (Messer). The H₂ consumption was measured with thermal conductivity detector (TCD) while the gas composition was determined in all analyses by the mass spectrometer (Pfeiffer Vacuum Thermostar), after all condensable products were separated in a cold trap, that was being cooled down with the mixture of isopropanol and liquid nitrogen (−80 °C) in a Dewar flask.

Theoretical calculations

The revised Perdew-Burke-Ernzerhof (RPBE) functional [2] as implemented in VASP.5.4.1 was used to describe the exchange-correlation interaction, using the projector augmented wave method for the interaction between valence electrons and the core. An energy cutoff of 450 eV sufficed for well-converged results. The force convergence threshold for geometry optimization was set to 0.03 eV/Å. The calculated lattice constants for Re were 4.457 Å and 2.755 Å, which is consistent with the experimental values 4.456 and 2.761Å to within 0.1 %. The catalyst was modelled as four layers of Re(0001), where the bottom two layers were frozen in their bulk positions and the top two were allowed to relax. For small fragments, a 3x3 supercell was constructed and sampled with a 4x4x1 Monkhorst-Pack mesh [3], while a 6x6 supercell sampled at the gamma point was used for the derivates of mucic acid. The Van der Waals interactions were accounted for by the Grimme D3 method. [4] Standard corrections for the dipole moment were employed. [5] Solvation effects were not modelled explicitly.

For small fragments, all possible adsorption sites were considered (fcc, hcc, top, bridge) and the most stable one studied. For the C₆ molecules, a dozen adsorption positions were pre-optimized, subjected to first-principles molecular dynamics and then optimized to find the most probable adsorption site.

Transition states were roughly found with the nudged elastic band method (0.20 eV/Å) and further refined using the dimer method (0.03 eV/Å). [6] They were verified by the vibrational analysis (displacement of ±0.01 Å) to contain precisely one imaginary frequency and to correspond to the desired reaction (and not some spurious surface diffusion or similar).

Vibrational analysis was used to calculate the zero-point energy (ZPE) corrections. For the partition functions, used for obtaining entropic contributions (and consequently the Gibbs free energies), translational, rotational and vibrational contributions were taken into account. For adsorbates, the harmonic approximation (vibrational contributions only) were used, while the gaseous species were treated in the ideal gas limit. [7]
The zero-point energy correction (ZPE) of molecule with $N$ atoms was calculated as

$$\Delta E_{ZPE} = \sum_{i}^{3N} \frac{h\nu_i}{2}$$

$h$ denotes Planck’s constant and $\nu$ is a vibrational frequency.

The Gibbs free energy is calculated as $G = H - TS = U + PV - TS$, where $U$ is the complete internal energy, $P$ and $V$ are pressure and volume, respectively (negligible for reactions of adsorbates on a surface because $\Delta V \approx 0$), $T$ is temperature and $S$ is entropy.

In the harmonic approximation, we have

$$U = E_0 K + \Delta E_{ZPE} + \sum_{i}^{3N} \frac{\epsilon_i}{\exp(\frac{\epsilon_i}{k_B T}) - 1}$$

and

$$S = k_B \left( \frac{\epsilon_i}{k_B T \left( \exp(\frac{\epsilon_i}{k_B T}) - 1 \right)} - \ln \left( 1 - \exp(-\frac{\epsilon_i}{k_B T}) \right) \right)$$

where $\epsilon_i = h\omega_i$, $h$ is the Planck constant, $k_B$ is the Boltzmann constant and $T$ the temperature.

In the ideal gas approximation, enthalpy is calculated as

$$H = E_0 K + \Delta E_{ZPE} + \int_0^T C_p \, dT$$

where $C_p = k_B + C_{V,\text{translational}} + C_{V,\text{rotational}} + C_{V,\text{vibrational}}$. Translational heat capacity is $1.5 \, k_B$, rotational heat capacity is $k_B$ or $1.5 \, k_B$ for linear and non-linear molecules, respectively, and the vibrational heat capacity is

$$\int_0^T C_{V,\text{vibrational}} \, dT = \sum_{i}^{3N} \frac{\epsilon_i}{\exp(\frac{\epsilon_i}{k_B T}) - 1}$$

Entropy is calculated as

$$S(T, p) = S_{\text{translational}} + S_{\text{rotational}} + S_{\text{vibrational}} + S_{\text{electronic}} - k_B \ln \frac{p}{1 \text{ atm}}$$

where

$$S_{\text{translational}} = k_B \left( \ln \left( \frac{2\pi M k_B T}{h^2} \right)^{1.5} \frac{k_B T}{1 \text{ atm}} + \frac{5}{2} \right)$$
\[ S_{\text{rotational,linear}} = k_B \left( \ln \left( \frac{8\pi^2 I k_B T}{\sigma h^2} \right) + 1 \right) \]

\[ S_{\text{rotational,non-linear}} = k_B \left( \ln \left( \frac{\sqrt{\pi I_A I_B I_C}}{\sigma} \left( \frac{8\pi^2 k_B T}{h^2} \right)^{1.5} \right) + 1.5 \right) \]

\[ S_{\text{vibrational}} = k_B \left( \frac{\epsilon_i}{k_B T \left( \exp(\epsilon_i/k_B T) - 1 \right)} - \ln \left( 1 - \exp(\epsilon_i/k_B T) \right) \right) \]

\[ S_{\text{electronic}} = k_B \ln(2s + 1) \]

where \( M \) is the molar mass, \( I \) (and \( I_A \), \( I_B \), and \( I_C \)) are the moment of inertia, \( \sigma \) is the symmetry number and \( s \) the total spin.

