

## Supplementary information SI – Experimental Section

### 1. Synthesis of the macro-/mesoporous silica monolith

5 46.3 g distilled H<sub>2</sub>O and 4.6 g HNO<sub>3</sub> (68%, Aldrich) were  
mixed for 15 min at 0 °C and 4.79 g of PEO (20 000, Aldrich  
99%) were added and stirred for 1 h. Then 37.7 g TEOS (Aldrich  
99%) were added and the mixture was stirred for 1 h. The  
10 resulting solution was poured into PVC tubes of 10 cm length and  
8 mm internal diameter and kept at 40 °C for 3 days. The  
monoliths were then washed in water and treated in an ammonia  
solution (0.1 M) at 40 °C for 20 h. The monoliths were dried at  
40 °C for 24 h and calcined at 550 °C for 8 h. These silica  
monoliths (10 cm length and 6 mm internal diameter) were cut in  
15 pieces of desired size and are hereafter named as parent monolith  
or MonoSil.

### 2. Synthesis of CuBTC crystals via DMSO protocole

A precursor solution was prepared in a 50 mL beaker by mixing  
20 1,3,5-benzenetricarboxylic (BTC) acid (named also trimesic acid)  
(0.58 g, 2.76 mmol, Aldrich 99%) with 5 g DMSO under slight  
heating until a complete dissolution was obtained, then the  
solution was cooled down and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (1.22 g, 5 mmol,  
Aldrich 99%) was added slowly to avoid any nucleation, which  
25 could start due to the heat produced by solvation. The resulting  
clear solution of precursors is stable for at last 8 months (proven  
by DLS). The solution was then poured in a Petri dish and  
evaporated at 120°C for 72 h. The obtained blue powder was  
transferred to into a round bottom flask with reflux condenser and  
30 was heated under reflux for 1 h with 30 mL ethanol. The powder  
was then dried at 80 °C for 24 h.

### 3. Synthesis of CuBTC-MonoSil

The parent monolith (MonoSil, 2 cm, 0.160 mg) was  
35 activated at 150 °C for 4 h under reduced pressure, and immersed  
in 4 mL of the previous CuBTC precursor solution in a  
polypropylene reactor and then heated to 100 °C for 3 h until the  
monolith becomes totally transparent revealing complete  
diffusion of the solution within the pores. The monolith was then  
40 retrieved from the solution, dried at 80°C for 2 h and kept at 120  
°C for 12 h to allow Cu-BTC crystallisation by solvent  
evaporation. A subsequent washing in boiling ethanol was  
performed by transferring the impregnated monolith into a round  
bottom flask with reflux condenser and heating for 1 h under  
45 reflux with 30 mL ethanol to remove unreacted Cu(NO<sub>3</sub>)<sub>2</sub>. The  
latter was visible in the SEM pictures of the unwashed monolith  
as needles deposited in the macropores. The monolith was then  
dried at 80 °C for 24 h. For the use as flow reactor, the monoliths  
50 were ended with two glass tubes and clad with a heat-  
shrinkable Teflon clad (Plastimeuse) (Fig. S4) at 180 °C for 2 h.  
For comparison CuBTC powder was prepared by evaporating the  
precursor solution at 120 °C for 12 h; the same washing and  
drying procedures as for the CuBTC-MonoSil were performed.

