

## Electronic Supplementary Information (ESI)

### Solvent-free synthesis of hierarchical zeolite Y by carbochlorination

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## S.1 Chlorination temperature

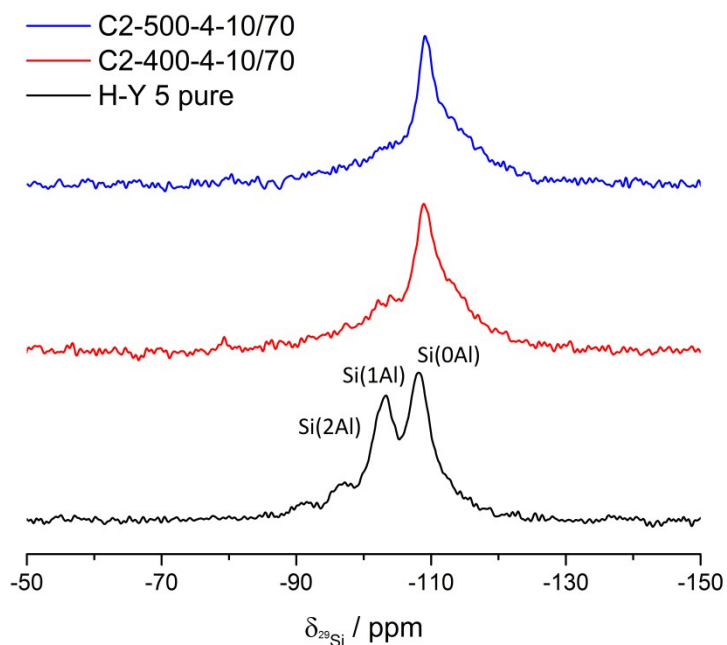


Fig. S1  $^{29}\text{Si}$  CP-MAS NMR spectra of the parent zeolite and composite 2 prepared at 400 and 500 °C. Si(nAl) species have been assigned according to [S1]

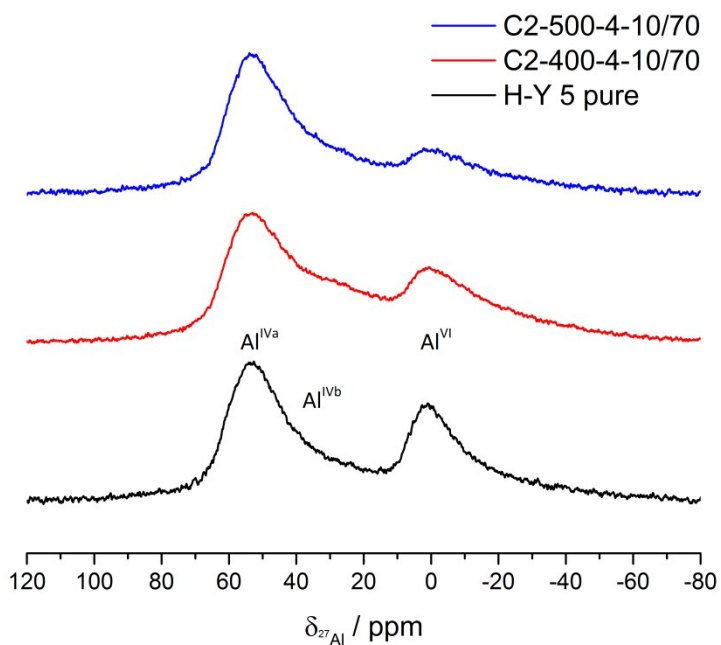


Fig. S2  $^{27}\text{Al}$  CP-MAS NMR spectra of the parent zeolite and composite 2 prepared at 400 and 500 °C. Al species have been assigned according to [S2]

