

Supporting Information

N₂-physisorption measurements of Covalent Triazine-based Frameworks (CTFs) before and after sulfonation in the gas-phase:

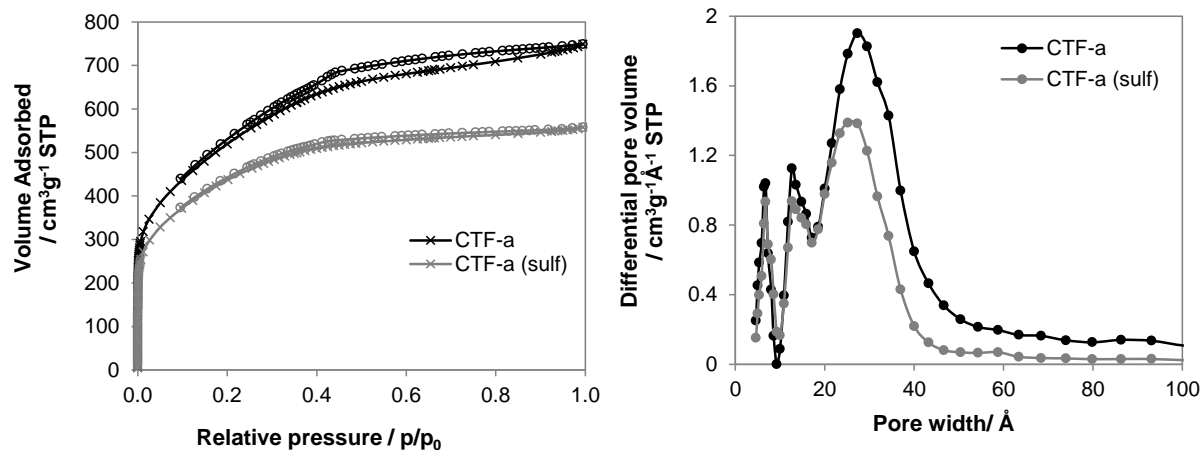


Figure S1: N₂-physisorption isotherm (left) and pore size distribution calculated via N₂-DFT model (right) of an untreated CTF based on 1,3-dicyanobenzene (CTF-a) and after sulfonation in the gas-phase (CTF-a (sulf)).

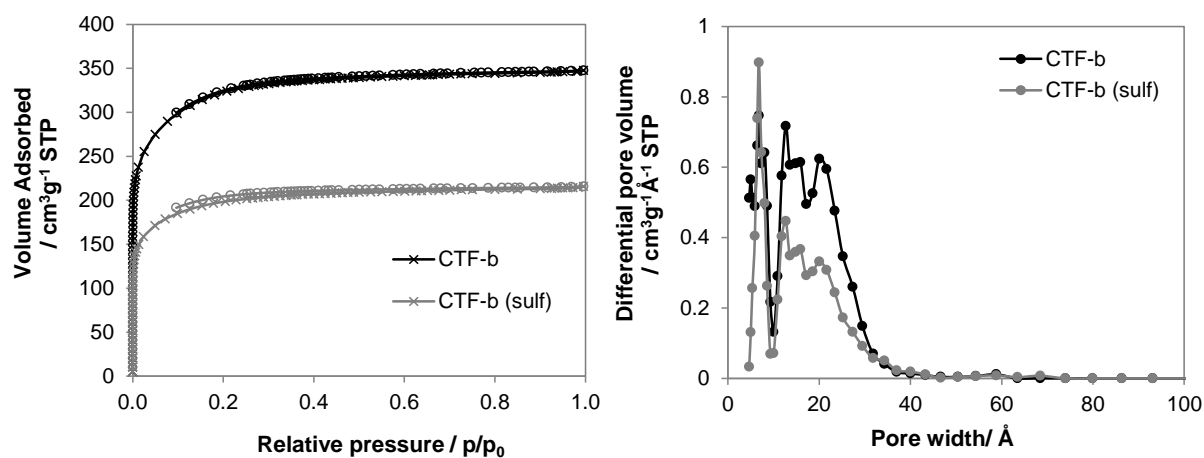


Figure S2: N₂-physisorption isotherm (left) and pore size distribution calculated via N₂-DFT model (right) of an untreated CTF based on 2,6-dicyanopyridine (CTF-b) and after sulfonation in the gas-phase (CTF-b (sulf)).

