Supporting information

Contents

3D printing methodologies

Preparation of the 3D-printed structured FTS catalyst (3D-Co cat)

A paste was prepared by combining Puralox TH100/150 (Sasol) as γ-Al_2O_3 precursor and Disperal P2 (Sasol) as permanent binder in a 80/20 ratio respectively. An organic binder (methyl cellulose, Merck) was added to achieve the required rheology and provide green strength prior to calcination. As a solvent, demineralized water was used to which the solid ingredients were added gradually to achieve a solid content of 52.5%. Mixing was performed using a centrifugal mixer (Thinky ARE-250) for 2 minutes at 1900 rpm. Following the paste preparation, the paste was transferred to a syringe suitable for 3D-printing.

As a 3D-printing technology, Direct Ink Writing (DIW) was chosen since it is considered the most developed manufacturing technique for directly printing catalysts or catalyst supports. The developed viscous paste is transferred to a syringe and extruded through a thin nozzle. By computer-controlled movement of the nozzle, the structure is built up layer by layer adapting to the programmed CAD design. The alumina supports were printed in a 1:3:5 stacking using a 800 µm nozzle and a 800 µm interfiber distance. After printing, a calcination step was performed at 550°C with a dwell time of 3 hours to thermally decompose the organic binder and convert the boehmite to γ-Al_2O_3. The resulting alumina supports showed a BET value of 203 m^2/g and a pore volume of 0.54 ml/g.

To achieve the required Co-Ru loading onto the alumina supports, a one-step incipient wetness impregnation was performed using Cobalt(II) nitrate hexahydrate (Sigma Aldrich) and Ruthenium (III) nitrosyl nitrate (31.3%, Thermo Scientific) as Co and Ru precursor. A certain volume of 12% Co and 0.3% Ru solution in water was prepared based on the Archimedes pore volume of the alumina supports. After impregnation, an additional calcination step was performed at 160°C (3h dwell) and 250°C (3h dwell) to remove the nitrates from the Co and Ru precursors. ICP showed a metal loading of 8.6% Co and 0.22% Ru after calcination which is slightly lower than the commercial reference catalysts and probably caused by small losses during the impregnation procedure.

Preparation of the 3D-printed Cu internals (3D-Cu)

For the development of 3D-printed Cu contactors, a paste was prepared using pure Cu powder (Safina, particle size < 15 µm) combined with a binder solution consisting of two types of hydroxypropyl cellulose (HPC) and an organic additive for lubrication. As a first step, a binder solution of 2 wt% HPC (370.000 MW, Sigma Aldrich) and 7.8 wt% HPC (100.000 MW, Sigma Aldrich) in 1-propanol (Sigma Aldirch) was prepared to which Cu powder was added gradually until a solid content of 94.6% was reached. After each step, the paste was mixed using a planetary-centrifugal mixer (Hauschild Speedmixer DAC1100) at atmospheric pressure followed by a degassing step to ensure minimal entrapped air bubbles. The paste was transferred to the syringe and 3D-printed structures were developed using the described DIW technology. Cu structures were printed in a 1:1-configuration with a 400 µm nozzle and 1.2 mm interfiber distance. After printing, a calcination and sintering step was performed to remove the organic binder and obtain a highly conductive dense Cu structure. The calcination was performed in air up to 500°C at a heating rate of 30°C/h resulting in an oxidized Cu structure. To restore the metallic properties and enhance the thermal conductivity, a reduction of the copper oxide to metallic copper combined with a sintering treatment was performed under hydrogen atmosphere. A sintering temperature of 1030°C was used with a constant hydrogen flow of 100L/h. After sintering, wire-EDM was employed to tailor the outer diameter.

