Supporting Information

Tailored monolith supports for improved ultra-low temperature water-gas shift reaction

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1 Continuous gas-phase catalytic test rigs

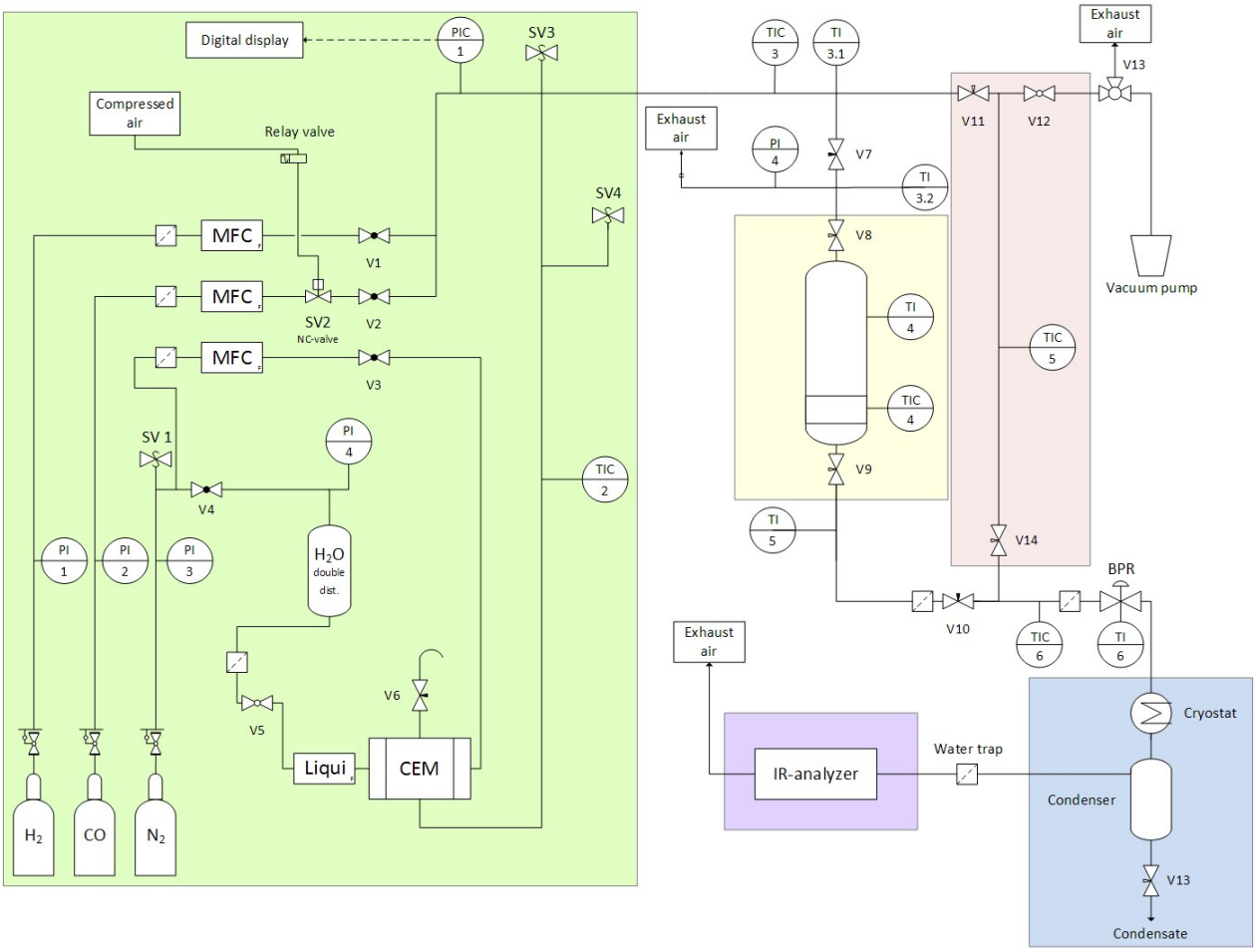


Figure S1. Flow scheme of the continuous packed-bed reactor for the catalytic evaluation of the different samples. Green: gas dosing and mixing section, red: bypass section, yellow: packed-bed reactor, blue: condenser section, purple: IR analyzer section.

