

Electronic Supplementary Material for:

Hydrodeoxygenation (HDO) of aliphatic oxygenates and phenol over NiMo/MgAl₂O₄: Reactivity, inhibition, and catalyst reactivation

Trine Marie Hartmann Dabros^{1,a}, Mads Lysgaard Andersen¹, Simon Brædder Lindahl¹, Thomas Willum Hansen², Martin Høj¹, Jostein Gabrielsen³, Jan-Dierk Grunwaldt^{4,5} and Anker Degn Jensen^{1,*}

¹ Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), Søtofts Plads, Building 229, DK-2800 Kgs. Lyngby, Denmark; trar@topsoe.com (T.M.H.D); maanlysgaard@gmail.com (M.L.A); Simonb.lindahl@hotmail.com (S.B.L.); mh@kt.dtu.dk (M.H.); aj@kt.dtu.dk (A.D.J.)

² National Centre for Nano Fabrication and Characterization (DTU Nanolab), Technical University of Denmark (DTU), Fysikvej - Building 307, DK-2800 Kgs. Lyngby, Denmark; thwh@dtu.dk (T.W.H)

³ Haldor Topsøe A/S, Haldor Topsøes Allé 1, DK-2800 Kgs. Lyngby, Denmark; joga@topsoe.com (J.G.)

⁴ Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstraße 20, Karlsruhe, D-76131, Germany; grunwaldt@kit.edu (J.-D.G.)

⁵ Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz Platz 1, Eggenstein-Leopoldshafen, D-76344, Germany; grunwaldt@kit.edu (J.-D.G.)

* Correspondence: aj@kt.dtu.dk; Tel.: 0045-45-25-28-41

^a Current affiliation: Haldor Topsøe A/S, Haldor Topsøes Allé 1, DK-2800 Kgs. Lyngby, Denmark; trar@topsoe.com (T.M.H.A)

Test of catalytic activity

A simplified process diagram of the reactor setup is shown in Figure S1. The oxide catalyst precursor (0.5 g) was mixed with SiC (150-250 µm) and loaded into the stainless steel reactor tube with steel wool acting as bed support. The reaction temperature was measured at the middle of the catalyst bed, with a position adjustable thermocouple placed in a thermo pocket outside of the reactor tube (inside of the reactor pressure shell, Figure S2). Catalyst activation was performed in-situ in the catalytic activity setup, approximately at near atmospheric pressure, in a flow of 10-12 % H₂S formed by decomposition of dimethyl disulfide (DMDS, Sigma-Aldrich, ≥ 99.0 %) in H₂, giving a total flow rate of around 830 NmL/min. 1 NmL is defined as 1 mL at normal conditions (1 atm pressure and 0 °C), and from the ideal gas law thus corresponds to 44.6 µmol. Initial heating was performed in 100 NmL/min N₂ from room temperature to 200 °C. The temperature was then increased to 360 °C (by 5 °C/min) and held at 360 °C until an increasing amount of unconverted DMDS was detected in the separator tube. After sulfidation, the temperature and pressure was increased to obtain reaction conditions.

The liquid model compound feed was fed (with an HPLC pump) into the reactor tube via a dip tube (Figure S2). The gas feeds (≥ 99.9 % H₂, ≥ 99.95 % N₂, and 2 % H₂S/H₂) were mixed at a three-way valve and sent to the bottom of the reactor pressure shell, thus being preheated inside the pressure shell before reaching the reactor inlet in the top (Figure S2). The reactor effluent was cooled (to 10-15 °C) and separated into gas and liquid. The gas was analysed online by gas chromatography (GC) using a Shimadzu (Kyoto, Japan) GC-2014 equipped with a 2 m 0.53 mm ID Shincarbon ST column and a thermal conductivity detector (TCD). N₂, H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆, and C₃H₈ were detected and quantified. The analysis frequency was typically two GC-TCD measurements per hour. A valve manifold (V1-V8) was used to collect liquid products, typically using a 4-5 h collection period in each sample bottle. The mass and density (Anton Paar DMA 4100) of the liquid samples were measured to get the volumetric flow rate. The liquid composition was analysed by GC-FID/MS using a Shimadzu (Kyoto, Japan) 2010 GCMS-QP2010 Ultra equipped with a Supelco Equity®-5 30 m x 0.32 mm column with d_{film} 0.5 µm and a flame ionisation detector (FID) and a parallel mass spectrometer (MS).