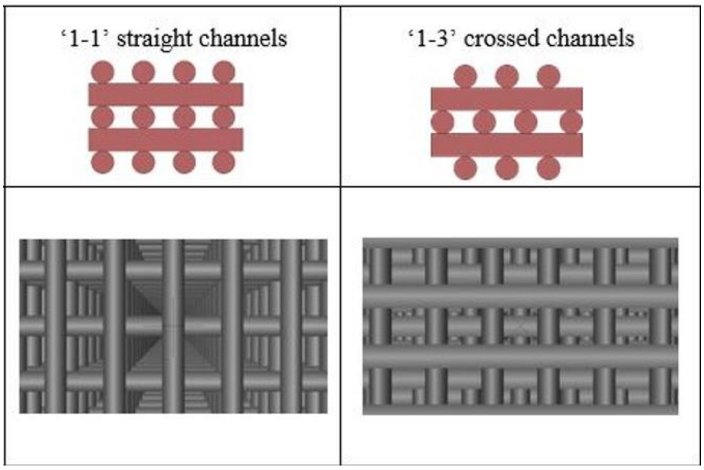


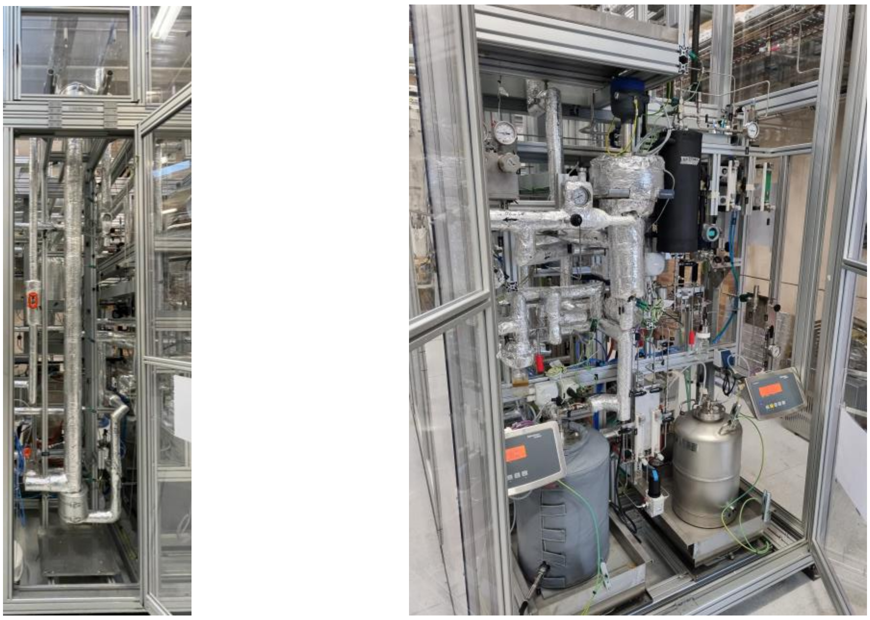
Figure 1S: Example of DIW writing fiber stacking configurations.

Reactor setup

For the catalytic experiments, a tubular fixed bed reactor (wall-cooled) with an internal diameter of 26 mm and a length of 2.5 m was used, loaded with the four individual catalyst systems. In each experiment with the different catalyst systems, only a part of the available reactor length was used. A thermal oil flowing through a jacket around the reactor tube (shell side) provides the required heating and cooling of the reactor wall, as also seen in Figure 3S.

Radially placed thermocouples, 11 in total with a spacing of 240 mm, monitor the temperature in the centerline of the packed bed and an additional 2 thermocouples monitor the thermal oil at the inlet and outlet. The inlet gas composition is set by individual mass-flow controllers through ratio control, with the inlet gas flow rate set using a Coriolis mass-flow controller upstream the reactor. Downstream the fixed-bed reactor condensation of the wax and light hydrocarbons from the reactor outlet gas occurs in a hot (170 °C, 20 barg) and cold (5 °C, 5 barg) separator. Reactor pressure is set by the backpressure regulator downstream the hot separator with a second backpressure regulator for the pressure in the cold separator. Gas samples downstream the cold separator were measured by GC in order to follow conversion and product selectivity. Additionally, an atmospheric Ritter flow meter is placed in the off-gas line (not drawn).

The gas samples were measured using an online GC equipped with separate channels for the detection of N2, Ar, CO2, CH4, CO (HS-N column with TCD detector), H2 (Molsieve 5A column with TCD detector) and C1–C4 (PlotQ column with FID detector). The applied GC method run time was 15 minutes, meaning one GC injection with FTS process gas every 15 minutes. Condensates from the hot (wax) and cold separators (lights and water) were not considered in this work as the conversion and selectivity were determined based on the gas analysis only.



