Supporting information

Synthesis of co-precipitated Rh@Al$_2$O$_3$ catalysts [1]

The alumina rhodium slurry was prepared by dispersing 0.005 wt% rhodium in alumina. Subsequently, aluminiumchloride was added in a molar ratio of 3.14:1 and the solution was stirred for 3h. Then, 25% ammonia was added to adjust the pH to 10. This was subsequently filtered and washed with deionized water and ethanol. The precipitate was thereafter dried in a vacuum oven and calcined at 900°C for 4h.

The acid wash was performed by pouring 120 mL 1M HCl over the catalyst in a funnel. Thereafter, the catalyst was neutralized with water and dried at 120°C for 1 hour.

CO-Yield evaluation

The CO yield was determined by comparing the CO output flow with the CH$_4$ and CO$_2$ input flow into, see eq.1

$$\frac{CO_{out}}{CO_{2,in} + CH_{4,in}} * 100\%$$

eq S1

Whereas for the turnover frequency the total molecular amount of CO was produced per rhodium site per second, see eq. 2

$$\frac{CO_{out}}{mol_{Rh} * time\ (s)} * 100\%$$

eq S2

The amounts were based on the signal in a thermal conductivity detector in a GC, where the carrier gas N$_2$ was used as an internal standard.

Electron Paramagnetic simulation

The simulation was done in EasySpin [2]. All X-band EPR spectra were obtained at 10 K with mod. amp. 4.000 G and power 0.6325 mW. Microwave freq. 9.643733 (fresh), 9.647212 (activated), 9.644264 (activated, washed), 9.648861 (activated, washed, activated) GHz.