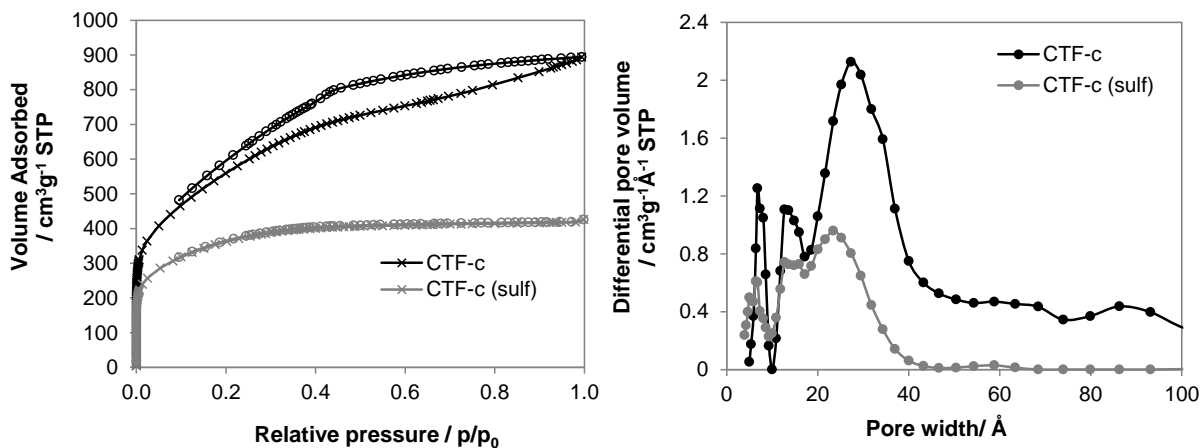


Figure S3: N₂-physorption isotherm (left) and pore size distribution calculated via N₂-DFT model (right) of an untreated CTF based on 1,4-dicyanobenzene (*CTF-c*) and after sulfonation in the gas-phase (*CTF-c (sulf)*).

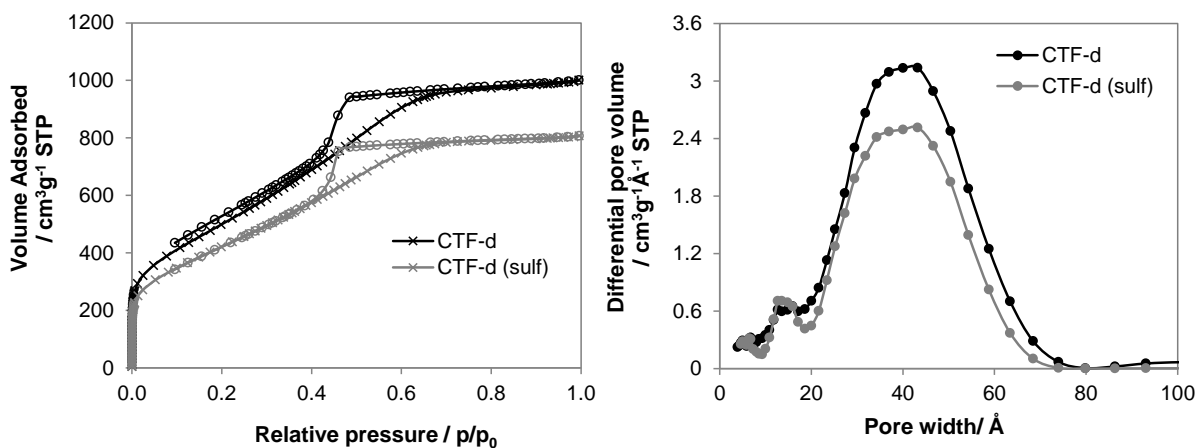


Figure S4: N₂-physorption isotherm (left) and pore size distribution calculated via N₂-DFT model (right) of an untreated CTF based on 4,4'-dicyanobiphenyl (*CTF-d*) and after sulfonation in the gas-phase (*CTF-d (sulf)*).