**Table S14.** Calculated ZPE-corrected reaction energies and activation barriers for methanol decomposition and hydrogen adsorption.

| #  | Reaction                                      | \( \Delta E \) (eV) | \( E_a \) (eV) |
|----|-----------------------------------------------|---------------------|--------------|
| 1  | \( \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OH}^* \) | -0.36               | n/a          |
| 2  | \( \text{CH}_2\text{O} \rightarrow \text{CH}_2\text{O}^* \) | -1.41               | n/a          |
| 3a | \( \text{CH}_3\text{OH}^* \rightarrow \text{CH}_3\text{O}^* + \text{H}^* \) | -0.70               | 0.19         |
| 3b | \( \text{CH}_3\text{OH}^* + \text{OH}^* \rightarrow \text{CH}_3\text{O}^* + \text{H}_2\text{O}^* \) | +0.00               | 0.03         |
| 4a | \( \text{CH}_3\text{O}^* \rightarrow \text{CH}_2\text{O}^* + \text{H}^* \) | +0.03               | 0.67         |
| 4b | \( \text{CH}_3\text{O}^* + \text{OH}^* \rightarrow \text{CH}_2\text{O}^* + \text{H}_2\text{O}^* \) | -0.22               | 1.01         |
| 5  | \( \text{CH}_3\text{O}^* + \text{CH}_3\text{O}^* \rightarrow \text{CH}_2\text{O}^* + \text{CH}_3\text{OH}^* \) | +0.03               | 0.89         |
| 6  | \( \text{OH}^* + \text{H}^* \rightarrow \text{H}_2\text{O}^* \) | +0.95               | 1.25         |
| 7  | \( \text{H}^* + \text{H}^* \rightarrow \text{H}_2^* \) | +0.92               | 0.89         |
| 8  | \( \text{H}_2 \rightarrow \text{H}_2^* \) | -0.39               | n/a          |
| 9  | \( \text{N}_2 \rightarrow \text{N}_2^* \) | -0.63               | n/a          |
| 10 | \( \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^* \) | -0.24               | n/a          |
Figure S12. Mechanism of dehydroxylation of mucic acid (in a diester form) and hydrogenation of the ensuing muconate on Re(0001). The most probable pathway shown with bolded arrows with shaded compounds. The (ZPE-corrected) activation barriers, $E_a$ and reaction energies, $\Delta E$, (in parenthesis) for each elementary step in eV (lateral interaction between co-adsorbed products/reactants included). Free H* and OH*, involved in the reaction, not shown for clarity.
Figure SI3. Potential energy surface ($E_{ZPE}$ and $\Delta G$) for the entire catalytic cycle using a) $H_2$ or b, c) $CH_3OH$ as a hydrogen source on Re(0001). Dehydroxylation is exergonic in both cases, hydrogenation is exergonic with CH$_3$OH. In panel c), the reactions are not grouped by type but shown as they occur.

Key for adsorbed species/steps in Figure SI3a, Figure SI3b and Figure SI3c is as follows:
|   |   |
|---|---|
| 1 | Start |
| 2 | Mucic |
| 3 | Mucic + 4 H2 |
| 4 | TS |
| 5 | Mucic-1OH + OH + 4 H2 |
| 6 | TS |
| 7 | Mucic-1,2OH-a + 2OH + 4 H2 |
| 8 | Mucic-1,2OH-b + 2OH + 4 H2 |
| 9 | TS |
| 10 | Mucic-1,2,3-OH + 3OH + 4 H2 |
| 11 | TS |
| 12 | Muconic + 4OH + 4 H2 |
| 13 | TS |
| 14 | Muconic + 4OH + 2H + 3 H2 |
| 15 | TS |
| 16 | Muconic + 4 OH + 4 H + 2 H2 |
| 17 | TS |
| 18 | MuconicH1 + 4 OH + 3H + 2H2 |
| 19 | TS |
| 20 | MuconicH1H2 + 4 OH + 2H + 2H2 |
| 21 | TS |
| 22 | MuconicH1H2H3 + 4 OH + H + 2H2 |
| 23 | TS |
| 24 | Adipic + 4 OH + 2H2 |
| 25 | TS |
| 26 | Adipic + 4 OH + 2H + H2 |
| 27 | TS |
| 28 | Adipic + 4 OH + 4H |
| 29 | TS |
| 30 | AAdipic + 3OH + 3 H + H2O |
| 31 | TS |
| 32 | AAdipic + 2OH + 2H + 2H2O |
| 33 | TS |
| 34 | AAdipic + OH + H + 3H2O |
| 35 | TS |
| 36 | Adipic + 4 H2O |
| 37 | Adipic + 3 H2O |
| 38 | Adipic + 2 H2O |
| 39 | Adipic + 1 H2O |
| 40 | Adipic |
| 41 | End |