Experiments were terminated by flushing the reactor with N₂ at ambient pressure and ≥ 400 °C for ½ h to desorb any condensed species from the catalyst pores. The flushing was then continued, as the temperature was decreased to ambient conditions.

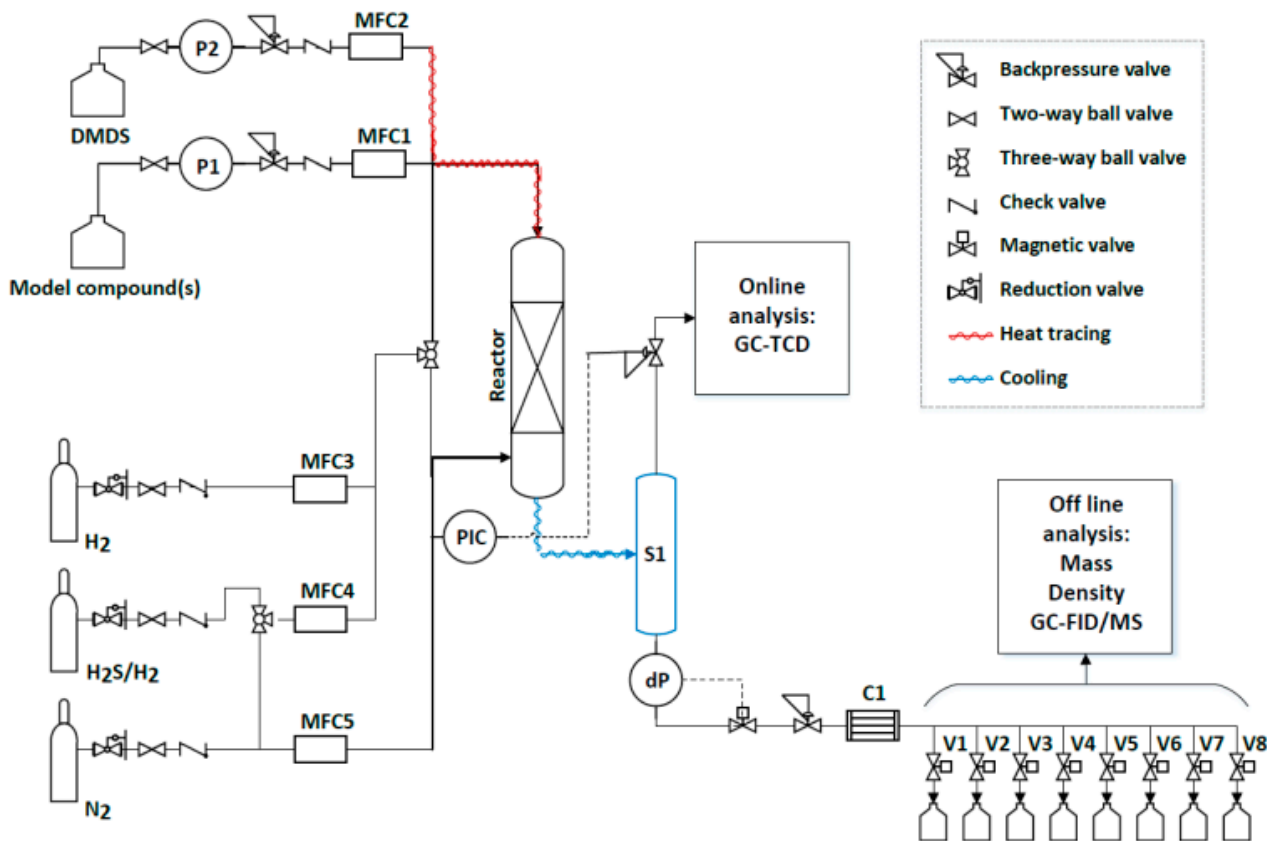


Figure S1. Simplified process diagram of the continuous flow fixed bed reactor setup. P: pump. MFC: Mass flow controller. PIC: Pressure indicator and controller. S1: Separator. dP: Differential pressure cell. C1: Condenser. V1-V8: Magnetic valves.