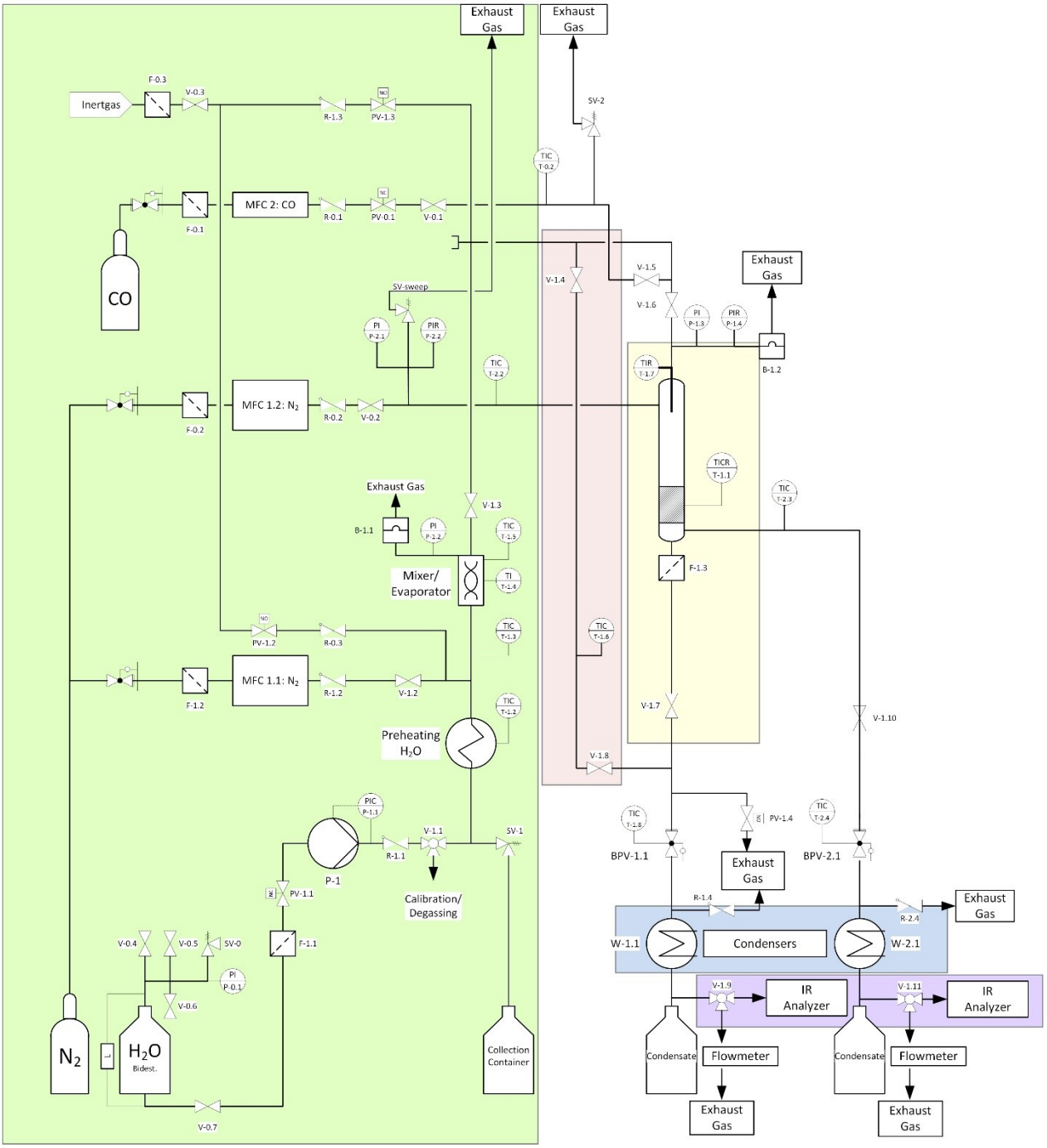
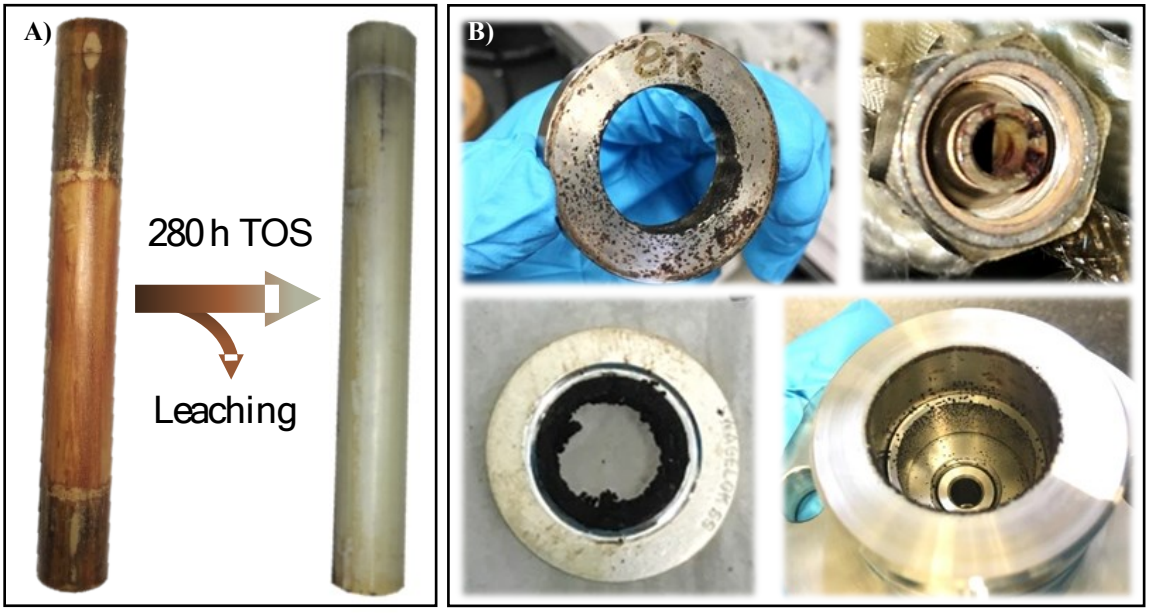