The (insulated) FT reactor tube

The hot separator (insulated) and cold separator (insulated black)

Figure 2S: Photos of the tubular fixed bed FTS reactor (2.5 m long, 26 mm I.D., left) and the corresponding gas/liquid separators (right).

Reactor loadings

Reference catalyst system

For the packed bed reference catalyst system, the FTS catalyst and SiC (diluent) pellets were crushed and sieved to 500-800 µm. The FT reactor was filled with catalyst and diluent from the top with the thermocouples already in place. Inside the reactor, the bottom 240 mm was filled with only SiC granules, see also Figure 3. On top of this inert layer, the catalyst mixture was then loaded with a final bed length of 620 mm and a catalyst loading 0.30 $g_{cat}/mL_{reactor}$. This catalyst mixture consisted of 100 g FTS catalyst granules homogeneously mixed with the 312 g SiC granules at a combined bulk density of 1.2 g/mL.

Catalyst system 3D Co-cat

The 3D-printed structured FTS catalysts were prepared and supplied by VITO with a similar catalyst composition to the FTS reference catalyst for comparison reasons. Each cylindrical catalyst structure, at a 25.0 mm O.D. and a length of 26.0 mm, was printed in a 1,3,5-configuration with 800 µm fibers and 800 µm spacing. Each structure was 10 g providing an undiluted catalyst loading of 0.78 $g_{cat}/mL_{reactor}$. Because of this higher catalyst density, the individual structures were spaced at 240 mm, each on top of a thermocouple, with the space between the structure filled with 3 mm SiC pellets as diluent, see also Figure 3. In total, 8 structures were placed, at a total weight of 80 g (Figure 3). That is, because the structures themselves could not be diluted, it was decided to dilute the space between the structures.

Catalyst system Co-cat//Al-foam

The aluminum open cell foam (16 pores/cm, 93% void) was obtained from GoodFellow.com with dimensions of 150x150x30 mm from which cylinders of 30x26.1 mm (LxD) were cut using electrical discharge machining. Slight compressibility of the Alu foams allowed for placing the 26.1 mm foam contactors inside the 26.0 mm I.D. reactor for the best possible wall contact. In total, 7 foam cylinders were placed inside the reactor on top of a stainless-steel mesh (<100 µm) providing a total bed length of 210 mm (Figure 3). A thermocouple (TI04) was placed in the center of the middle Aluminium foam after carefully drilling a hole into the foam.

Finally, 30.7 g FTS catalyst was homogenously mixed with 29.8 g of ɣ-alumina, both in the 212-425 µm sieve fraction. This mixture, with a bulk density of 0.60 g/mL (0.58 g/mL_{void} inside foam), was poured into the foam to achieve a catalyst loading of 0.28 $g_{cat}/mL_{reactor}$. Here, ɣ-alumina was used as diluent to avoid demixing upon loading the catalyst into the aluminum foam.

Catalyst system Co-cat//3D-Cu

In system D, 3D-printed Cu contactors were applied and loaded with catalyst and diluent particles. These 3D-printed Cu contactors were printed in a 1:1-configuration with a 400 µm nozzle and 1.2 mm spacing resulting in a total 66% void and subsequently cut using electrical discharge machining to a O.D. of 26.05 mm and an average length of 43.8 mm. Slight compressibility of the Cu contactors allowed for placing the 26.05 mm foams inside the 26.0 mm I.D. reactor for the best possible wall contact. In total, 5 contactors were placed in the FT reactor on top of a stainless-steel mesh (<100 μm) providing a total bed length of 219 mm (Figure 3). A thermocouple (TI04) was placed in the center of the middle contactor.

Finally, 30.7 g FTS catalyst was homogeneously mixed with 11.5 g ɣ-alumina, both in the 212-425 μm sieve fraction. This mixture, with a bulk density of 0.61 g/mL (0.55 g/mL_{void} inside Cu contactor), was poured into the Cu contactors to obtain a catalyst loading of 0.26 $g_{cat}/mL_{reactor}$. A smaller amount of diluent was used, to keep the catalyst loading similar to the other systems.