Simulation parameters for the activated sample were: S=0.5, g=[2.016 2.001 1.901], Nucs=Rh, n=1 A=[68 0 0] MHz, g$_{Strain}$=[0.004 0.004 0.040]
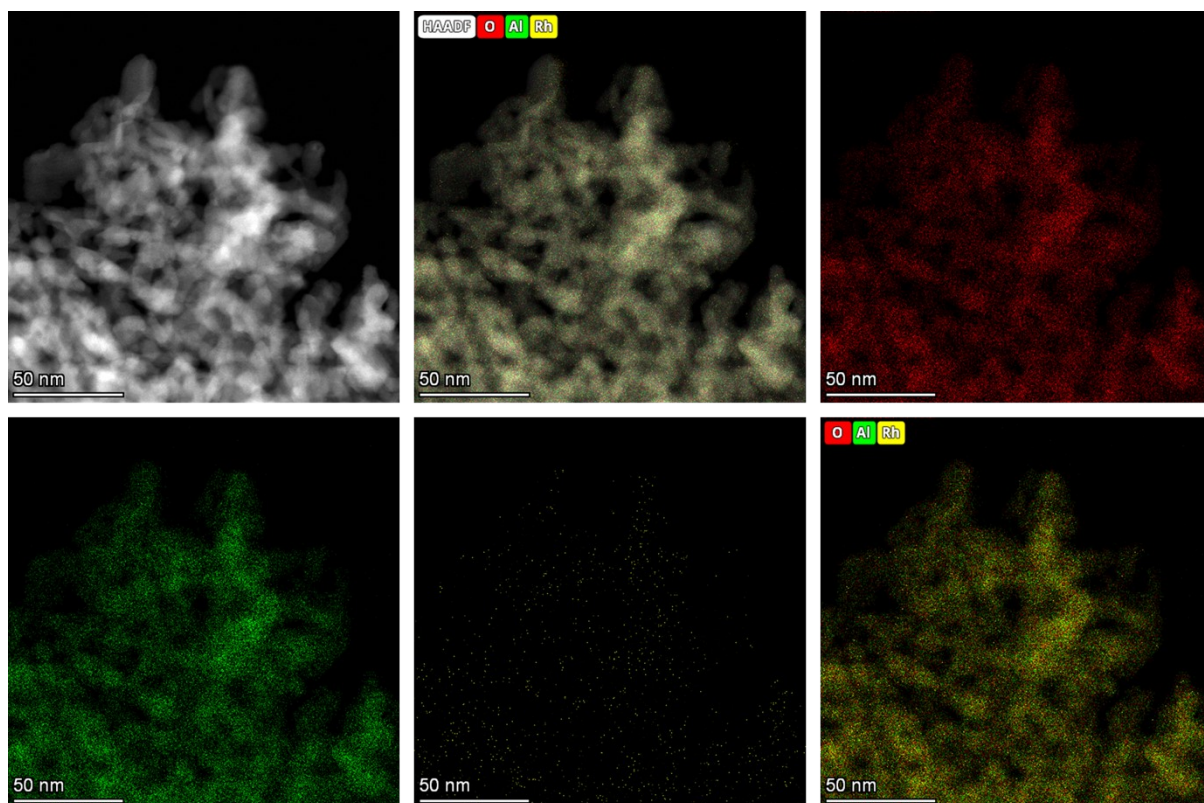
Figure S1 – TEM-EDX mappings of the zoomed-out photo in Figure 1c. No signs of Rh agglomeration above the noise level was observed.
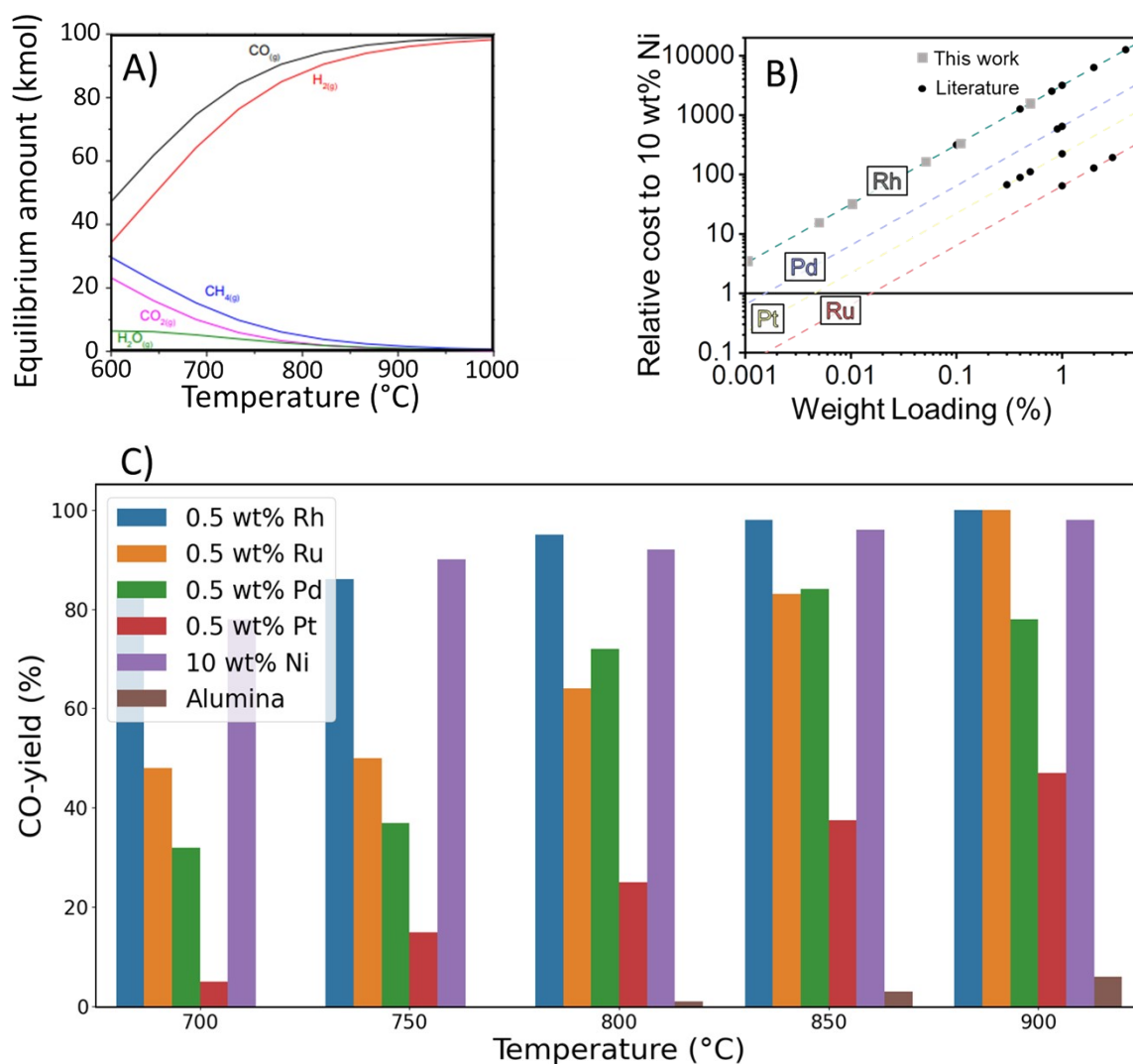