N₂ was used as an internal standard in the GC-TCD measurements. The molar flow of H₂ and gaseous (g) products ($F_{g,i}$) could thus be determined as:

$$F_{g,i} = y_i \cdot \frac{F_{N_2,feed}}{y_{N_2}}$$

The total effluent molar gas flow was based on the known molar feed flow of N₂, $F_{N_2,feed}$, and the fraction of N₂, y_{N_2} , as determined by GC-TCD. The concentration of detected products in the liquid effluent were determined based on the effective carbon number [1]. The molar flow of each compound was then calculated from the concentration, C_i (mol/L), and the total volumetric flow rate, Q , determined from the mass, m_l , and density, ρ_l , of the collected liquid product and the time, t , of collection:

$$F_{l,i} = C_i \cdot Q = C_i \cdot \frac{m_l}{\rho_l \cdot t}$$

Reactor design

A schematic drawing of the reactor is shown in Figure S2. The reactor was constructed from 316L stainless steel, as was the piping of the entire setup. The reactor consists of a vertical pressure shell and an internal reactor tube, in which catalyst bed was placed. The pressure shell consists of an 80 cm straight tube with flanges welded to the top and bottom respectively. The internal reactor tube is a 91.5 cm long straight tube with internal diameter 0.8 cm and outer diameter 1.0 cm. A support pin located 42.15 cm from the outlet of this tube enables fixation of the catalyst bed in the isothermal zone of the furnace using steel wool.