Thermogravimetric analysis of Covalent Triazine-based Frameworks (CTFs) before and after sulfonation in the gas-phase:

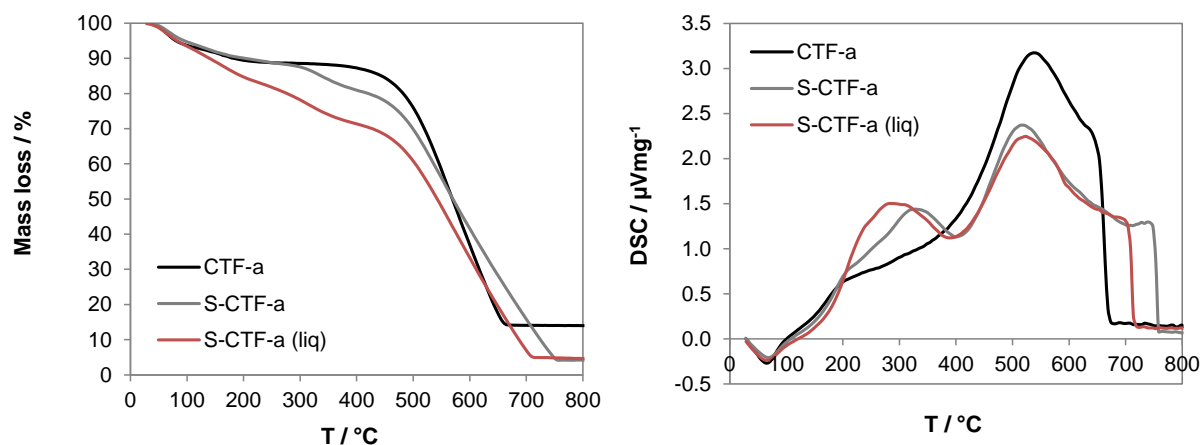


Figure S5: Thermogravimetric analysis of an untreated CTF based on 1,3-dicyanobenzene (*CTF-a*) and after sulfonation in the gas-phase (*S-CTF-a*) and liquid phase (*S-CTF-a (liq)*); temperature dependent mass loss (left) and differential scanning calorimetry (right).

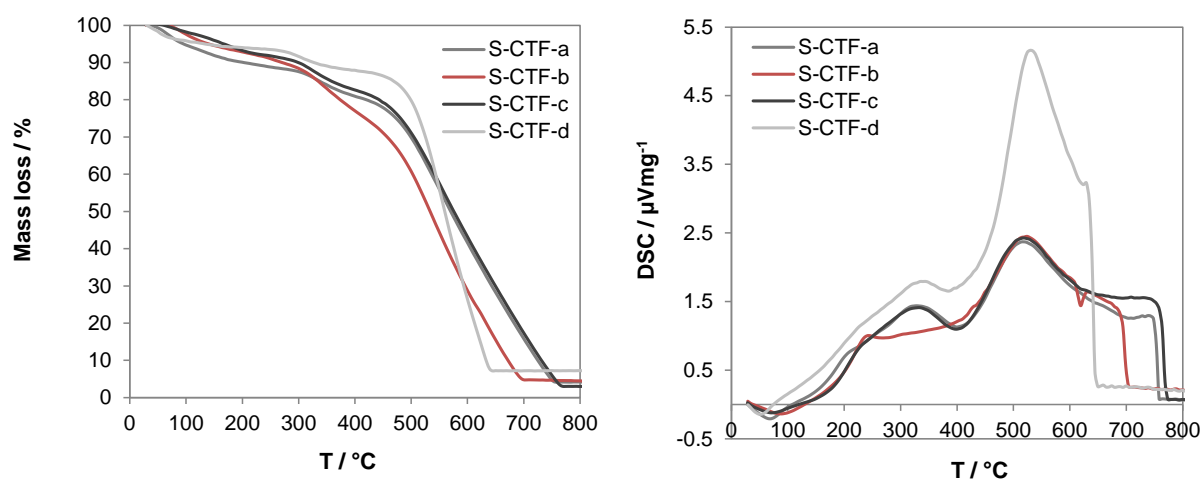


Figure S6: Thermogravimetric analysis of sulfonated CTFs based on 1,3-dicyanobenzene (*S-CTF-a*), 2,6-dicyanopyridine (*S-CTF-b*), 1,4-dicyanobenzene (*S-CTF-c*) and 4,4'-dicyanobiphenyl (*S-CTF-d*); temperature dependent mass loss (left) and differential scanning calorimetry (right).