Figure S2 – Theoretical temperature dependent CO-yield and the respective gas compositions for DRM (a). Relative costs for 10 wt% Ni supported on Al$_2$O$_3$ compared to similar weight loading in terms of maximal atom occupancy (b). Temperature dependent conversions of the individual noble metals on Al$_2$O$_3$. This approached the theoretical yield (c).
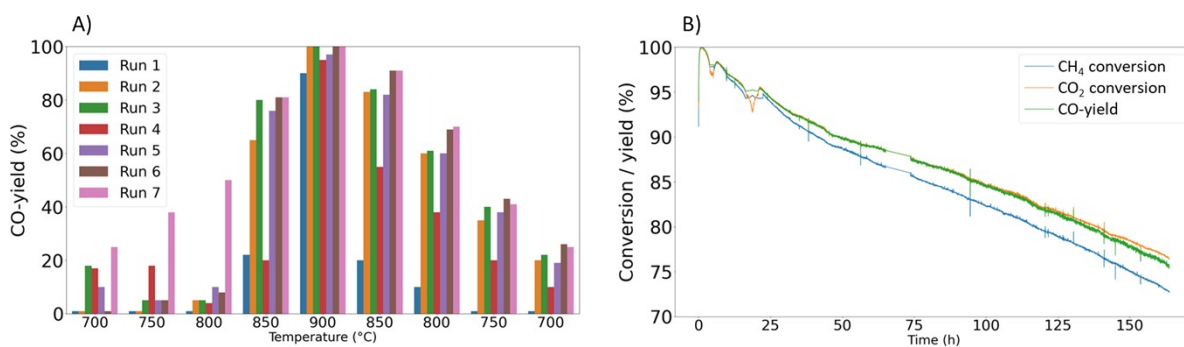