### 55 4. Materials characterization

The physicochemical properties of the monoliths were  
characterized by X-Ray Diffraction (XRD), nitrogen sorption at  
77K, scanning electron microscopy (SEM) and  
thermogravimetric analysis (TGA). XRD patterns were taken on  
60 a Bruker AXS D8 diffractometer by using CuK $\alpha$  radiation  
(wavenumber  $\lambda = 1.5405 \text{ \AA}$ ) and Ni filter from 4 to 50° in 2 theta  
with a step of 0.02° and 2 s per step. The adsorption–desorption  
isotherms of nitrogen at 77 K were determined using a  
Micromeritics ASAP 2020 instrument after outgassing the  
65 samples (30 mg) at 100°C under high vacuum (0.5 Pa) for 8 h to  
remove the water in the channels of Cu-BTC with pressure  
between 0.001 <math>p/p\_0</math> <math>< 0.9959</math> with an equilibrium interval of 5 s  
and 36 points in adsorption and 30 points in desorption. The  
mesopore and /or micropore volume was taken at the end of the  
70 filling of the pore. Surface area was determined by the BET  
method considering the Rouquerol law to be able to compare  
materials possessing microporosity.<sup>1</sup> The mesopore diameter was  
determined using the desorption branch and the Broekhoff and  
De Boer method.<sup>2</sup> The morphology of the monoliths was  
75 examined using a Hitachi S-4500 I SEM. The chemical analysis  
by EDX of the Cu-BTC monolith was performed on different  
parts of cut pieces of the monolith using a FEI instrument Quanta  
200F (15 kV) in retrodiffusion. TGA analysis was carried out  
using a NETZSCH Iris TG 209C in the temperature range 25-900  
80 °C with a ramp of 10 °C min<sup>-1</sup>. TEM images have been obtained  
with a JEOL 1200 EX II at 100 kV after grinding the monolith,  
dispersing the powder in ethanol and deposition on a carbon grid.

### 5. Friedländer reaction

85 The CuBTC-MonoSil (2 cm, 0.160 g) was activated under  
reduced pressure at 100 °C for 4 h in a Schlenk tube. The  
monolith was then placed in the setup for catalysis in flow in a  
chamber heated at 80 °C (see Fig. S4). A solution consisting of 2-  
aminobenzophenone (87 mmol, 17.14 g, Aldrich 97%) and an  
excess of acetylacetone (8.53 mol, 737 g, Aldrich 99%) was  
90 prepared and passed through the monolith with a flow rate of 0.5  
mL min<sup>-1</sup>. Concentrations of reactants and products in the  
resulting mixture were determined by sampling periodically the  
reaction. The resulting solutions were analyzed by GC using a  
95 VARIAN 3900 apparatus and an apolar column HP-5 (phenyl-  
methylpolysiloxane) of 0.32 mm internal diameter and 30 m  
length. The conversion of the reactant was followed within time  
thanks to a calibration curve prepared with dodecane as standard.  
The products were first identified by GC/MS with a  
100 SHIMIDAZU QP2010Plus instrument.

### References/

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2. a) J.C.P. Broekhoff and J. H. De Boer, *J. Catal.*, 1968, 10, 377. b)  
A. Galarneau, D. Desplandier, R. Dutartre, F. Di Renzo, *Micropor.*  
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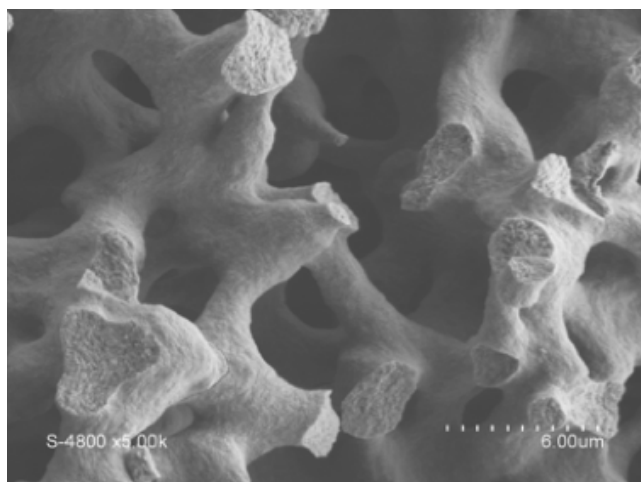