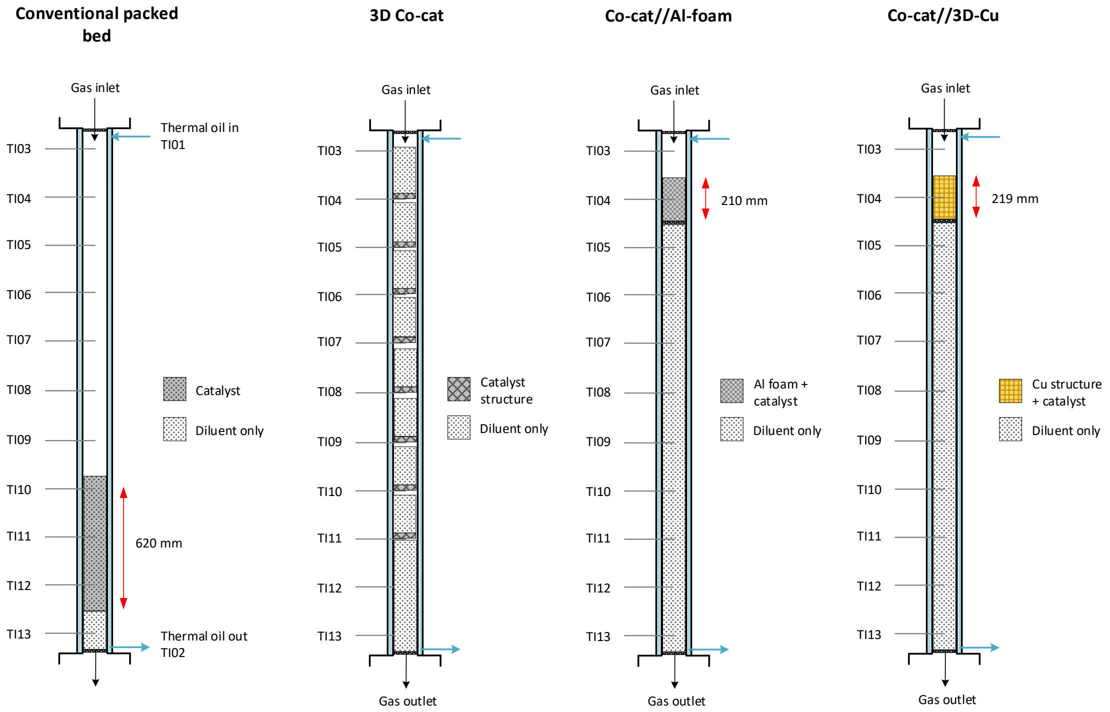


Figure 3S: Catalyst systems A-D applied in the FTS reactor. The systems contain respectively, a packed bed of diluted FTS catalyst. The 3D Co-cat system contains 3D-printed catalysts spaced at 240 mm with diluent in between. The Co-cat//Al-foam system contains Aluminum foams filled with diluted catalyst and the Co-cat//3D-Cu contains the 3D-printed Cu contactors filled with diluted catalyst.

Table 1S: FTS reactor loadings and applied reaction conditions.

Catalyst system	Catalyst [g]	Catalyst loading [$g_{cat}/mL_{reactor}$]	Gas flow rate [g/h]	WHSV
Packed bed	100	0.30	500	6.5
3D Co-cat	80	0.39	500	6.3
Co-cat//Al-foam	30.7	0.30	200	6.5
Co-cat//Al-foam (high flow)	30.7	0.30	500	16.3
Co-cat//3D-Cu	30.7	0.26	200	6.5

At a constant composition of 32 vol% CO, 63 vol% H_2, 5 vol% Ar and pressure of 20 barg.

The detailed temperature profiles for the catalyst systems with all relevant thermocouple data can be found in Figure 4S.