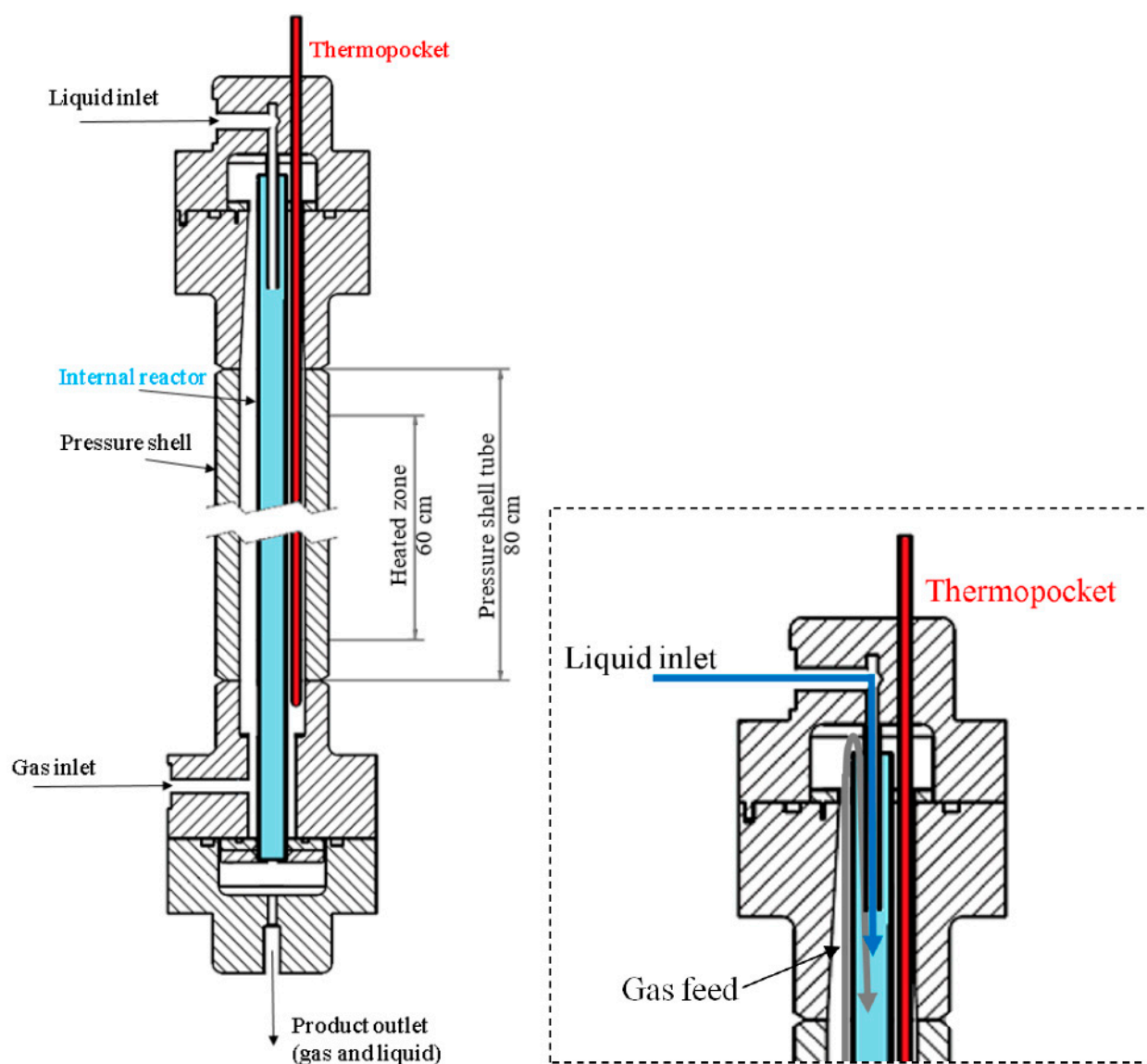


Figure S2. Schematic drawing of reactor design including pressure shell, internal reactor, and thermo pocket. The gas and liquid inlets are shown. The insert to the right shows the gas and liquid feed flow paths at the internal reactor tube inlet.

Temperature profile during experiment start-up

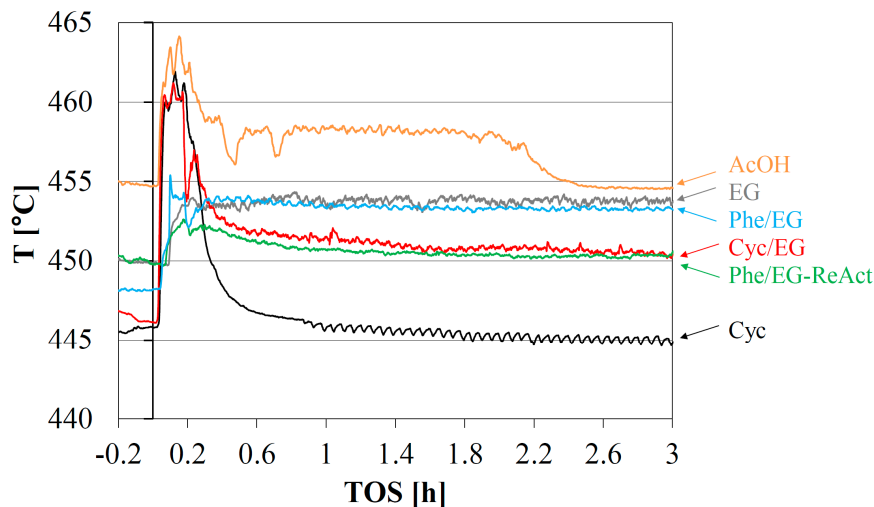


Figure S3. Initial temperature profiles. In the experiment with acetic acid (AcOH), the acetic acid feed was stopped at TOS ≈ 2.2 h.

Effectiveness factor

The effectiveness factor, η_{eff} , was used to assess the severity of the internal mass transfer limitation. The effectiveness factor can be expressed by the Thiele modulus, Φ , for a first order reaction over a spherical catalyst particle [2]:

$$\eta_{\text{eff}} = \frac{3}{\Phi^2} (\Phi \coth(\Phi) - 1)$$

$$\Phi = r_p \left(\frac{k \rho_c}{D_e} \right)^{1/2}$$

k is the mass based reaction rate constant, D_e is the effective diffusion coefficient, r_p is the catalyst particle radius, and ρ_c is the catalyst density. The feed gas consisted of approximately 65 % H_2 and 32 % N_2 in all experiments. The effectiveness factor was calculated by considering diffusion in pure hydrogen.