Fig. S1 SEM of CuBTC-MonoSil at higher magnification

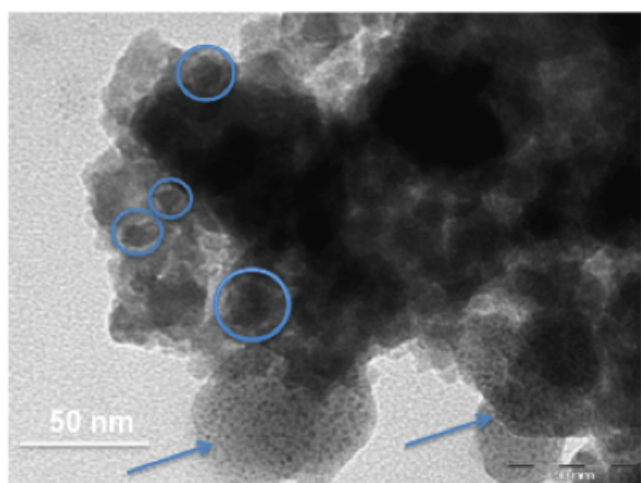
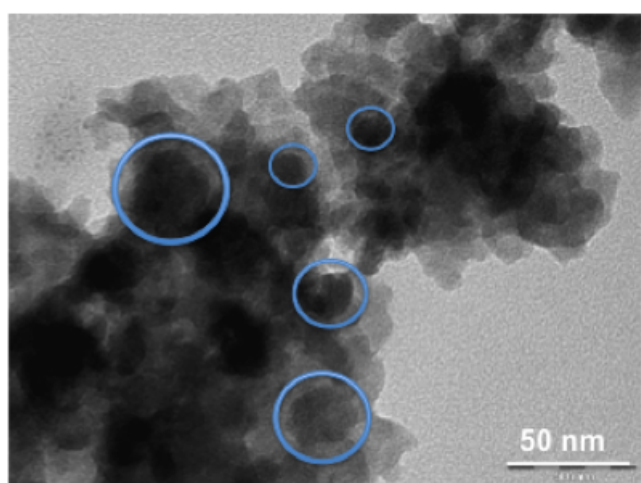


Fig. S2 TEM images of CuBTC-MonoSil. (Top) The majority of the images show small faceted crystals of CuBTC of 7 to 12 nm (shown by circles) in between the nanoparticles of silica, which form the skeleton of the monolith. (Bottom) In a few pictures some larger (50 nm) hexagonal crystals of CuBTC (shown by arrows) have grown at the surface of the skeleton.

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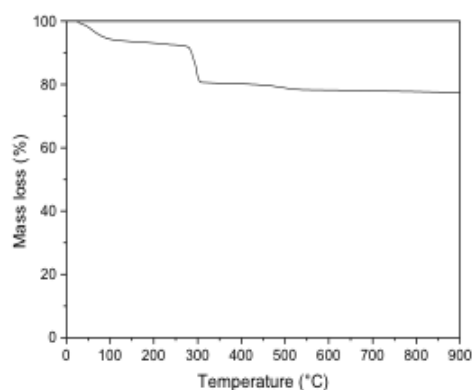
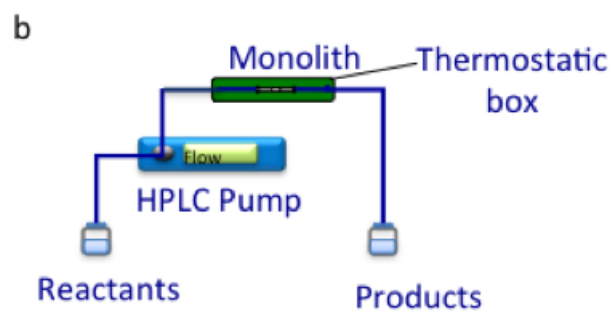
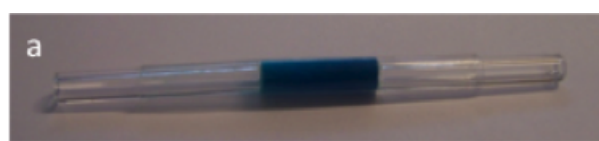


Fig. S3 TGA curve of CuBTC-MonoSil



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Fig. S4 Cladded CuBTC-MonoSil of 2 cm length and 6 mm diameter (a). Setup for the in-flow catalysis (b).

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