Figure S2. Flow scheme of the continuous reactor for the catalytic evaluation of the monolithic samples. Green: gas dosing and mixing section, red: bypass section, yellow: monolith-reactor, blue: condenser section, purple: IR analyzer section.



2 Corrosion effects due to leaching from SiO_2/SiC monolith-SILP

Figure S3. Corrosion effects during WGS reaction test with SiO_2/SiC monolith-SILP. A) Picture of the monolith before (left) and after (right) reaction with total TOS of more than 280 h, B) pictures of the reactor and its periphery showing pitting and surface corrosion after the experiment.

3 Novel monolithic supports development

The requirements to be met for the new compositions were good plasticity of the dough, easy drying to crack-free and straight monoliths, calcined body resistant both to compressive forces and to immersion in water and in the catalyst solvent, no catalyst leak, and activity comparable to benchmark alumina. Ideally, the surface roughness would also be low enough to allow the coating of a polymeric membrane for operation of a catalytic membrane.[7, 11] Pure γ-alumina mesoporous monoliths were successfully obtained and the mechanical properties were sufficient to fit the monolith in the reactor, but not to withstand pressurization. Therefore, a thorough screening of binders for alumina was performed by manual extrusion of pellets. Inexpensive natural clays, which facilitate extrusion and drying and confer mechanical stability to the extrudates, were added in different proportions for the formulation of alumina-rich extrudates to improve the crushing strength while maintaining a similar porous distribution and chemistry. Their main properties are collected in Table S1.

Table S1. Composition and textural properties of the natural clays used as binders.