Key for adsorbed species/steps for Figure SI3a

Key for adsorbed species/steps for Figure SI3b
|   |   |
|---|---|
| 3 | TS |
| 4 | Mucic-1OH + OH |
| 5 | Mucic-1OH + OH + CH3OH |
| 6 | TS |
| 7 | Mucic-1OH + H2O + CH3O |
| 8 | Mucic-1OH + CH3O |
| 9 | TS |
| 10 | Mucic-1,2OH-a + OH + CH3O |
| 11 | TS |
| 12 | Mucic-1,2OH-a + H2O + CH2O |
| 13 | Mucic-1,2OH-a + CH2O |
| 14 | Mucic-1,2OH-a |
| 15 | Mucic-1,2OH-b |
| 16 | Mucic-1,2OH-b + CH3OH |
| 17 | TS |
| 18 | Mucic-1,2,3OH + OH + CH3OH |
| 19 | TS |
| 20 | Mucic-1,2,3OH + H2O + CH3O |
| 21 | Mucic-1,2,3OH + CH3O |
| 22 | TS |
| 23 | Muconic + OH + CH3O |
| 24 | TS |
| 25 | Muconic + H2O + CH2O |
| 26 | Muconic + CH2O |
| 27 | Muconic |
| 28 | Muconic + CH3OH |
| 29 | TS |
| 30 | MuconicH1+CH3O |
| 31 | Muconich1 + CH3O + CH3OH |
| 32 | TS |
| 33 | Muconich1H2 + CH3O + CH3O |
| 34 | TS |
| 35 | Muconich1H2+CH2O+CH3OH |
| 36 | Muconich1H2+CH3OH |
| 37 | TS |
| 38 | Muconich1H2H3+CH3O |
| 39 | Muconich1H2H3+CH3OH+CH3O |
| 40 | TS |
| 41 | Adipic+CH3O+CH3O |
| 42 | TS |
| 43 | Adipic+CH3OH+CH2O |
| 44 | Adipic+CH3OH |
| 45 | Adipic |
| 46 | End |

Key for adsorbed species/steps for Figure SI3c
Results

Esterification of aldric acid

The formation of lactones were detected in our previous study, where water was used as a solvent (Hočevar, B., Grilc, M. & Likozar, B. Aqueous Dehydration, Hydrogenation, and Hydrodeoxygenation Reactions of Bio-Based Mucic Acid over Ni, NiMo, Pt, Rh, and Ru on Neutral or Acidic Catalyst Supports). When methanol was used as a solvent, the formation of lactones did not appear, lactones were not detected. The low solubility of aldric acid (mucic acid) in practically any solvent was however in this case an advantage, as the esterification proceed fast once the aldric acid dissolves in the solvent. Identification was done by NMR. After esterification (at different reaction times) the methanol was removed from reaction mixture by distillation and final product was analysed by NMR to identify the presence or absence of carboxylic groups. Total esterification appeared to be very fast in the presence of acid and/or catalyst, while in the absence of the acid and/or catalyst esterification at elevated temperature took significantly longer (2h and 24h respectively). One can approximately evaluate complete esterification also only visually by the absence of undissolved solid particles in the reaction mixture, while esters have significantly higher solubility in the solvent.

Figure SI4: Esterification of aldric acid in alcohols as solvents in the presence of 1.25 M HCl.
Figure S15: Yields of (2)-(7) obtained over different Re homogeneous and heterogeneous catalysts, when glucaric acid was used as a reactant.
Table SI5: Reaction conditions, catalyst type, and yields (color code as in Figure 2) for mucic acid dehydroxylation over homogeneous Re catalysts (the ratio between Re and mucic acid was kept constant, the same when homogeneous and heterogeneous catalysts were used).