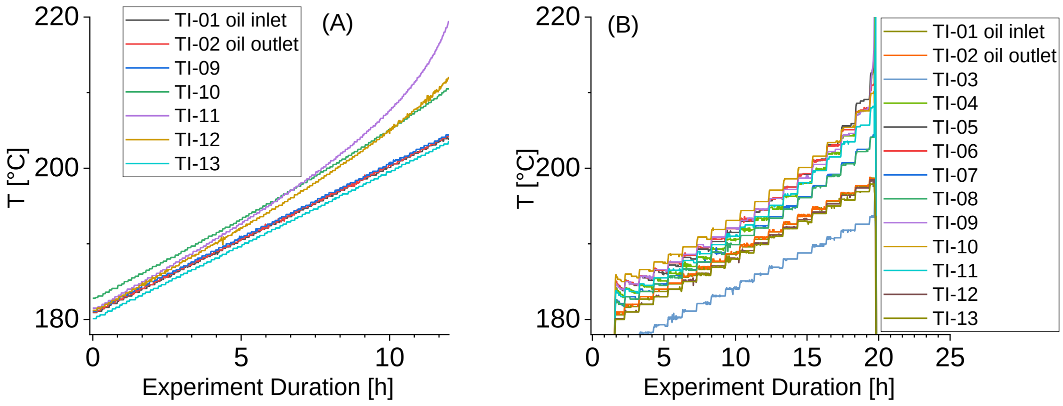


Figure 4S: Complete temperature profiles during the FTS startup experiments related to catalyst packed bed reference system (A) and system 3D Co-cat (B).

Catalyst characterization and results

Physicochemical analysis

Elemental analysis was performed via ICP-AES using a Thermo ICAP 6600. Samples were digested using HNO3-HClO4-HF in a 90:5:5 ratio in a microwave oven before measuring.

N_2 physisorption measurements were performed in an Autosorb-iQ-C unit (Quantachrome Instruments) at liquid nitrogen temperature (77 K). Prior to the experiment, ca. 0.1 g of the samples was degassed overnight in the degas station of the same Autosorb-iQ-C under vacuum at 623 K.

A summary of the physicochemical analysis of the catalyst can be found in Table 2S.

Table 2S: Textural, composition and crystallite size of Co+Ru/Al2O3 and 3D-printed catalyst measured by different techniques including N2 physisorption, ICP, and XRD techniques.

			ICP			**XRD**
Catalyst	**PV (mL/g)**	**BET (m2/g**	**Co (wt%)**	**Ru (wt%)**	**Al (wt%)**	**D (nm) Co3O4**
Co+Ru/Al_2O_3	0.46	189	11.7	0.27	48.4	9.8 ± 0.5
Co+Ru/Al_2O_3 (3D-printed catalyst B)	0.44	142	8.6	0.22	nd	10.4

Laser Flash Analysis (LFA)

For the Laser Flash Analysis (LFA), a Netsch LFA 467 was used which consists of a light source that produces a light flash for a small period of time (600 μs) and an infrared detector measures the temperature response on the opposite side of the detector. All samples were measured from 50 to 300 °C and back to 50 °C in 25 °C intervals. A duplo measurement was done at each condition with 2 minutes between each measurement. The penetration model was used as it provided the best fit.

Pyroceram and graphite were used as reference material, required when determining the specific heat values.

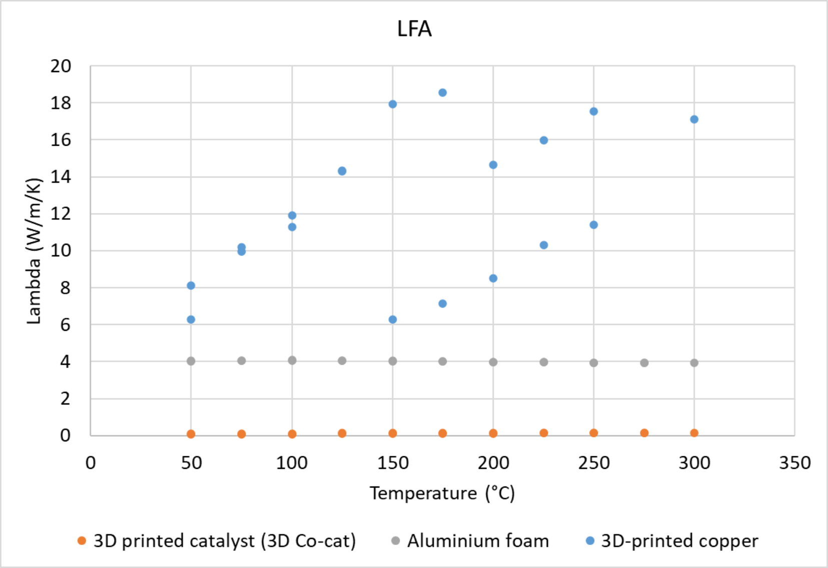


Figure 5S: Plot of the measured conductivity using LFA.

