Supplementary information SI – Experimental Section

1. Synthesis of the macro-/mesoporous silica monolith

A precursor solution was prepared in a 50 mL beaker by mixing 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$_3$)$_2$$\cdot$3H$_2$O (1.22 g, 5 mmol, Aldrich 99%) was added slowly to avoid any nucleation, which could start due to the heat produced by solvation. The resulting clear solution of precursors is stable for at least 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 was heated under reflux for 1 h with 30 mL ethanol. The powder was then dried at 80 °C for 24 h.

2. Synthesis of CuBTC crystals via DMSO protocol

A precursor solution was prepared in a 50 mL beaker by mixing 46.3 g distilled H$_2$O and 4.6 g HNO$_3$ (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 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 into pieces of desired size and are hereafter named as parent monolith or MonoSil.

3. Synthesis of CuBTC-MonoSil

The parent monolith (MonoSil, 2 cm, 0.160 mg) was 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 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 reflux with 30 mL ethanol to remove unreacted Cu(NO$_3$)$_2$. 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 were cut into pieces of desired size and are hereafter named as parent monolith or MonoSil.

5. Friedländer reaction

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 prepared and passed through the monolith with a flow rate of 0.5 mL min$^{-1}$. 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 SHIMADZU QP2010Plus instrument.

References


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 a Bruker AXS D8 diffractometer by using CuKα radiation (wavenumber $\lambda = 1.5405$ Å) 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 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 <p/r< 0.9959 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 filling of the pore. Surface area was determined by the BET method considering the Rouquerol law to be able to compare materials possessing microporosity. The mesopore diameter was determined using the desorption branch and the Broekhoff and De Boer method. The morphology of the monoliths was 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 Quantas 200F (15 kV) in retrodiffusion. TGA analysis was carried out using a NETZSCH Iris TG 209C in the temperature range 25-900 °C with a ramp of 10 °C min$^{-1}$. 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.
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.

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

Fig. S3 TGA curve of CuBTC-MonoSil