| Exp. | Catalyst type | t (h) | T (°C) | $P_{\text{initial}}$ (MPa) | Yield (mol %) 2,4-hexadienoic acid dimethyl ester (2) | Yield (mol %) 2-hexenedioic acid dimethyl ester (E) (3) | Yield (mol %) 2-hexenedioic acid dimethyl ester (Z) (4) | Yield (mol %) 3-hexenedioic acid dimethyl ester (E) (5) | Yield (mol %) 3-hexenedioic acid dimethyl ester (Z) (6) | Yield (mol %) Hexenedioic acid dimethyl ester (7) | Total yield (mol %) (2) – (7) |
|------|---------------|------|--------|--------------------------|---------------------------------------------------|------------------------------------------------------|------------------------------------------------------|---------------------------------------------------|---------------------------------------------------|-------------------------------------|-------------------------------|
| 1 M  | MeReO₃ (12)   | 4    | 120    | 0.5 H₂                   | 2.1                                               | 0.4                                                  | 0.0                                                  | 0.0                                               | 0.0                                               | 0.5                                 | 3.0                            |
| 2 M  | MeReO₃ (12)   | 4    | 120    | 0.5 H₂                   | 3.9                                               | 0.0                                                  | 0.0                                                  | 0.0                                               | 0.0                                               | 1.0                                 | 4.9                            |
| 3 M  | MeReO₃ (12)²  | 4    | 120    | 0.5 H₂                   | 4.1                                               | 0.0                                                  | 0.0                                                  | 0.0                                               | 0.0                                               | 0.5                                 | 4.6                            |
| 4 M  | MeReO₃ (12)¹  | 4    | 120    | 0.5 H₂                   | 3.7                                               | 0.0                                                  | 0.0                                                  | 0.0                                               | 0.0                                               | 1.9                                 | 5.7                            |
| 5 M  | MeReO₃ (12)   | 72   | 100    | 0.5 H₂                   | 8.2                                               | 2.8                                                  | 0.3                                                  | 0.9                                               | 0.0                                               | 4.0                                 | 16.2                           |
| 6 M  | MeReO₃ (12)   | 72   | 120    | 0.5 H₂                   | 7.3                                               | 3.5                                                  | 0.4                                                  | 1.3                                               | 0.4                                 | 6.3                                 | 19.2                           |
| 7 M  | MeReO₃ (12)   | 72   | 140    | 0.5 H₂                   | 8.4                                               | 2.4                                                  | 0.5                                                  | 0.9                                               | 0.4                                 | 0.5                                 | 13.1                           |
| 8 M  | MeReO₃ (12)   | 72   | 120    | 0.5 N₂                   | 42.7                                              | 0.4                                                  | 0.0                                                  | 0.0                                               | 0.0                                               | 0.0                                 | 43.1                           |
| 9 M  | MeReO₃ (12)   | 72   | 120    | 1.0 H₂                   | 12.5                                              | 18.4                                                 | 1.5                                                  | 5.8                                               | 0.0                                               | 16.9                                | 55.1                           |
| 10 M | MeReO₃ (6)    | 72   | 120    | 0.5 H₂                   | 2.5                                               | 0.0                                                  | 0.0                                                  | 0.0                                               | 0.0                                               | 0.2                                 | 2.7                            |
| 11 M | MeReO₃ (18)   | 72   | 120    | 0.5 H₂                   | 13.2                                              | 2.2                                                  | 0.5                                                  | 0.9                                               | 0.5                                 | 0.9                                 | 18.3                           |
| 12 M | MeReO₃ (12)   | 72   | 120    | 0.5 H₂                   | 8.7                                               | 7.8                                                  | 0.7                                                  | 2.3                                               | 0.9                                 | 4.2                                 | 24.6                           |
|     | Pd/C (5)      |      |        |                         |                                                   |                                                      |                                                      |                                                    |                                                    |                                                    |                                  |
| 13 M | MeReO₃ (12)   | 72   | 120    | 0.5 H₂                   | 0.8                                               | 8.2                                                  | 0.7                                                  | 2.4                                               | 0.0                                               | 18.1                                | 30.3                           |
| 14 M | MeReO₃ (10)   | 72   | 120    | 0.5 H₂                   | 1.5                                               | 6.6                                                  | 0.4                                                  | 1.8                                               | 0.0                                               | 19.2                                | 29.5                           |
| 15 M | MeReO₃ (12)   | 72   | 120    | 0.5 H₂                   | 24.5                                              | 9.6                                                  | 1.2                                                  | 4.9                                               | 2.2                                 | 4.5                                 | 46.8                           |
| 16 M | MeReO₃ (12)²  | 72   | 120    | 0.5 H₂                   | 11.3                                              | 19.4                                                 | 1.7                                                  | 8.7                                               | 3.7                                 | 9.1                                 | 53.9                           |
| 17 M | HReO₃ (12)    | 72   | 120    | 0.5 H₂                   | 4.9                                               | 2.8                                                  | 0.3                                                  | 0.7                                               | 0.3                                 | 0.8                                 | 9.9                            |
| 18 M | HReO₃ (12)    | 72   | 140    | 0.5 H₂                   | 0.3                                               | 0.1                                                  | 0.4                                                  | 1.1                                               | 1.8                                 | 6.9                                 | 10.6                           |
| 19 M | HReO₃ (12)    | 72   | 120    | 0.5 H₂                   | 3.4                                               | 11.4                                                 | 0.8                                                  | 3.4                                               | 1.2                                 | 5.1                                 | 25.3                           |
| 20 M | HReO₃ (12)    | 72   | 120    | 0.5 H₂                   | 0.3                                               | 2.9                                                  | 0.1                                                  | 0.6                                               | 0.0                                 | 6.7                                 | 10.6                           |
| 21 M | KReO₂ (12)    | 72   | 120    | 0.5 H₂                   | 12.0                                              | 2.9                                                  | 0.4                                                  | 1.5                                               | 0.6                                 | 0.4                                 | 17.8                           |
| 22 M | KReO₂ (12)    | 72   | 140    | 0.5 H₂                   | 17.4                                              | 4.9                                                  | 0.5                                                  | 2.1                                               | 0.9                                 | 0.7                                 | 26.5                           |
| 23 M | KReO₂ (12)    | 72   | 120    | 0.5 H₂                   | 8.4                                               | 23.1                                                 | 1.4                                                  | 6.2                                               | 1.9                                 | 3.8                                 | 44.7                           |
| 24 M | KReO₂ (12)    | 72   | 140    | 0.5 H₂                   | 0.2                                               | 23.0                                                 | 1.1                                                  | 5.9                                               | 0.0                                 | 21.2                                | 51.3                           |

1 Solvent: EtOH
2 Solvent: i-PrOH
3 Solvent: n-BuOH
Table S16: Conditions, catalyst type, and yields for mucic acid dehydroxylation over heterogeneous Re catalysts (the ratio between Re and mucic acid was kept constant, the same when homogeneous and heterogeneous catalysts were used).

