Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information

Shining light onto the low-temperature methanol aqueous-phase reforming using homogeneous Ru-pincer complexes – operando Raman-GC studies

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1. Calculations

Turnover Frequency (TOF)

For the calculation of the turnover frequency after x hours, the total moles of hydrogen produced within the time x where divided by the molar amount of catalyst used in the experiment.

$$TOF(x\,h) = \frac{n_{H2}(x\,h)}{n_{catalyst}}$$

KOH consumption

Each CO_2 molecule reacts with two OH^- molecules to CO_3^{2-} and H_2O. Since the purity of KOH was 84%, it is assumed that all OH^- is neutralized, when a third of the produced molar amount of hydrogen equals 0.5*84% of the added mass of KOH. The assumption that three molecules of H_2 correlate with one molecule CO_2 is valid only after the formate peak fully disappeared, so that no more CO_2 is "trapped" in formate.

For experiment 1 the formate signal disappears after approximately 24 hours. Until then 2.587 L or 0.051 moles H_2 were produced. That equals 0.017 moles of CO_2, which is in good agreement with 2.3g KOH $\rightarrow$ 0.5*0.84*2.3g/56.1 g/mol = 0.017 mol. This rough estimation shows that the assumption of full OH^- consumption is valid.

For experiment 2 the same calculation yields: 1.257 L H_2 or 0.035 moles of CO2, against 4.5g KOH $\rightarrow$ 0.5*0.84*4.5g/56.1 g/mol = 0.0335 mol.

2. Figures

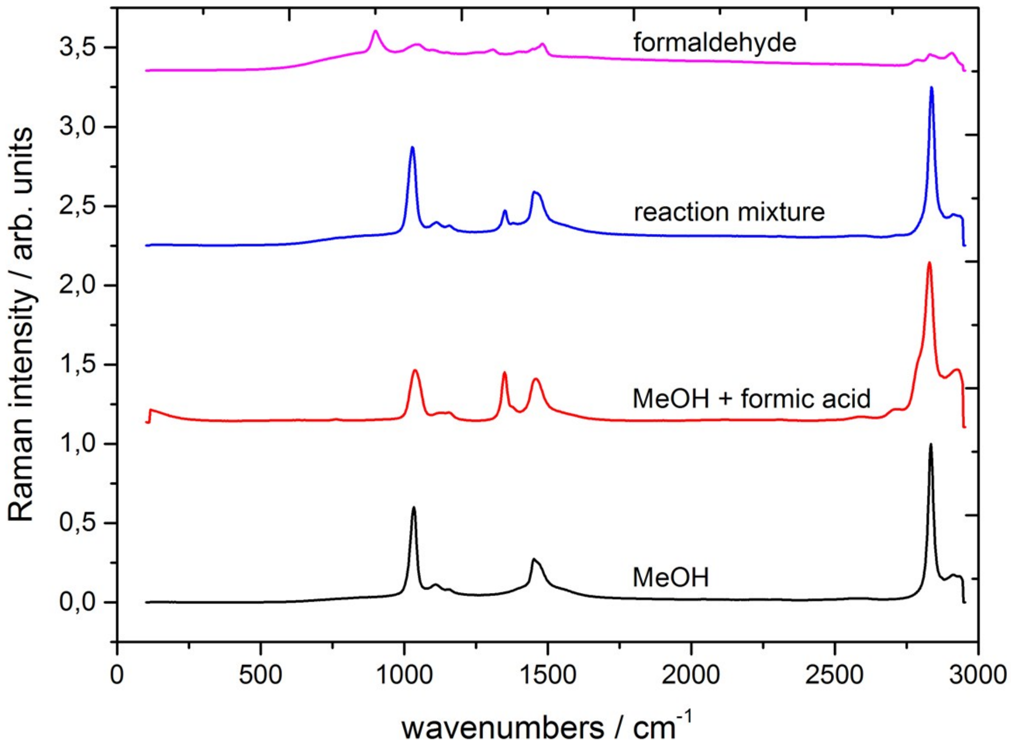

Figure S1. Raman spectra of reaction of formaldehyde (magenta), reaction mixture (blue), reaction mixture with formic acid (red) and pure Methanol (black)

Figure S2. K_2CO_3 precipitation on the inner wall of the reactor after an experiment