Figure S3 – (A) Complete runs and (B) the stability test for the 0.005wt% Rh/Al$_2$O$_3$ loaded catalysts at 900°C in terms of performance of all yields and conversions. A decrease in activity due to agglomeration was observed.
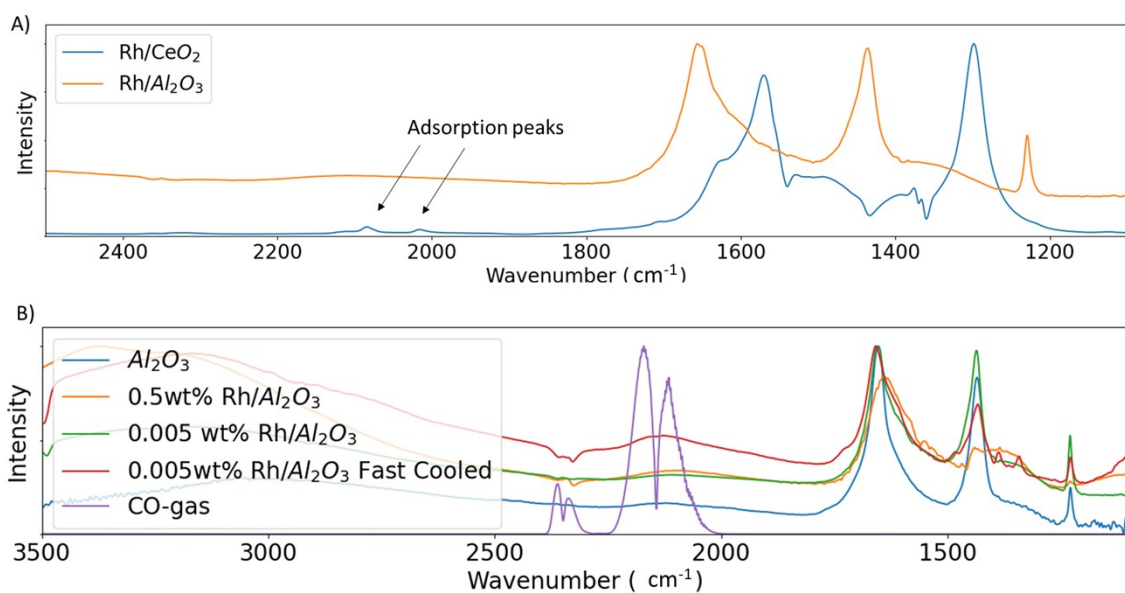
Figure S4 – (A) CO-DRIFTS on Rh/CeO$_2$ and Rh/Al$_2$O$_3$ catalysts showing the differences in adsorption and dissolution behavior. (B) Comparable overlap of adsorbed CO molecules with CO-gas.
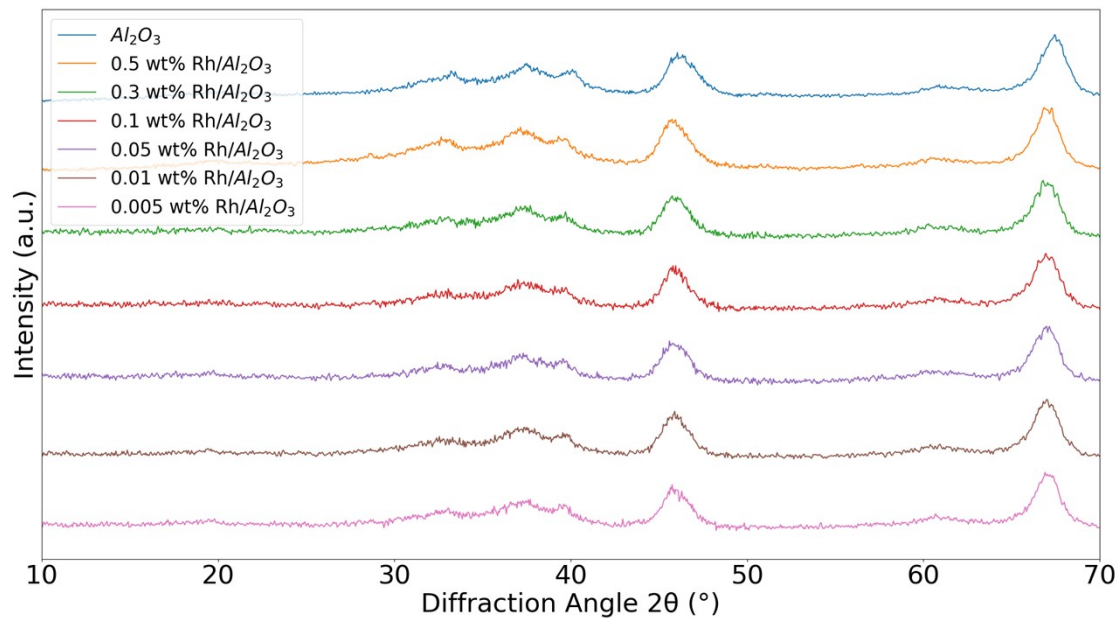