| Exp. | Catalyst | t (h) | T (°C) | $P_{\text{initial}}$ (MPa) | $P_{\text{final}}$ (MPa) | Yield (mol %) | Yield (mol %) | Yield (mol %) | Yield (mol %) | Yield (mol %) | Yield (mol %) | Total yield (mol %) |
|------|----------|-------|--------|-----------------------------|-----------------------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------------|
| 25_m | Re/SiO$_2$ (0.42) | 72 | 120 | 0.5 | 0 | 4.6 | 0.6 | 0.1 | 0.8 | 0.4 | 0.1 | 6.5 |
| 26_m | Re/SiO$_2$ (0.42) | 72 | 140 | 0.5 | 0 | 1.4 | 0.9 | 0.1 | 0.3 | 0.1 | 0.2 | 2.9 |
| 27_m | Re/Al$_2$O$_3$ (0.42) | 72 | 120 | 0.5 | 0 | 3.9 | 0.8 | 0.1 | 0.7 | 0.4 | 0.1 | 6.0 |
| 28_m | Re/Al$_2$O$_3$ (0.42) | 72 | 140 | 0.5 | 0 | 0.3 | 1.6 | 0.1 | 0.7 | 0.0 | 1.7 | 4.5 |
| 29_m | Re/C (0.42) | 72 | 120 | 0.5 | 0 | 17.1 | 10.3 | 1.1 | 22.5 | 8.2 | 2.9 | 62.2 |
| 30_m | Re/C (0.42) | 72 | 140 | 0.5 | 0 | 2.0 | 13.4 | 1.3 | 31.0 | 10.3 | 2.2 | 60.2 |
| 31_m | Re/C (0.42) | 72 | 140 | 1 | 0 | 0.0 | 18.5 | 1.4 | 20.2 | 5.7 | 7.2 | 53.1 |
| 32_m | Re/C dried (0.42) | 72 | 120 | 0.5 | 0 | 0.7 | 26.1 | 2.1 | 27.7 | 7.9 | 19.0 | 83.5 |
| 33_m | Re/C red. (0.42) | 72 | 120 | 0.5 | 0 | 0.2 | 24.0 | 1.5 | 23.8 | 8.6 | 25.1 | 83.3 |
| 34_m | Re/C (0.42) | 72 | 120 | 0.5 | 0 | 9.4 | 0.4 | 5.5 | 0.0 | 43.6 | 58.9 |
| 35_m | Pd/C (0.052) | 72 | 140 | 0.5 | 0 | 0.2 | 16.8 | 0.9 | 6.4 | 2.8 | 24.0 | 51.2 |
| 36_m | Pd/C (0.038) | 72 | 120 | 0.5 | 0 | 0.3 | 3.5 | 0.2 | 4.4 | 0.0 | 45.3 | 53.8 |
| 37_m | Pd/C dried (0.42) | 72 | 120 | 0.5 | 0 | 0.0 | 2.8 | 0.0 | 0.2 | 0.0 | 60.5 | 63.6 |
| 38_m | Pd/C red. (0.42) | 72 | 120 | 0.5 | 0 | 0.2 | 4.1 | 0.3 | 4.8 | 0.0 | 57.9 | 67.4 |
| 39_m | Re/C (0.42) | 72 | 120 | 0 | 0.5 | 43.8 | 2.4 | 0.7 | 0.7 | 0.5 | 0.6 | 48.6 |
| 40_m | Re/Cred. (0.42) | 72 | 120 | 0 | 0.5 | 67.0 | 0.5 | 0.3 | 0.0 | 0.0 | 0.2 | 67.9 |
| 41_m | Re/C red. (0.42) | 72 | 120 | 0 | 0.5 | 62.4 | 16.8 | 1.2 | 6.8 | 3.1 | 2.5 | 92.8 |
| 42_m | Re/C red. (0.42) | 72 | 120 | 0 | 0.5 | 80.0 | 1.4 | 0.3 | 5.6 | 2.8 | 0.6 | 90.6 |
| 43_m | Re/C red. (0.42) | 72 | 150 | 0 | 0.5 | 63.0 | 0.0 | 0.0 | 1.4 | 1.3 | 0.1 | 65.8 |
| 44_m | Re/C red. (0.42) | 72 | 175 | 0 | 0.5 | 3.8 | 8.3 | 1.6 | 28.4 | 14.6 | 0.3 | 56.9 |
| 45_m | Re/C red. (0.42) | 72 | 175 | 0 | 0.5 | 0.5 | 32.0 | 2.8 | 22.7 | 9.0 | 30.9 | 98.0 |
| 46_m | Re/C red. (0.42) | 72 | 120 | 0 | 0.5 | - | - | - | - | - | - | 85.8 |
| 47_m | Re/C red. (0.42) | 72 | 120 | 0 | 0.5 | - | - | - | - | - | - | 81.3 |
| 48_m | Re/C red. (0.42) | 336 | 120 | 0 | 0.5 | 2.7 | 18.6 | 2.0 | 50.2 | 16.0 | 1.3 | 90.9 |

1. Solvent: i-ProOH
2. Catalyst dried over night at 120 °C in a N$_2$ flow
3. Catalyst pre-reduced at 400 °C for 3 h in a 200 ml min$^{-1}$ H$_2$ flow
4. Catalyst pre-reduced at 350 °C for 3 h in a H$_2$ flow, transferred into the autoclave in an argon atmosphere (glove box) to prevent air exposure and oxidation. The reactant was placed in the autoclave in a glove box, while methanol was placed into external container, purged with nitrogen, vacuumed to remove air and placed in the autoclave.
5. Only propyl esters of 2,4-hexadienedioic acid detected
6. Only butyl esters of 2,4-hexadienedioic acid detected
7. Catalyst pre-reduced at 400 °C for 3 h in a H$_2$ flow.
Figure SI6: Composition of gaseous phase after reaction catalyzed by unreduced Re/C (blue) and by reduced Re/C (green). Catalyst reduction was performed in a 200 mL min$^{-1}$ H$_2$ flow for 3 h at 400 °C.

Figure SI7: Hydrogen formation in MeOH reactions over Re/C catalyst. Detected products (by GCMS) are framed.
Figure S18: H-NMR shifts of: a) esterified reactant (mucic acid ester – red) and b) product (blue).
Recycling tests and catalysts leaching

Rhenium is a metal known for its propensity towards leaching from solid supports. A comprehensive review by Sharkey and Jentoff [8] on deactivation by leaching during rhenium-catalyzed deoxydehydration (DODH) studied hot filtration and centrifugation recycling tests were done and found out that there is no difference between the hot filtration test and the separation by using room temperature separation. Cooling the reaction mixture does not cause a precipitation or redisposition of rhenium species. The measurements made after separation at room temperature therefore properly represent the amount of Re leached under reaction conditions.