The calculated effectiveness factor as a function of particle size (Figure S4) was 0.83-0.95 for ethylene hydrogenation and 0.71-0.90 for cyclohexanol dehydration in the applied particle size range. Thus, the kinetic results presented in the main manuscript (Table 1 and Table 3) are assumed to give a fair estimate of the intrinsic reactivity, however with slight influence by mass transfer limitations. In the case of pure cyclohexanol dehydration, however, there was approximately 100 % conversion during the entire activity test independent of temperature. To be sure that mass transfer limitations did not restrict this experiment, it should be repeated at lower conversion with different grain sizes.

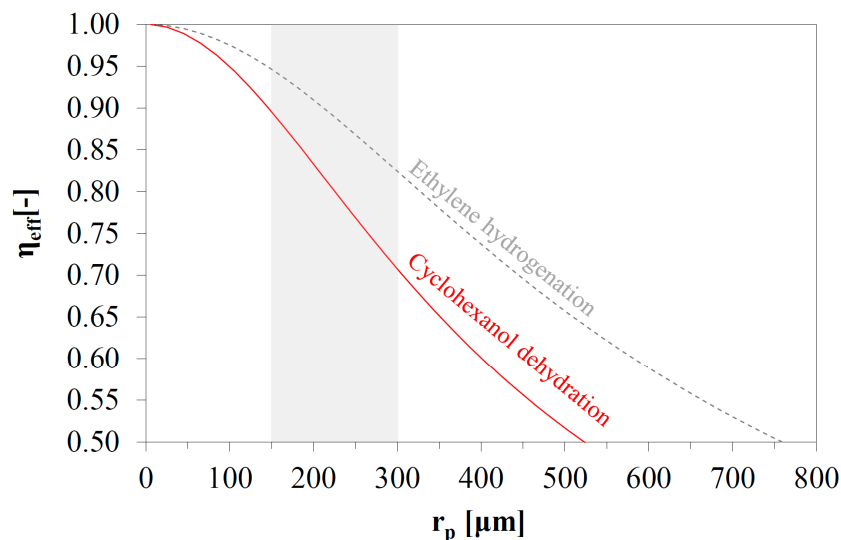


Figure S4. Effectiveness factor estimated for the fastest reaction in the conversion of ethylene glycol (dashed line) and cyclohexanol (solid line) as a function of catalyst particle radius. The actual particle radius used in HDO activity tests (150–300 μm) is shaded.

Arrhenius plots for ethylene glycol HDO

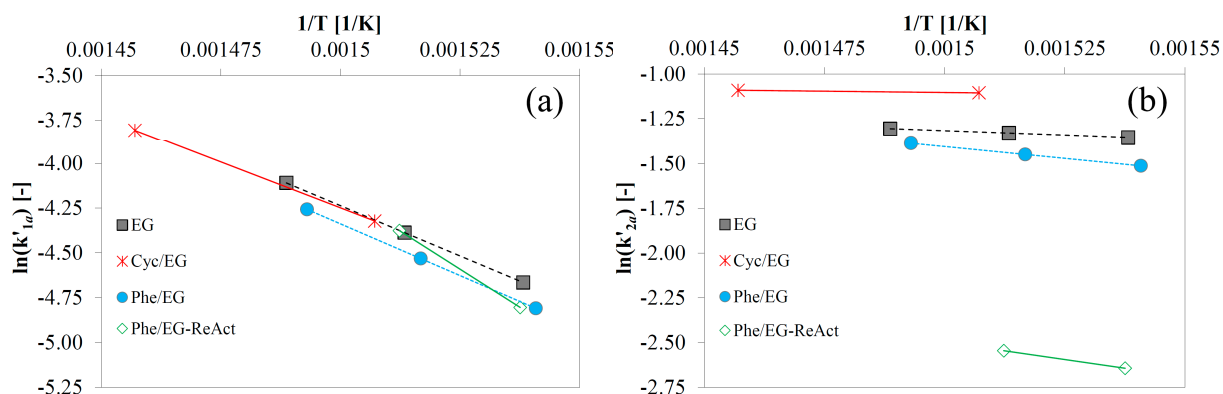


Figure S5. Arrhenius plots for the rate constants presented in the main manuscript (Table 1). (a) k'_{1a} : Initial dehydration and hydrogenation of $\text{C}_{2,\text{ox}}$ into ethylene. (b) k'_{2a} : Hydrogenation of ethylene into ethane.