	Sepiolite	Kaolinite	Bentonite
SiO_2, %	57.9	49.0	60.9
MgO, %	20.2	0.3	3.2
Al_2O_3, %	7.1	35.0	19.8
CaO, %	4.7	0.3	1.0
Fe_2O_3, %	2.1	1.6	4.2
K_2O, %	1.4	1.2	0.3
Na_2O, %	0.3	0.2	3.4
Mn_2O_3, %	0.1	0.0	0.0
TiO_2, %	0.4	1.5	0.2
L.O.I.*, %	5.8	12.0	6.0
S_{BET} / m^2 g^{-1}	240	48	40
Particle size / μm	38 – 125	< 0.5	50 - 150

* Loss on ignition

A common temperature of 550 ºC was selected for the heat treatment of all the extrudates, as it guarantees the permanent dehydration of the silicates, which improves their stability, and the formation of the desired γ-alumina phase from boehmite, according with the TGA results included in Figure S4.

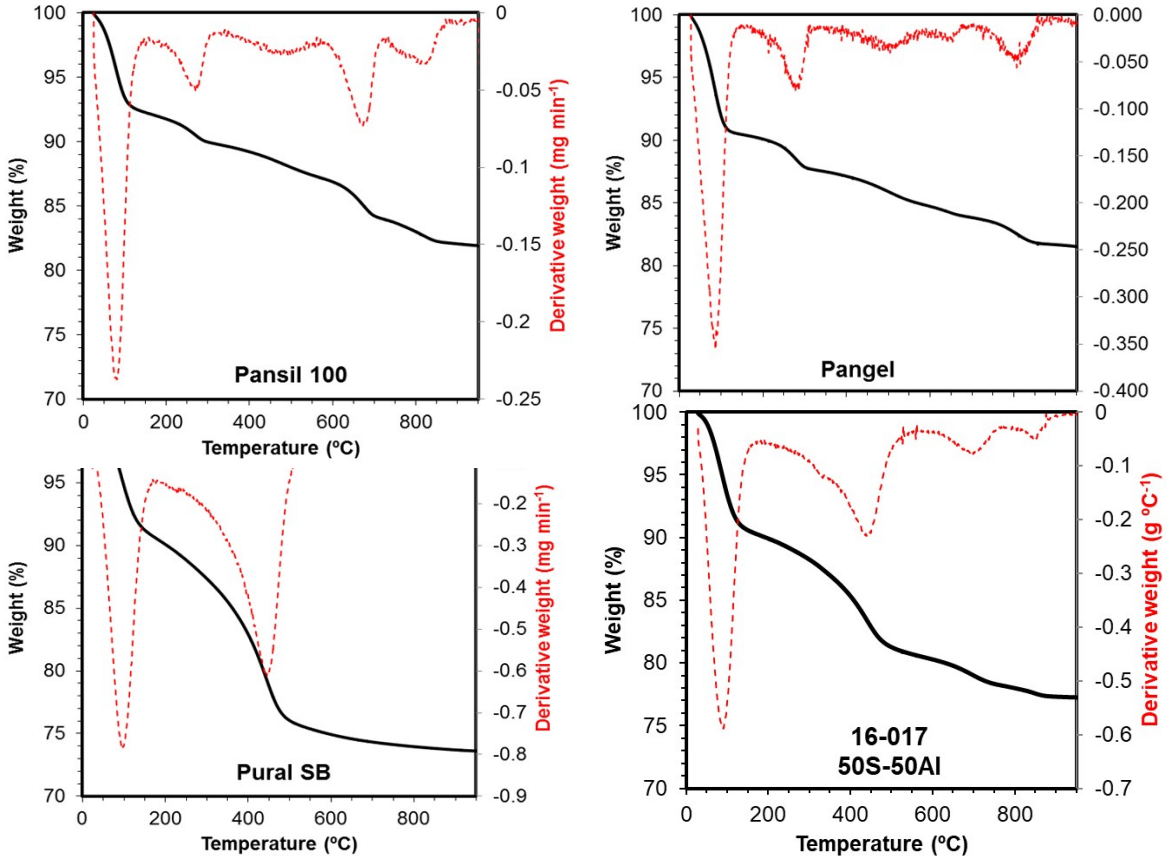


Figure S4. TGA of fresh extrudates made of natural sepiolite clay (top), the alumina precursor (bottom, left) and a 50% mixture (bottom right).