In our dehydroxylation (deoxydehydration) reactions, methanol was used as a solvent. Methanol has a very low boiling point (TBP = 64.7 °C), which makes it difficult to perform hot filtration tests, as also mentioned by Sharkey and Jentoff. Therefore, the catalyst was removed from the reaction mixture by centrifugation at room temperature and dried (and reduced if needed) before reuse (recycling tests). The amount of the rhenium species was determined before and after the reaction using ICP-MS analysis. The results showed that from 8 to 14 % of rhenium had been lost from the catalyst surface (carbon was used as a support). The concentration of the rhenium species in the liquid phase determined by ICP-MS was 18 % of the total Re on the catalyst surface. The difference between the obtained values on the

Figure SI9: NMR shifts for the product 39M (brown) and mucic acid ester (green).
solid catalyst and in the liquid reaction mixture is probably due to small solid particles of Re/C that remained in the liquid phase after the separation. The diameter of the catalyst particles used in the experiments was below 100 µm, therefore we believe the catalyst could not be 100 % efficiently removed from the liquid phase. If this obtained values of the leached rhenium species and the insights from the study by Sharkey and Jentoff \cite{8} are taken into account, the homogeneously catalysed contribution when Re/C is used as a catalyst is minimal. The amount of the leached catalyst is low. Moreover, homogeneous catalysis was shown to be less efficient than heterogeneous (at the same Re : aldaric acid ratio). A prior reduction of the catalyst (Re/C) reduces the oxidation state of the rhenium species on the support, lowering its solubility. This was also proved with the recycling test, where the catalyst activity retained the same for two cycles, contrary to the unreduced catalyst. Rhenium on the unreduced catalyst (untreated catalyst/fresh catalyst) has a higher oxidation state, as proved by the XPS analysis (Figure 8) and is therefore easily leached. However, in the recycling tests, the mass ratio between catalyst (Re/C) and aldaric acid (mucic acid) was kept constant and the potential loss of Re from the surface was not considered.

**Hot filtration test**

In addition, the hot filtration test was carried out and another reaction with supernatant was performed to take into account the possible homogeneous reaction catalyzed with leached rhenium. The catalyst used in this experiment was sieved into particles between 40 and 100 µm. The reaction was carried out at 120 °C and a standard concentration of mucic acid for 24 h. The autoclave was connected to another autoclave, with two filters in-between; pore diameter of 15 µm and 2 µm respectively. It was assumed that the filters would efficiently filter the particles with a diameter > 40 µm. The reaction mixture was filtered at the reaction temperature (120 °C) and at elevated reaction pressure (9.4 bar). After filtration, when the gas pressure equilibrium was established, the second autoclave was opened. The reaction mixture was filtered efficiently; no solid particles were found in the liquid reaction mixture. The filtered liquid mixture was further purged with nitrogen, filled with fresh nitrogen up to 5 bar and heated up again to 120 °C. A further 24 h of reaction was carried out to consider the potential homogeneous reaction.
In parallel, an uninterrupted experiment was carried out under the same reaction conditions. During the two experiments, liquid samples were collected and analyzed by GCMS (as described above). The results obtained were compared. It can be seen (Figure SI11 a & b) that no further dehydroxylation occurred after hot filtration. Only the hydrogenation of one double bond took place to a small extend, while other dehydroxylated-hydrogenated products were not detected (Figure SI11 c & d). The final product (dimethyl adipate) was also not detected.

When reduced catalyst is used a high concentration of hydrogen is formed (see Figure SI6), which can remain dissolved in the liquid phase even after hot filtration. This could be sufficient for minor hydrogenation even without the catalyst (as it was shown in our previous study. [9] The concentration of hydrogenated products is 0.035 mol L⁻¹, which is 0.0042 mol of formed hydrogenated products in the reaction mixture (V_liquid = 0.12 L). The hydrogenation of one double bond in each product needs 1 mol of H₂, thus the same amount of H₂ (0.0042 mol) was needed for hydrogenation after hot filtration. Taken into account the solubility of hydrogen [10], the amount of dissolved H₂ at the corresponding conditions (cold MeOH) was sufficient (0.004 mol) for hydrogenation.
Figure SI11: The formation of dehydroxylated products during uninterrupted (red dot) and filtered (black square) test.

**Catalyst characterization results**

**XRD**

Samples for the XRD analysis (fresh, reduced and red&ox Re/C) were prepared in glovebox where they were sealed with Kapton film. The analyses were performed on the PANalytical X’Pert Pro instrument using CuKα1 radiation source between 10° to 90°.

From Figure SI12 we can see that different treatments cause only minor changes on XRD diffractograms. We can see that the samples include quartz (99-101-2030) [11] and graphite (99-100-5714) [11]. The quartz is contaminant of the commercial Re/C catalyst and is due to a minor quantity disregarded as a influencing factor on the catalysis.
Figure SI12: XRD diffractograms shows only small differences between samples and the evidence of quartz and graphite.
**TPR**

H₂ TPR was performed on fresh, reduced and red-ox (reduced and exposed to air) Re/C catalyst samples. Figure SI13 shows H₂ TPR analysis results of the reduction of fresh Re/C. Increased heating in H₂/Ar mixture first started with production of CO₂, following with the H₂ consumption at 300 °C due to Re reduction. The moment when Re was reduced, the CO₂ production was funnelled to the production of CH₄ and at higher temperatures to production of CO. Due to a complex nature of hydrogen consumption due to CH₄ and CO formation we take H₂ consumption below 400°C only as an indicator of rhenium state. All samples exhibit sharp peak below 400°C.

![Graph showing TCD and MS signal vs. temperature](image1.png)

**Figure SI13:** H₂ TPR includes in addition to the reduction of rhenium also reduction carbon species to form CH₄ and CO.

Figure SI14 shows the comparison between result from calibrated mass spectrometer and thermal conductivity detector. The TCD signal is higher than MS due to CH₄ and CO contribution.