Reproducibility experiments for CTF synthesis and sulfonation procedure with SO_3 in the gas phase:

Table S1. CHN elemental analysis, specific surface area, total pore volume of reproduced CTF materials as well as the sulfur content after modification with SO_3 in the gas-phase of these reproduced materials.

Material	C ^[a] [wt.%]	H ^[a] [wt.%]	N ^[a] [wt.%]	S _{BET} ^[b] [m ² g ⁻¹]	V _P / V _{P(micro)} ^[c] [cm ³ g ⁻¹]	S ^[a,d] [wt.%]	S ^[d] [mmolg ⁻¹]	S-degree ^[d] [%]
CTF-a	71.86	2.73	8.53	1543	0.98 / 0.35	-	-	-
S-CTF-a	-	-	-	1227	0.68 / 0.35	1.67	0.52	6.6
S-CTF-a ^[e]	-	-	-	969	0.54 / 0.28	3.07	0.96	12.2
CTF-b	61.80	2.40	20.91	876	0.46 / 0.32	-	-	-
S-CTF-b	-	-	-	699	0.37 / 0.27	0.72	0.23	2.8
CTF-c	62.51	3.03	8.44	1276	0.71 / 0.36	-	-	-
S-CTF-c	-	-	-	1221	0.67 / 0.33	1.76	0.54	6.9
CTF-d	80.11	1.98	3.65	1861	1.45 / 0.31	-	-	-
S-CTF-d	-	-	-	1679	1.29 / 0.28	1.32	0.41	8.5

[a] Determined with elemental analysis. [b] Specific surface area identified by Brunauer-Emmet-Teller (BET) method. [c] Total pore volume determined at $p/p_0=0.98$ and micropore volume determined via N_2 -DFT model. [d] Determined after sulfonation with SO_3 . A reference of non-sulfonated CTF contained <0.01 wt.% sulfur. [e] Sulfonated in the liquid phase with 20% oleum (containing 20 wt.% SO_3).

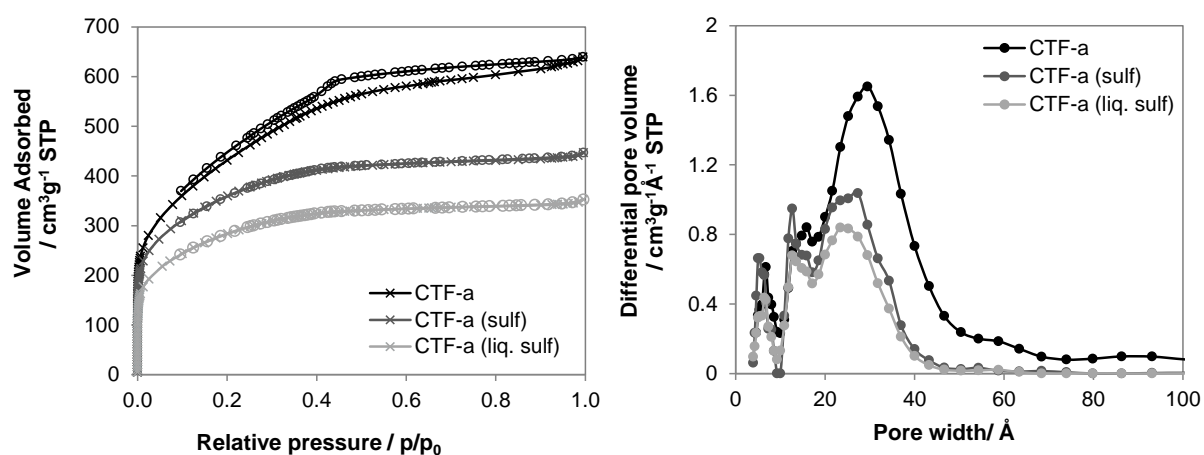


Figure S7: Representative N_2 -physorption isotherm (left) and pore size distribution calculated via N_2 -DFT model (right) for reproduction experiments of a CTF based on 1,3-dicyanobenzene (CTF-a) prior and after sulfonation in the gas-phase (CTF-a (sulf)).