Acceptable samples regarding dough plasticity and mechanical resistance of the dried extrudates were further calcined and characterized in terms of porous structure and crushing strength. Table 2 in the results part contains a list of the shaped support samples selected to be crushed, impregnated, and then tested in the packed-bed reactor for catalytic activity in the WGS reaction. Figure S5 compiles the textural properties of the different pure sepiolite and carbon-sepiolite composite samples, while Figure 3 in the manuscript show the textural properties of the alumina-containing samples.

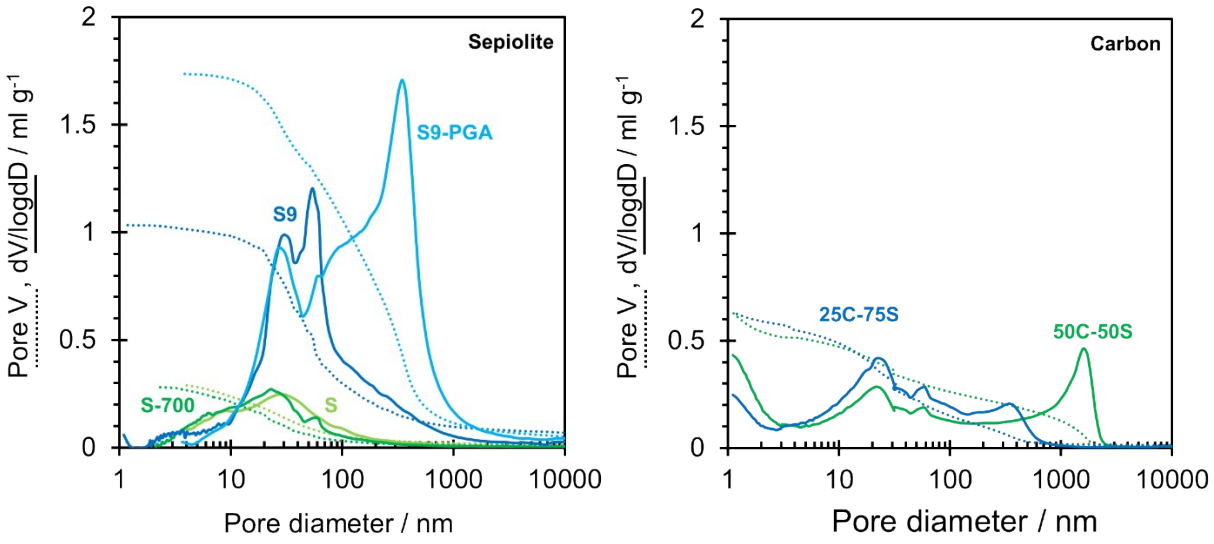


Figure S5. Pore volume and pore size distribution of single-component sepiolite monoliths (left) and carbon+sepiolite monoliths (right).

Among the screened SILP particles, the support composition of the best performing sample was selected to be shaped as full monolith to obtain an optimized monolithic-SILP for WGS. The material shrinkage during the thermal treatment was measured to design the extrusion die, the results are shown in Figure S6.

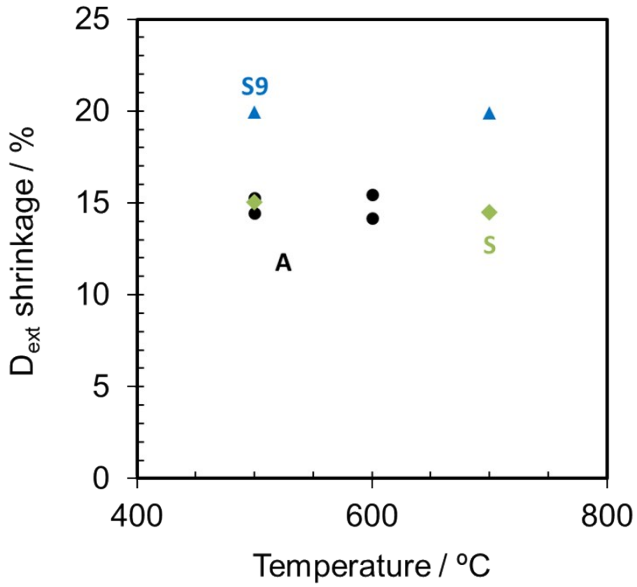


Figure S6. External diameter reduction with the calcination temperature of single-component monoliths of sepiolite Pangel S9 (S9, blue), sepiolite Pansil 100 (S, green), and γ-alumina (A, black).