![Graph showing H₂ consumption vs. time](image2.png)

**Figure SI14:** H₂ Consumption based on MS and TCD measurements; TCD includes also contributions of CH₄ and CO at higher temperatures.
**CO TPD**

![Graph showing CO TPD](image)

**Figure SI15:** CO temperature programmed desorption on the reduced Re/C sample. Peak below 250 °C corresponds to desorption from rhenium, while peak above 400 °C corresponds to decomposition of functional groups on carbon.

**SEM**

Catalyst morphology of the fresh catalyst was determined using FE-SEM (Supra 35 VP). Catalyst has rough surface, which is in line with high BET surface area (649 m² g⁻¹). The catalyst particles have different sizes ranging from below 1 μm to 100 μm (Figures SI12-14).

![SEM micrograph of fresh Re/C sample at high magnification](image)

**Figure SI16:** SEM micrograph of fresh Re/C sample at high magnification.
Figure SI17: SEM micrograph of fresh Re/C sample at medium magnification.

Figure SI18: SEM micrograph of fresh Re/C sample at low magnification.

XPS

The X-ray photoelectron spectroscopy (XPS) analyses were performed on the PHI-TFA XPS spectrometer (Physical Electronics Inc.). To eliminate oxidation of Re on the air, samples were prepared in a glove box and transferred under the protective atmosphere of Ar to ultra-high vacuum spectrometer. The analyzed depth was about 3-5 nm. Sample surfaces were excited by X-ray radiation from monochromatic Al source at photon energy of 1486.6 eV. The binding energies accuracy was about ±0.3 eV. Quantification of surface composition
(reported in Table 1 in main text) was obtained from XPS peak intensities multiplied by sensitivity factors provided by the instrument manufacturers.

Deconvolution of XPS Re 4f was performed in XPSPEAK 4.1\textsuperscript{[15]. The baseline was described by Shirley background. The peak area ratio between 4f\textsubscript{7/2} and 4f\textsubscript{5/2} was locked to the theoretical ratio of 4/3 and the peak width was locked to the same value. The oxidic Re 4f peaks were described by symmetric Lorentzian-Gaussian function while the metallic Re 4f peaks were described by asymmetric Lorentzian-Gaussian function. The deconvolution spectra can be found in figures SI20-SI22 and the peak position, peak area and compound abundancy is in the table SI7. The deconvoluted peaks at 40.5, 41.3, 43.1, 44.7 and 46.5 eV were corresponded to the 4f\textsubscript{7/2} binding energies of Re\textsuperscript{0}, Re\textsuperscript{3+}, Re\textsuperscript{4+}, Re\textsuperscript{6+} and Re\textsuperscript{7+}\textsuperscript{[16,17]. Rhenium in fresh and red&ox samples is mostly in Re\textsuperscript{6+} state (100% and 92% respectively), while in the reduced state it is mostly in Re\textsuperscript{0} state (67.6%).
**Figure SI20.** Deconvoluted Re 4f spectra of fresh Re/C sample. Rhenium can be found in Re$^{6+}$ oxidation states.

**Figure SI21:** Deconvoluted Re 4f spectra of red&ox Re/C sample. Rhenium can be found in Re$^{6+}$, Re$^{3+}$ and Re$^{0}$ oxidation states.
Figure S122: Deconvoluted Re 4f spectra of reduced Re/C sample. Rhenium can be found in Re$^{3+}$ and Re$^{0}$ oxidation states.

Table S17: The peak position, peak area and compound abundancy obtained by the deconvolution.

| Sample               | Peak name          | Position (eV) | Area [au] | Compound abundancy [%] |
|----------------------|--------------------|---------------|-----------|------------------------|
| fresh                | ReO$_3$-Re 4f$_{7/2}$ | 44.65         | 1.621     | 100                    |
|                      | ReO$_3$-Re 4f$_{5/2}$ | 47.08         | 1.216     |                        |
| reduced and oxidized | ReO$_3$-Re4f$_{7/2}$ | 44.84         | 1.753     | 92.0 (ReO$_3$)         |
|                      | ReO$_3$-Re4f$_{5/2}$ | 47.27         | 1.315     |                        |
|                      | Re-Re4f$_{7/2}$     | 40.5          | 0.083     | 4.3 (Re)               |
|                      | Re-Re4f$_{5/2}$     | 42.93         | 0.062     |                        |
|                      | Re$_2$O$_3$-Re4f$_{7/2}$ | 41.3  | 0.07     | 3.7 (Re$_2$O$_3$)     |
|                      | Re$_2$O$_3$-Re4f$_{5/2}$ | 43.73    | 0.052     |                        |
| reduced              | Re-Re4f$_{7/2}$     | 40.45         | 1.25      | 67.6 (Re)              |
|                      | Re-Re4f$_{5/2}$     | 42.88         | 0.938     |                        |
|                      | Re$_2$O$_3$-Re4f$_{7/2}$ | 41.3  | 0.5      | 27.0 (Re$_2$O$_3$)    |
|                      | Re$_2$O$_3$-Re4f$_{5/2}$ | 43.73    | 0.375     |                        |
|                      | ReO$_2$-Re4f$_{7/2}$ | 43.1          | 0.1       | 5.4 (ReO$_2$)          |
|                      | ReO$_2$-Re4f$_{5/2}$ | 45.53         | 0.075     |                        |
MeOH reduction capability of ReO\textsubscript{x}

Methanol does not only serve as a solvent but can also act as a reducing agent and therefore reduces Re to its metallic form. This was demonstrated with the reduction test of oxidized Re/C sample with MeOH and verification of sample’s oxidation state with a H\textsubscript{2}-TPR test. The reduction was performed in MeOH vapour (22 kPa) at 175 °C for 5 h. As the reduction took place in the gas phase it is clear that the observed reduction rate is conservative compared to significantly higher availability of liquid MeOH in the slurry reactor during the activity tests.