XRD and Rietveld Refinement procedure

X-ray diffraction (XRD) measurements were performed in an Empyrean diffractometer (Malvern Panalytical, Almelo, The Netherlands) using Co Kα radiation (λ = 0.17890 nm) on a spinning silicon wafer. Samples were calcined before measurement at 400 °C in air for 1 h. Samples were measured in the 2θ region from 5° to 120°. Rietveld refinement was used for the determination of the average crystallite size. Rietveld refinement has been performed by the MAUD Software [1-2]. The most reliable part of XRD patterns (2θ=20-50) has been determined and utilized for refinement. The CIF files of existing phases of cubic Co3O4 (COD Number: 1526734) and γ-alumina (COD Number: 1533936) have been applied for refinement. The GOF values ($\chi=\sqrt{R_{wp}^2/R_{exp}^2}$) around or less than 2 are representative of a good fitting (Table 2S) confirm the reliability of refinement. To more support, the differences of the experimental and calculated pattern are also illustrated in Figure 6S for all samples. It could be seen that the differences are almost zero within the 2θ range, which is indication of good refinement.

D denote crystallite size, χ=goodness of fit, a=lattice parameter of Co_3O_4 phase in Å

Table 3S: Rietveld refinement results + GOF values.

No	Sample	D(nm)		a (lattice Å)	χ (GOF) <3
XRD-1	3D-printed catalyst	14	±1	8,063	2.62
XRD-2	3D-printed catalyst spent	11,7	±1	8,075	2,27
XRD-3	Co+Ru/Al_2O_3	9,8	±0,5	8,073	1.37
XRD-4	Co+Ru/Al_2O_3 spent	16,4	±1	8,065	2.55