4 Activity tests of the benchmark system and novel supports

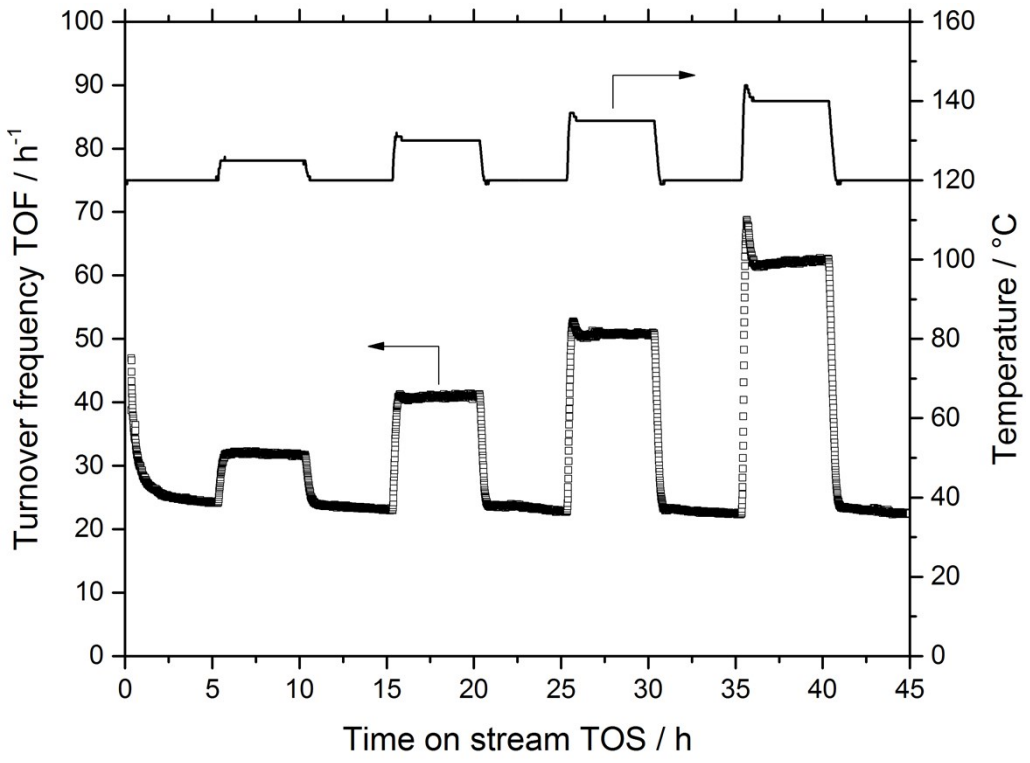


Figure S7. Catalytic activity data for the benchmark SILP WGS particulate catalyst. Turnover frequency (left y-axis) and bed temperature (right y-axis) over time-on-stream .p = 1 bar, precursor = $[Ru(CO)_3(Cl)_2]_2$, loading (Ru) = 0.02 $g\ g_{Support}^{-1}$, IL = $[C_4C_1C_1Im]Cl$, α = 0.34, m_{cat} = 2.0 g, p_{H2O}:p_{CO} = 2:1, $\dot{V}_{tot}$ = 174 $mL_N\ min^{-1}$.