Equilibrium calculations

HSC Chemistry v. 9.4.1 was used to calculate the thermodynamic equilibrium composition (Figure S6) of the reactions in Scheme 2 of the main manuscript. The feed composition (2.1 kmol cyclohexanol, 66.1 kmol H_2 , and 31.8 kmol N_2) was based on the molar feed concentration of the experiment with pure cyclohexanol, Cyc. Reaction products considered were H_2O , cyclohexane, cyclohexene, and benzene. The thermodynamic equilibrium prescribes full conversion of cyclohexanol.

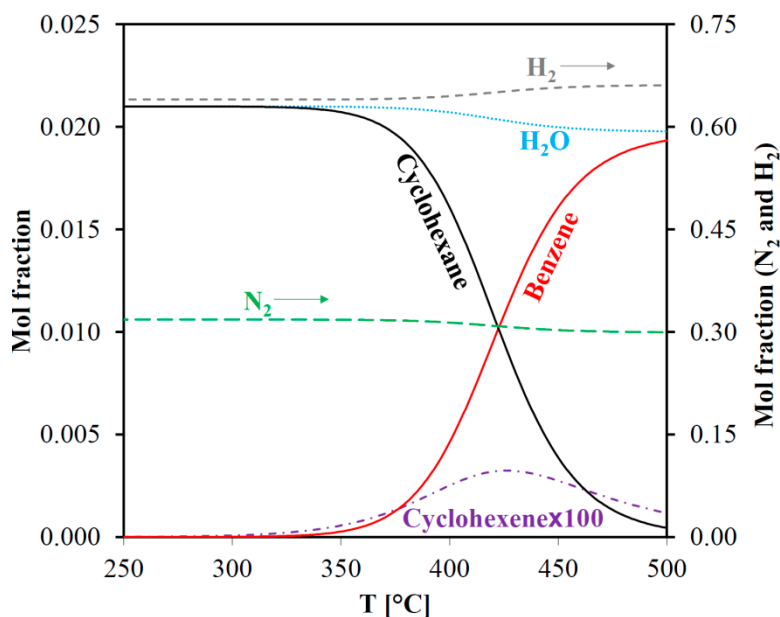


Figure S6. Equilibrium composition during cyclohexanol HDO calculated with HSC Chemistry v. 9.4.1. Feed composition: 2.1 kmol cyclohexanol, 66.1 kmol H_2 , and 31.8 kmol N_2 . Products included: H_2O , cyclohexane, cyclohexene, and benzene. The concentration of cyclohexene is multiplied with 100 for visualization.

HSC Chemistry v. 9.4.1 was also used to calculate the thermodynamic equilibrium composition (Figure S7) of the conversion of phenol into benzene and cyclohexane with a feed composition similar to that used in Phe/EG (excluding ethylene glycol). The thermodynamic equilibrium prescribes full conversion of phenol.