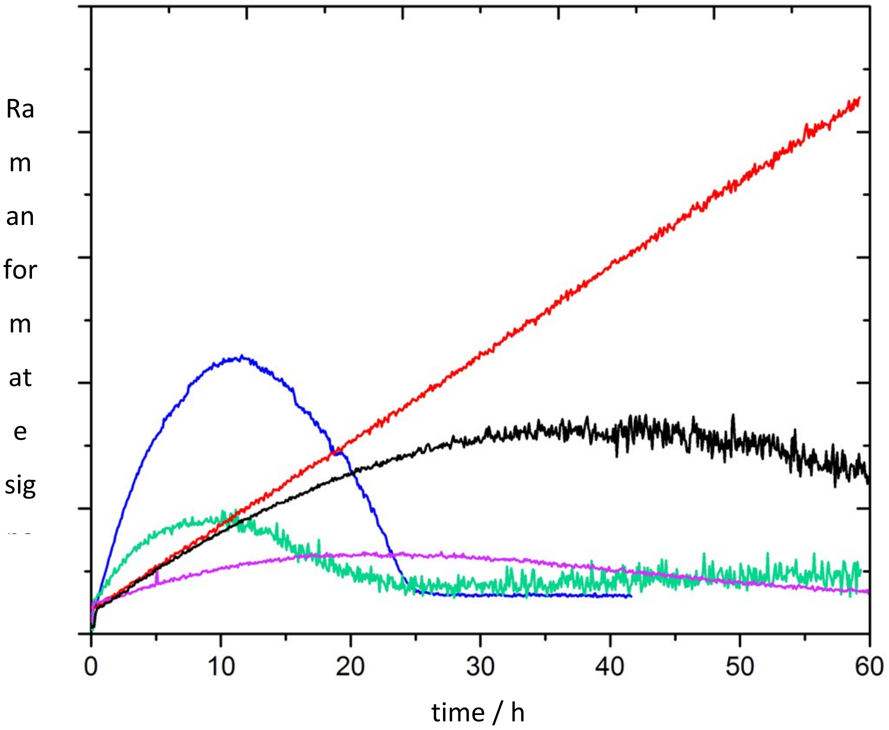

Figure S3. Concentration profiles for format in arb. units for all experiments. The reaction conditions are given in table 1 as follows: (green) entry 1, (blue) entry 2, (purple) entry 3, (black) entry 4, (red) entry 5

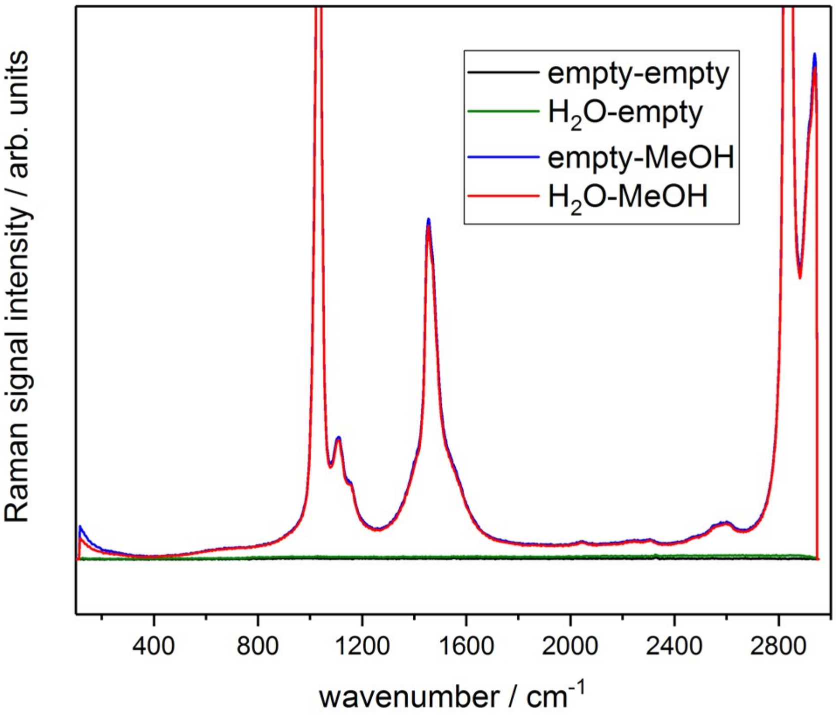

Figure S4. Raman spectra for the completely empty glass reactor (black), empty reactor, but water in the heating jacket (green), empty heating jacket with methanol in the reactor (blue) and water in the jacked and methanol in the reactor (red)

3. GC calibration

The gas chromatograph was calibrated solely for the H_2/CO_2 ratio. 3 calibration gases from Linde AG were used: 5,02%, 15,4% and 25,1% CO_2 in H_2 (The odd numbers are taken from the respective calibration certificate of the gas bottle).

Raw chromatogram data were loaded into MATLAB. Peak area of hydrogen and carbon dioxide was summed up and normed to 100% because no side products were generated. The ratio of these normed peak areas were calibrated with the known concentrations – and therefore ratios – of the calibration gas mixtures. The following diagram shows the calibration curves.

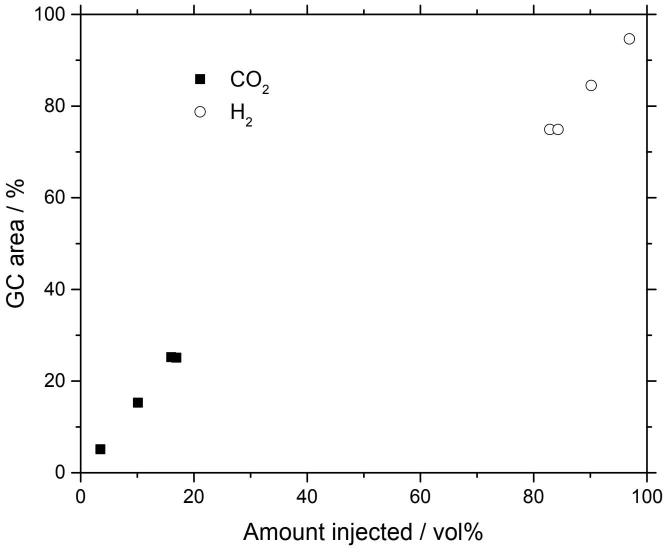

Figure S5. TCD area detected for different amounts of CO2 and H2 injected into the GC.