Homogeneous Ruthenium-based Water-Gas Shift Catalysts via Supported Ionic Liquid Phase (SILP) Technology at Low Temperature and Ambient Pressure.

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Supporting Information

1. Preparation of Supported Ionic Liquid Phase (SILP) WGS catalysts

For a typical experiment, 178 mg of the catalyst precursor $RuCl_3$-hydrate (Alfa Aesar, >99 %) was dissolved in 50 ml bi-distilled water and stirred in a Schlenk-tube for 10 min. 500 mg of the ionic liquid [BMMIM][OTf] (Solvent Innovation, >99%) was added to the dark brown to black solution. After 5 minutes of stirring 4 g of the highly porous support Silica 100 (Merck KgaA) was added. The suspension was stirred for another 15 min. The solvent was then removed in vacuo upon which a dry powder with a ruthenium loading of $w_{Ru} = mg_{Ru}\ g_{Support}^{-1} = 0.02$ and an ionic liquid loading of $\alpha = V_{IL}\ V_{pore}^{-1} = 0.1$ was obtained. The free-flowing dark brownish powder was stored under argon until further use. In Figure S1 a fresh catalyst (left) and a used catalyst (dark yellow to orange) is depicted.

Figure S1. Fresh (right) and used (left) SILP WGS catalysts.

2. Flowsheet of the continuous gas-phase SILP WGS reactor

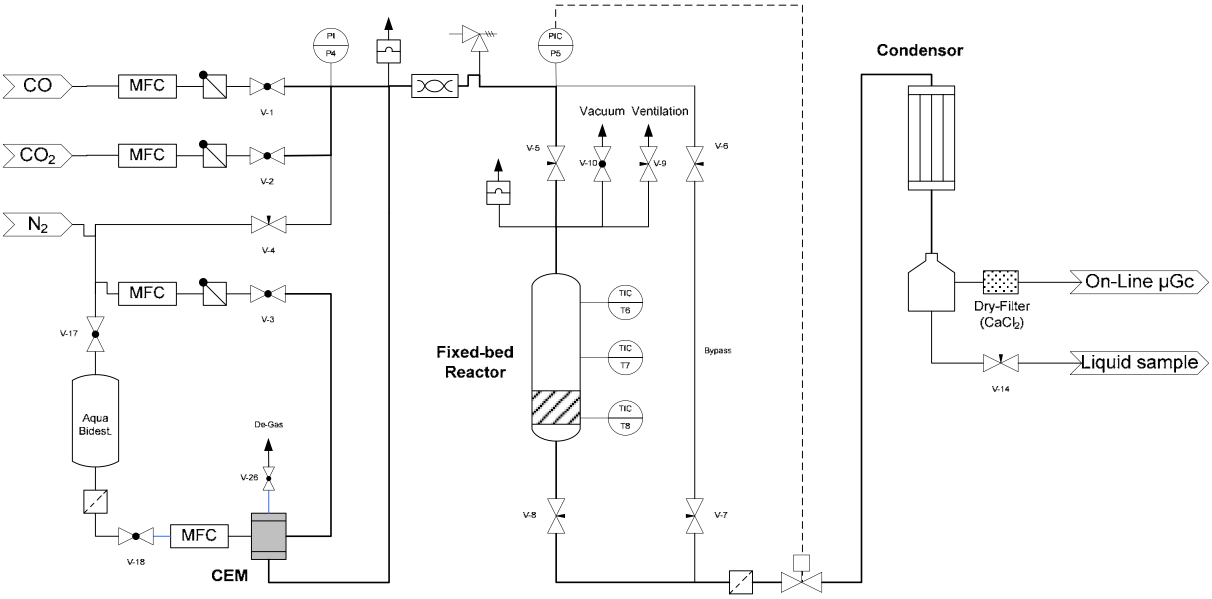

Figure S2. Flowsheet of the continuous SILP WGS reactor setup.

In a typical experiment the weighed SILP WGS catalyst was placed on the stainless steel frit (2 microns) of the tubular fixed bed reactor. The catalyst was covered with inert material and glass wool to prevent fluidization in case of vacuum being applied. The reactor was closed to the environment and heated under an inert gas flow. When the complete setup reached reaction temperature, the Controlled Evaporator and Mixer unit (Bronkhorst CEM / LiquiFlow HighFlow Series) was switched on and water was evaporated in the presence of nitrogen. The appropriate amount of CO was adjusted by means of a mass flow controller (Brooks 5850) and the gasses passed the bypass of the reactor until steady state conditions were achieved. This was verified by online analysis of the gas mixture in the MicroGC (Varian 4900). The bypass flow was then directed into the reactor and the reaction progress was monitored via MicroGC. Water was condensed at 1 °C after the reactor followed by a drying cartridge ($CaCl_2$) in order to avoid contamination of the microGC.

3. GC analysis

A Varian microGC (4900 Series) equipped with an MS5A (Molar sieves 5Å, 10m) and a PPQ (PolarPlot Q, 10m) column module was used for the analysis of the effluent gasses. Helium (Linde AG, 99.999%) was used as reference gas for the thermal conductivity detector and a carrier gas. GC details are given in Table S1.

Table S1. Representative parameters for WGS effluent gas analysis.

Gas chromatograph	Varian CP 4900	
Column	PPQ 10m	MS5A 10m
Detector	TCD	TCD
Temperature isothermal / °C	32	100
Column head pressure / kPa	250	300
Carrier and reference gas	Helium	Helium
Detection of	N_2, CO_2, Hydrocarbons	N_2, CO

In a typical 120 s analysis all components were detected and automatically integrated by use of the Varian Star 6.1 software. Using calibration curves produced by injection of calibration gas mixtures (Linde AG) a calibration factor was obtained. So a transformation of the peak area to a corresponding molar ratio and molar flow was possible.

4. Calculation of conversion (X) and turn over frequency (TOF)

The degree of conversion was calculated in two ways to ensure that the mass balance was complete:

a) Via molar flows $$X_{CO,MFC} = 1 - \frac{\dot{n}_{CO}}{\dot{n}_{CO,0,MFC}}$$

where $n_{CO,MFC,0}$ entitles the molar flow as calculated from the mass flow controller calibration and n_{CO} the molar flow as calculated from GC analysis.

b) Via normalized peak areas $$X_{CO,Area} = \frac{A_{CO_2} \cdot \kappa_{CO_2}}{\left(A_{CO} \cdot \kappa_{CO} + A_{CO_2} \cdot \kappa_{CO_2}\right)}$$

In both cases a good agreement of the calculated conversions was found.

Subsequently the turn over frequency (TOF) was calculated via the ratio of produced product (CO_2) per moles of Ruthenium:

$$TOF = \frac{\dot{n}_{CO_2}}{n_{Ru}} = \frac{X_{CO,Area} \cdot \dot{n}_{CO}}{n_{Ru}}$$