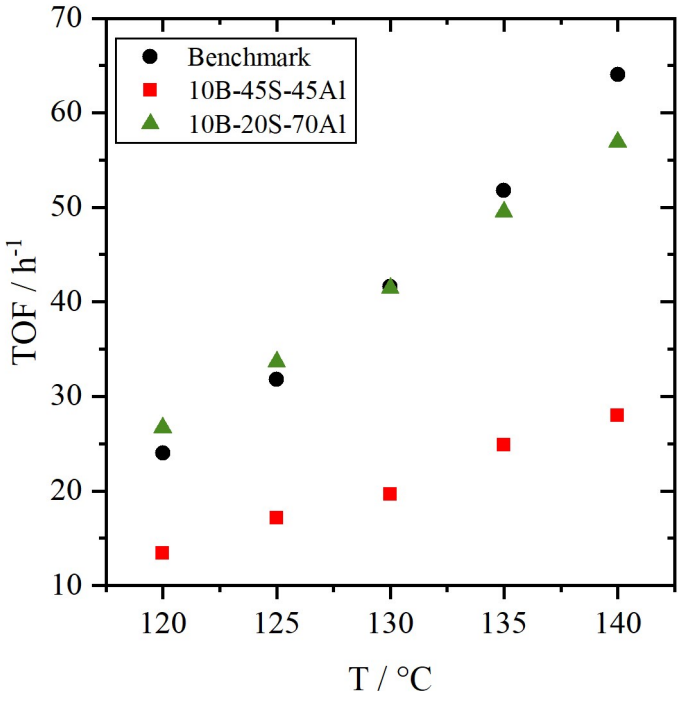


Figure S8. Comparison of the catalytic activity of the benchmark SILP WGS catalyst and the most promising novel catalytic support materials as particulates of 200-500 µm. Turnover frequency is plotted over time-on-stream. p = 1 bar, precursor = $[Ru(CO)_3(Cl)_2]_2$, loading (Ru) = 0.02 $g\ g_{Support}^{-1}$, IL = $[C_4C_1C_1Im]Cl$, α = 0.34, m_{cat} = 2.0 g, p_{H2O}:p_{CO} = 2:1, $\dot{V}_{tot}$ = 174 $mL_N\ min^{-1}$.

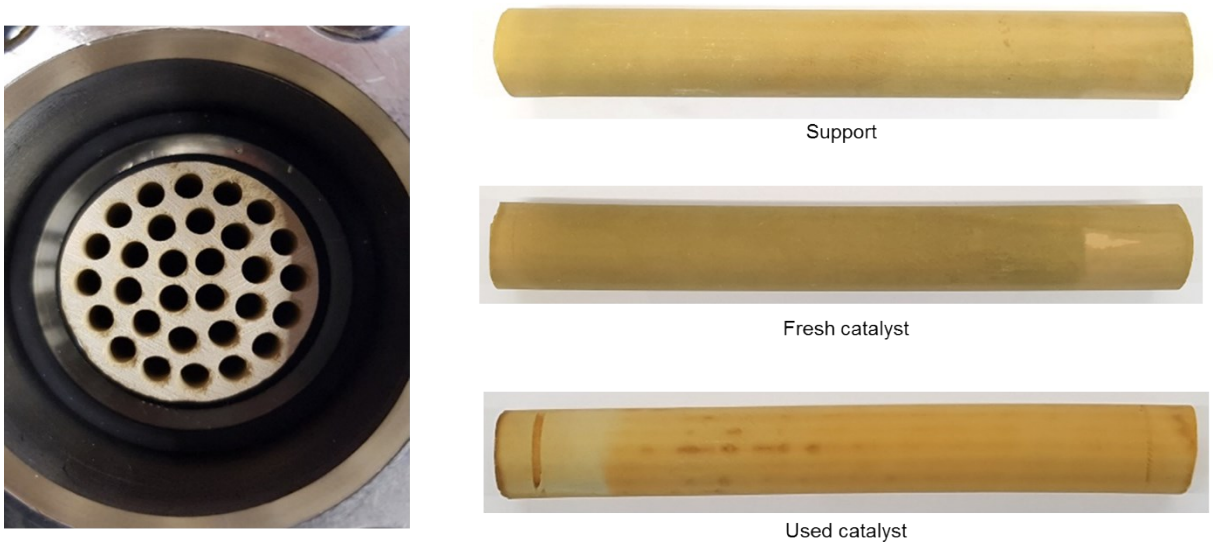


Figure S9. Left: γ-alumina-rich 10B-20S-70Al monolith calcined at 850 ºC and coated with the WGS catalyst fit in the reactor. Right: picture of the 10B-20S-70Al-850 monolith pristine (top) and coated with the catalyst before (middle) and after (bottom) reaction.