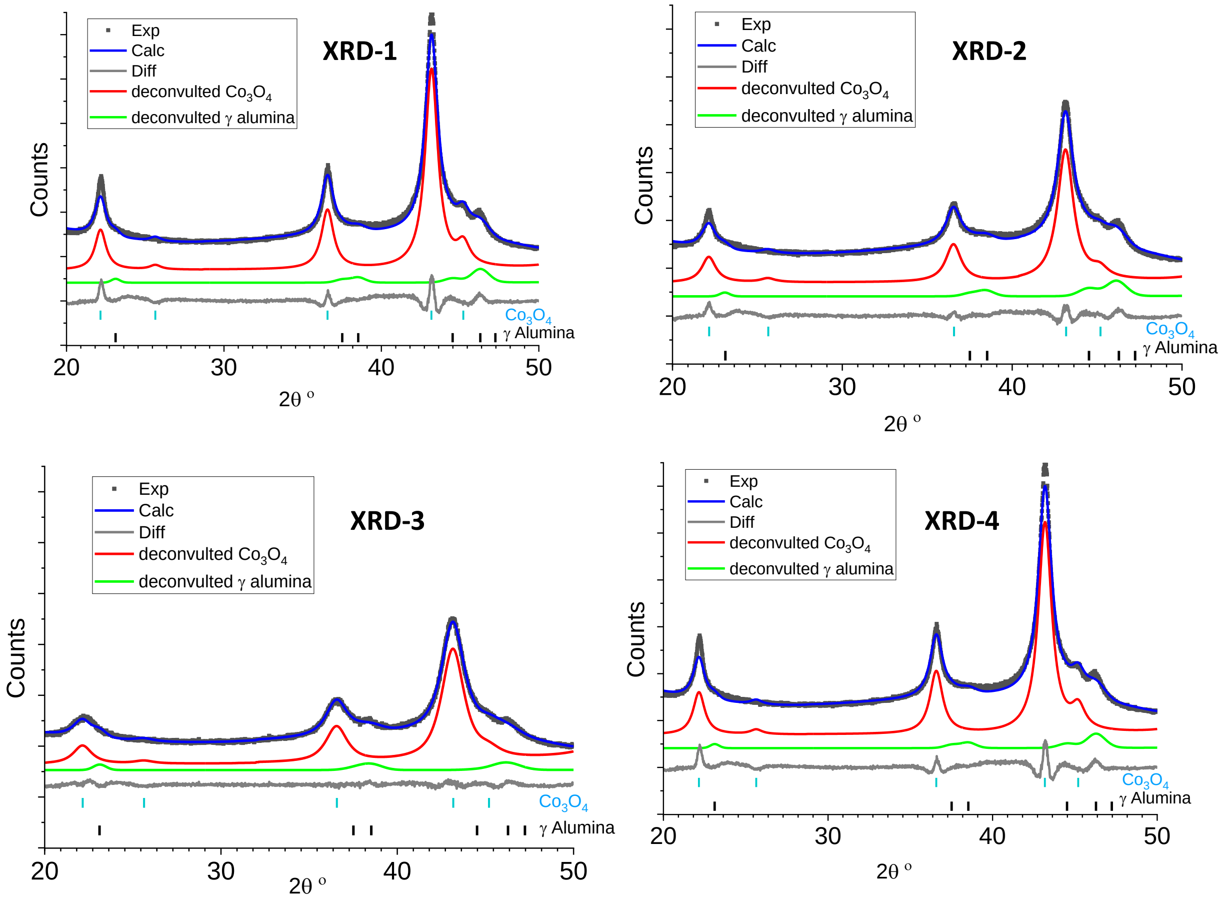


Figure 6S: Experimental XRD pattern (black x points), calculated XRD pattern (blue curve) and difference between experimental and calculated patterns (grey curve) for Rietveld refinement for sample XRD-1 to XRD-4.

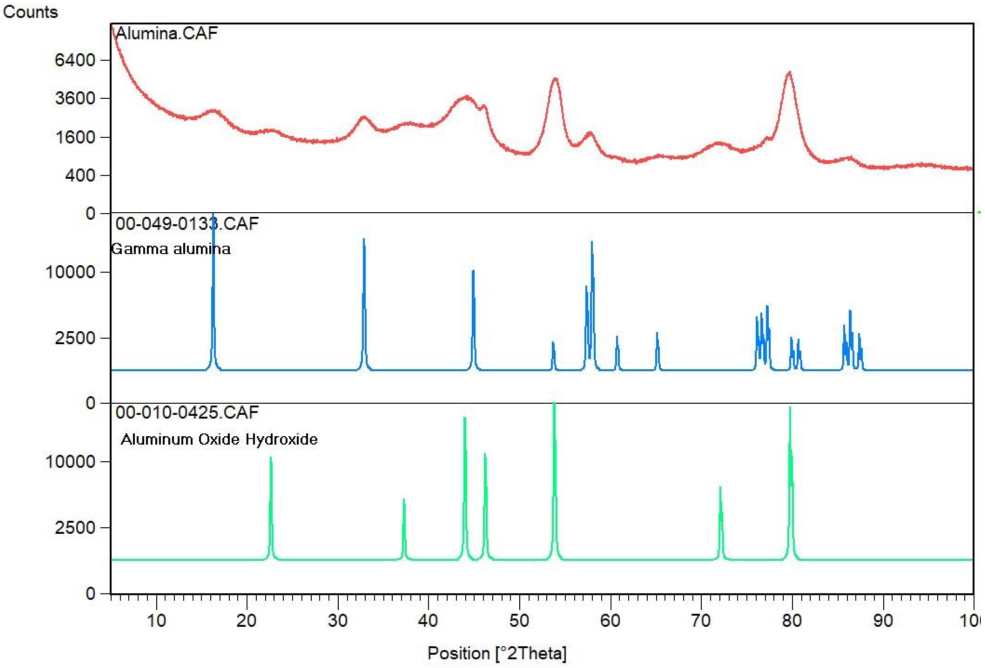


Figure 7S: Sample of Alumina is a mixture of γ-alumina and boehmite γ-AlO(OH) and non-pure γ-alumina

[1] Lutterotti L., Ceccato R., Maschio R.D., Pagani E. Mater. Sci. Forum 93 (1998) 278–281.

[2] Lutterotti L., Gialanella S. Acta Mater.46 (1998) 101–110.