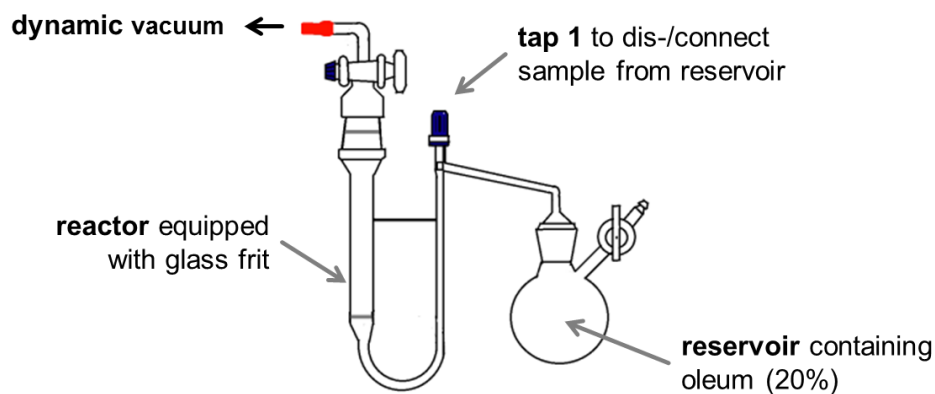


Figure S8: Schematic representation of the gas-phase sulfonation set-up used to obtain S-CTF materials. Set-up consists of a *reservoir* equipped with a stirring bar (containing oleum with 20 % SO₃) and a *reactor* equipped with a glass frit (containing 1 g of sample). The reactor is plugged to a vacuum pump to apply a *dynamic vacuum*. Both reactor and reservoir are interconnected through *tap 1* to enable evacuation of the sole sample or withdrawal of SO₃ from the oleum phase through the packed bed of solid sample.