Figure S5 – XRD of the different Rh loadings, showing the same diffraction pattern as Al$_2$O$_3$ for the differently loaded samples.

Survey spectrum (PE=500 eV)

Intensity (arb. units)

O 1s

O KLL

F KLL

F 1s

C 1s

Al 2s

Al 2p

1000 900 800 700 600 500 400 300 200 100 0
Binding Energy (eV)

*peaks charge corrected to adventitious carbon at 284.8 eV

- Detected small traces of F
- Al ~ 99.7 %
- Rh ~ 0.3 %

Rh 3d region (PE=300 eV)

Intensity (arb. units)

- data
- fit
- Rh_2O_3

308.7 eV

320 318 316 314 312 310 308 306 304
Binding Energy (eV)

Al 2p region (PE=300 eV)

Intensity (arb. units)

- data
- fit
- Al_2O_3

75.2 eV

80 79 78 77 76 75 74 73 72 71 70
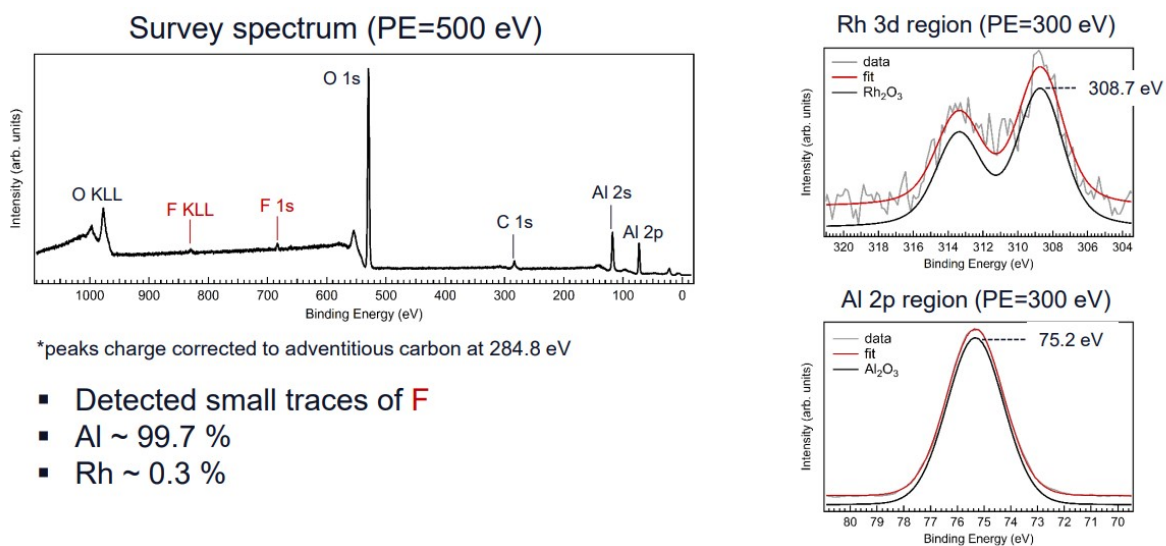Binding Energy (eV)

Figure S6 – XP spectrum of the Rh/Al_2O_3 powder. Two clear peaks are observed at 314 eV and 309 eV, matching the binding energies characteristic for Rh_2O_3. The surface content approximates 0.3 Rh/Al metal % (converting to approximately 0.5 wt% Rh/Al_2O_3), indicating Rh migration from the surface into the subsurface of Al_2O_3 (and not to the main bulk).

References

[1] A. Eftekhari, B. Modahedi, G. Dini, M. Milani, *J. Eur. Ceram. Soc.* **2018**, *38*, 3297-3304.

[2] S. Stoll, A. Schweiger, *J. Magn. Reson*. **2006**, 178, 42-55