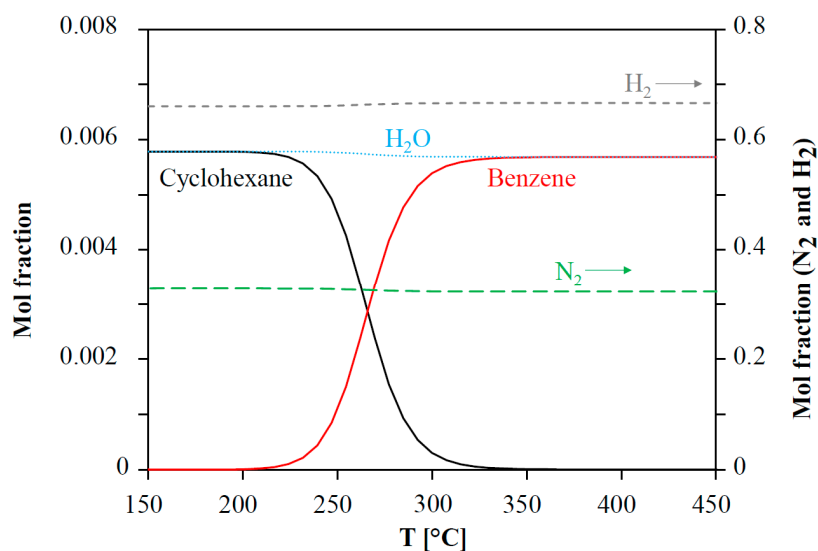


Figure S7. Equilibrium composition during phenol HDO calculated with HSC Chemistry v. 9.4.1. Feed composition: 0.55 kmol phenol, 65 kmol H_2 , and 31.2 kmol N_2 . Products included: H_2O , cyclohexane, benzene.

Transmission electron microscopy

Figure S8 reveals the consequence of carbon deposition: a ≈ 20 nm long, rectangular support particle sticking out of the bulk sample, having a double layer sulfide slab on each side, is covered by carbon. The deposited carbon thus limits the accessibility to the active sites of MoS_2 and inhibits HDO as well as other MoS_2 catalyzed reactions.

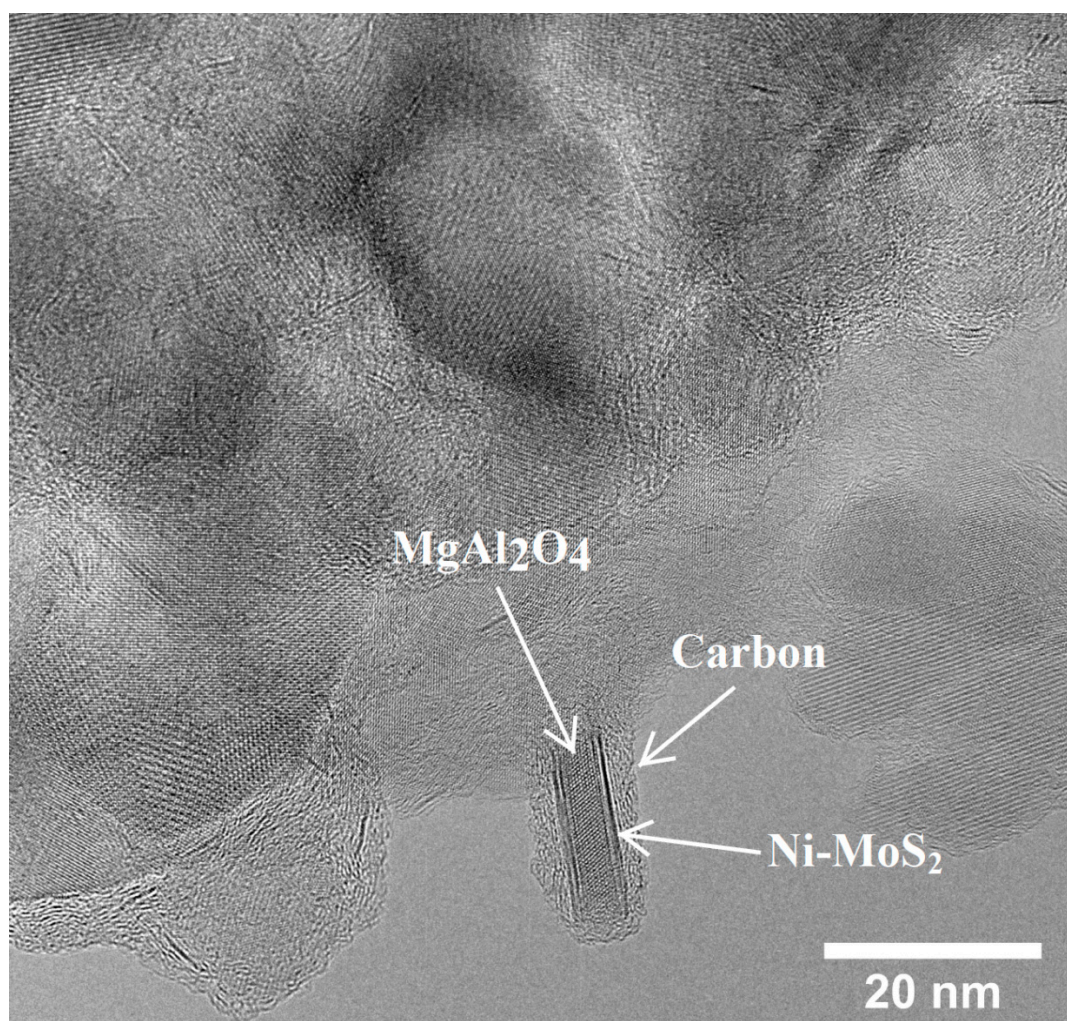
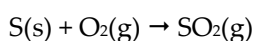
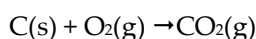
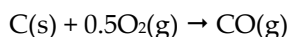