The experiment was performed in Autochem II 2920 (Micromeritics) coupled with a mass spectrometer (Thermostar, Pfeiffer Vacuum). 100 mg of fresh Re/C was inserted in the sample tube and reduced in 5% H\textsubscript{2}/Ar at 400 °C for 3 h. Sample was cooled-down to 40 °C and oxidized in 10% O\textsubscript{2}/He for 10 min, followed by the H\textsubscript{2}-TPR test that involved a heating-up (5 K/min) to 400 °C in 5% H\textsubscript{2}/Ar (exp.1). H\textsubscript{2}O production was measured by calibrated mass spectrometer, since H\textsubscript{2} consumption accounts besides ReO\textsubscript{x} reduction also CH\textsubscript{4} and CO formation on carbon supported Re. In this case no cold trap was installed to remove water vapours from outlet gas. After H\textsubscript{2} TPR, 10 min O\textsubscript{2} oxidation at 40 °C was repeated followed by MeOH treatment at 175 °C. Saturator heated to 30°C was used to increase partial pressure of MeOH to 22 kPa in a flow of He at overall pressure of 1 bar. Rhenium oxidation state after MeOH treatment was again addressed by H\textsubscript{2} TPR (exp. 2). To identify the contribution of the impurities to oxidation reactions we performed blank H\textsubscript{2} TPR reduction test without 10 min O\textsubscript{2} purging step (exp. 3) and additional blank desorption (exp. 4) to determine H\textsubscript{2}O formation not related to ReO\textsubscript{x} reduction. Blank H\textsubscript{2} TPR (exp. 3) was performed after H\textsubscript{2} TPR (exp. 2), with the sample heated to 175 °C and cooled to 40 °C with the same temperature ramp rate as after MeOH treatment in exp. 2 followed by H\textsubscript{2} TPR (exp. 3). Exp. 4 was carried out after H\textsubscript{2} TPR (exp. 3) with heating in 175 °C and cooling to 40 °C as in exp. 3. This is followed by heating in He instead in H\textsubscript{2}/Ar to determine amount of desorbed H\textsubscript{2}O, which does not result from ReO\textsubscript{x} reduction and is due to small leakages and impurities in gases. All gas mixtures are supplied by Messer with purity 5.0, except of He which has a purity grade of 6.0. Whole procedure is displayed in Figure SI23. H\textsubscript{2}O formation was monitored using a calibrated mass spectrometer (18 amu).

![Figure SI23: Procedure of determination of Re/C reducibility by MeOH.](image-url)
The comparison of the H\textsubscript{2}O formation is presented in Figure SI24. By comparing line 1 (exp. 1., no MeOH prereduction) and line 2 (exp. 2., MeOH prereduction) we can observe much lower H\textsubscript{2}O production in the case with MeOH prereduction, which is indicative of MeOH reduction capability of ReO\textsubscript{x}. The maximum H\textsubscript{2}O formation is observed at 250 °C, which is 50 °C lower than at H\textsubscript{2} TPR of fresh catalyst (figure SI14). The reason is used smaller heating rate (5 °C/min instead of 10 °C/min), where longer exposure results in reduction at lower temperature, as evidenced by 40 °C decreased temperature of CuO reduction, when heating rate is decreased from 10 °C/min to 5 °C/min.\textsuperscript{[15]} Additional reason is, that H\textsubscript{2} is adsorbed faster on metallic Re instead on the oxide. The 10 min exposure to O\textsubscript{2} for a 40 min results in around 44% oxidation of rhenium as calculated by comparing H\textsubscript{2} consumption from H\textsubscript{2} TPR of fresh sample and difference between H\textsubscript{2}O production of exp.1 and exp. 3 ((890-307)/1311=0.44, stoichiometric factor=1). Remaining metallic rhenium can activate H\textsubscript{2} and accelerate the reduction of ReO\textsubscript{x}.\textsuperscript{[16]} Remaining H\textsubscript{2}O formation can be explained by the desorption of H\textsubscript{2}O and decomposition of oxygen species introduced by small amount of impurities in used gasses (line 4, exp. 4., blank desorption 307 μmol/g). Additionally, H\textsubscript{2}O and O\textsubscript{2} impurities can also partially oxidize Re by observing the peak at 60 min (line 3, exp.3., blank H\textsubscript{2} TPR). The amount of water formation at H\textsubscript{2} TPR with MeOH prereduction (440 μmol/g) is almost equal to the formation at blank H\textsubscript{2} TPR (458 μmol/g) which demonstrates complete reduction of Re to Re\textsuperscript{0} by MeOH. As reported in the literature H\textsubscript{2} consumption in H\textsubscript{2} TPR of Re/Al\textsubscript{2}O\textsubscript{3},\textsuperscript{[17,18]} is observed as a single peak of rhenium oxide(s) reduction at temperatures below 350 °C, although rhenium oxide can be found several oxidation states. This suggests that there is no large difference between reduction rates of different rhenium oxides.

During prereduction by MeOH at 175 °C, a significant amount (up to 5.5 %) of H\textsubscript{2} was detected by mass spectrometer (Figure SI25), which can additionally influence rhenium oxidation state. As expected, we observed H\textsubscript{2}O formation due to reduction of rhenium and methanol decomposition. Additionally, we also observed increase of CO\textsubscript{2} concentration during MeOH addition, highly likely caused by methanol decomposition.
Figure SI25: Product concentrations in the outlet gas during prereduction of Re/C in MeOH.
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