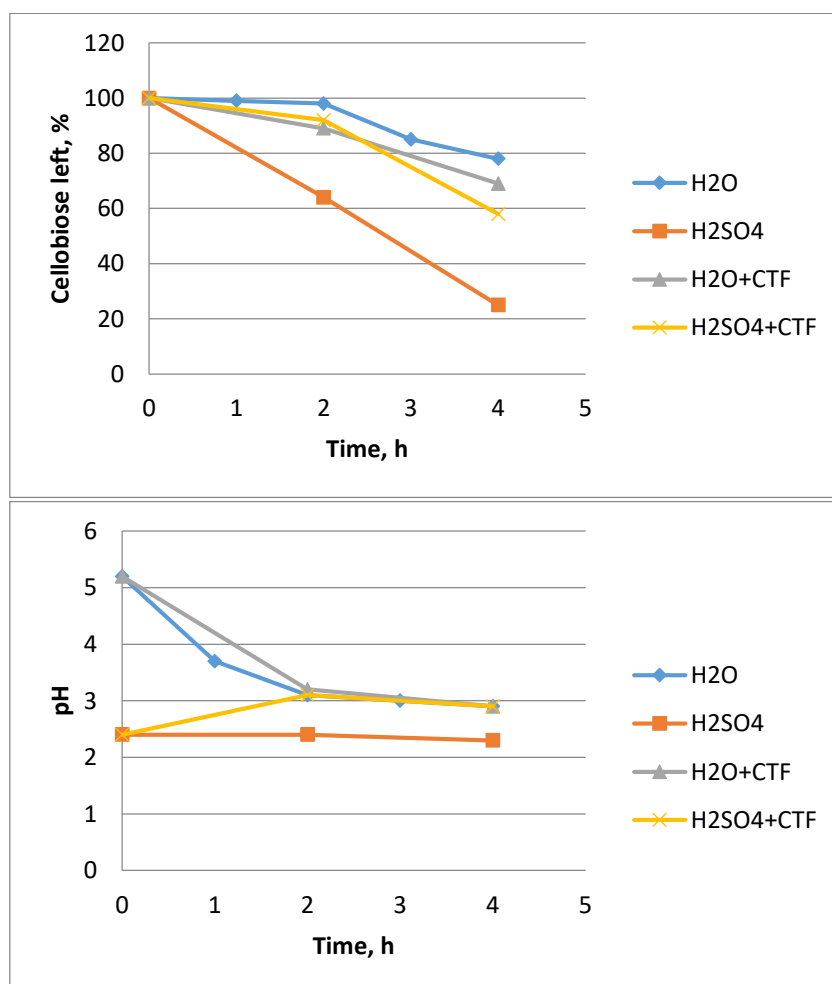


Figure S9: Conversion of cellobiose (up) and pH changes of the reaction mixture (down) as a function of time for homogeneous cellobiose hydrolysis.

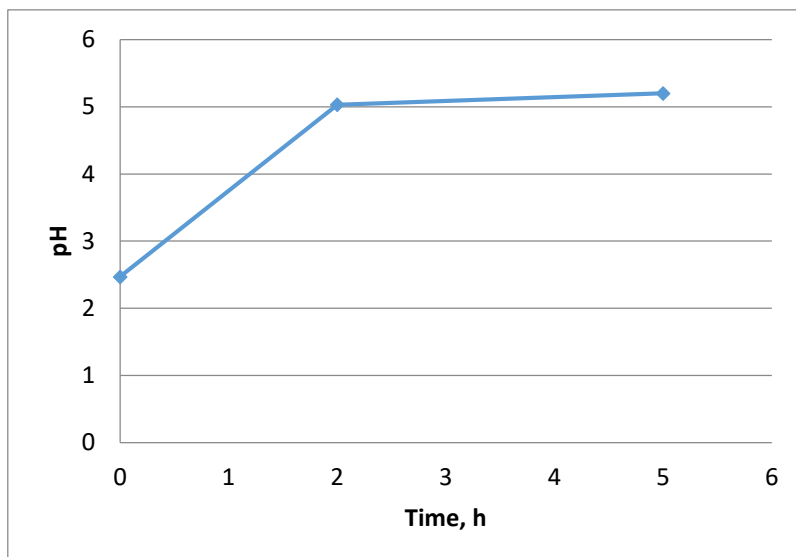


Figure S10: Neutralisation of H_2SO_4 (1.6 mM, 3 mL) upon stirring with CTF-a (30 mg) at room temperature.

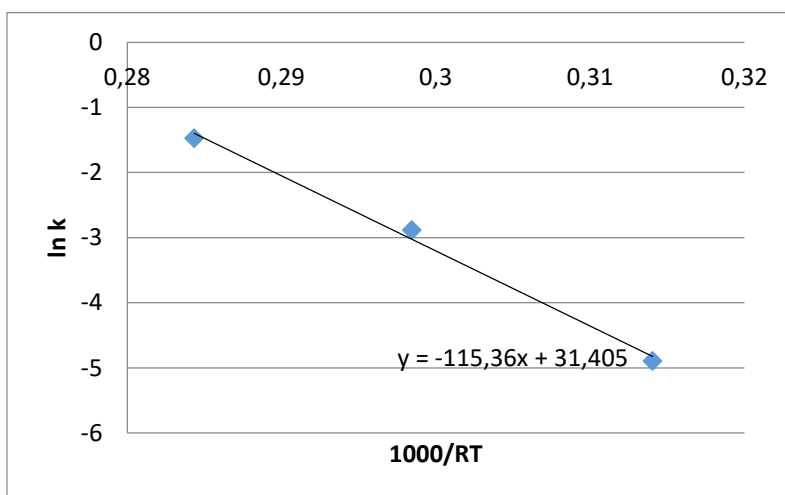


Figure S11: Arrhenius plot for estimation of activation energy for cellobiose hydrolysis over sulfonated CTF catalysts.