Figure S8. TEM image of spent catalyst from the experiment: EG.

Catalyst reactivation

First, the reactor was heated to 250 °C in a flow of 100 NmL/min N₂. Then the gas was switched to 1 NL/min 7.6 % O₂ in N₂, and slow heating with 1 °C/min was performed until 450 °C. After this point, the temperature was increased in small steps until 545 °C, where it was kept overnight. The concentration and temperature profiles are shown in Figure S9. At temperatures above 460 °C, no more carbon was burned off, but continued sulfur removal occurred as a function of temperature. The following reactions were assumed for the oxidation of deposited carbon and sulfur in MoS₂:



The carbon deposition on the catalyst was calculated based on the flow of N₂ and O₂ into the system, and on the concentrations of oxidation products and O₂ measured giving a carbon deposition of 15.4 wt%. The catalyst was then resulfided, and since the catalyst was only converted into a partial oxide phase, MoO_xS_y, by the oxidation step, the resulfidation took shorter time than the initial sulfidation. The catalyst activity was then tested again for the conversion of ethylene glycol and phenol.

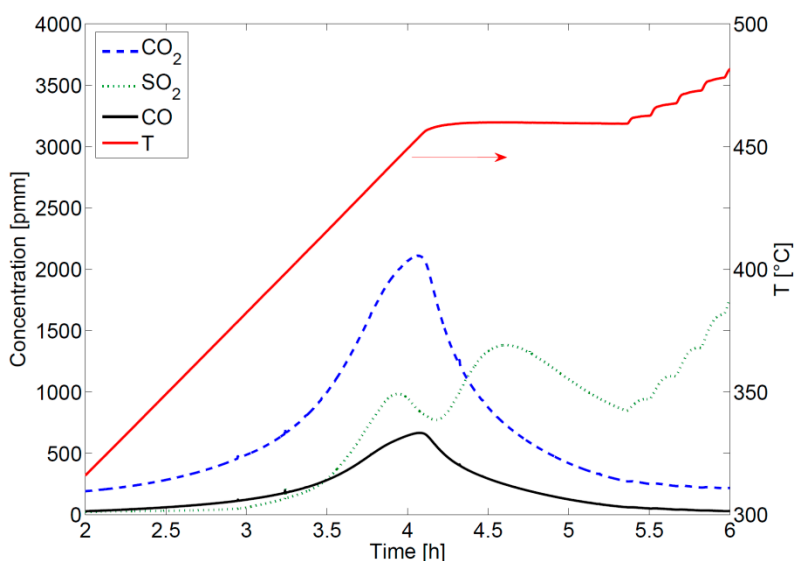


Figure S9. Off-gas concentration profiles and temperature profile from carbon burnoff from the spent catalyst after experiment Phe/EG (before Phe/EG-ReAct). Performed in-situ with 1 NL/min 7.6 %O₂ in N₂.

References

1. Schofield, K. The enigmatic mechanism of the flame ionization detector: Its overlooked implications for fossil fuel combustion modeling. *Prog. Energy Combust. Sci.* **2008**, *34*, 330–350.
2. Fogler, S.H. *Elements of Chemical Reaction Engineering*; 4th ed.; Pearson Education International, Prentice Hall: Westford, Massachusetts, 2010;