## S.2 Carbon Content in Composite

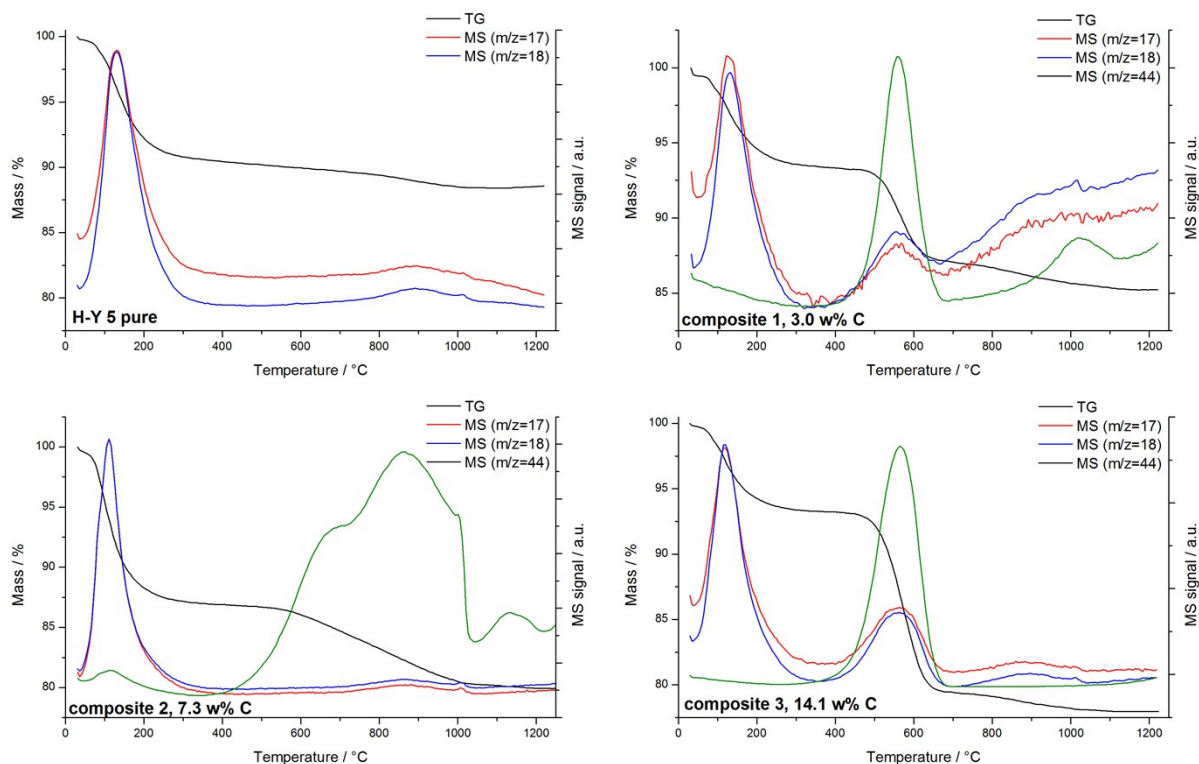


Fig. S3 TG/MS of parent material and all 3 composites with different carbon loadings under synthetic air from 25 to 1250 °C (heating rate 5 K min<sup>-1</sup>)

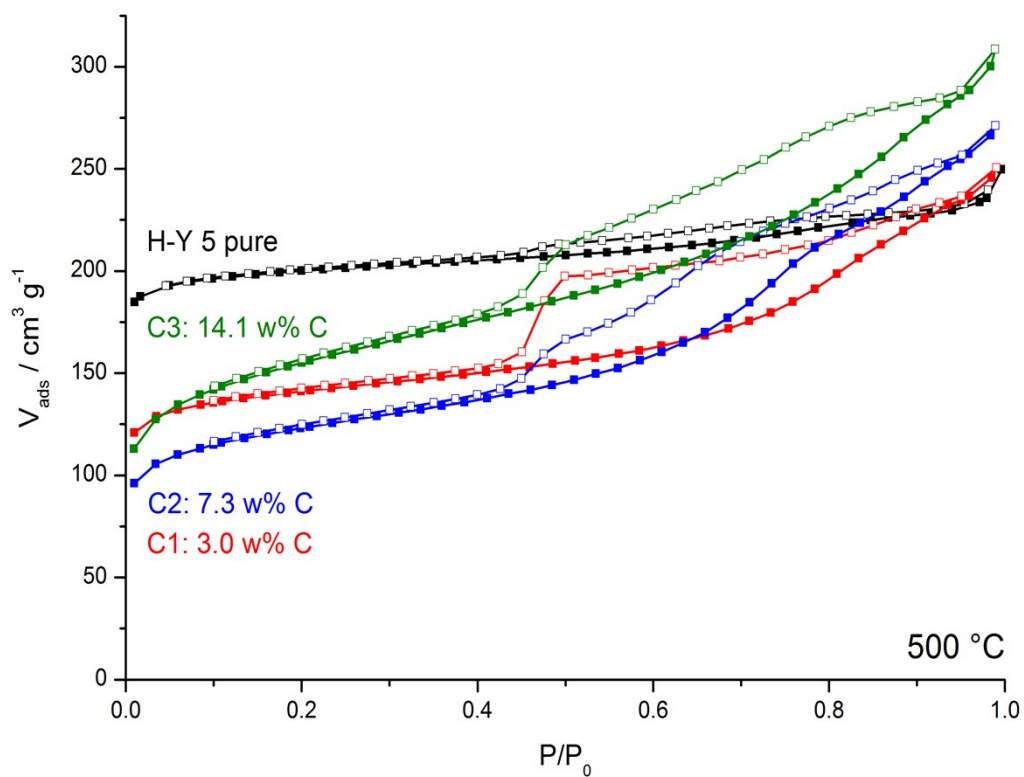


Fig. S4 N<sub>2</sub>-Isotherms at -196 °C of samples at 500 °C from different zeolite-carbon composite red (C1-500-4-10/70), blue (C2-500-4-10/70), green (C3-500-4-10/70)

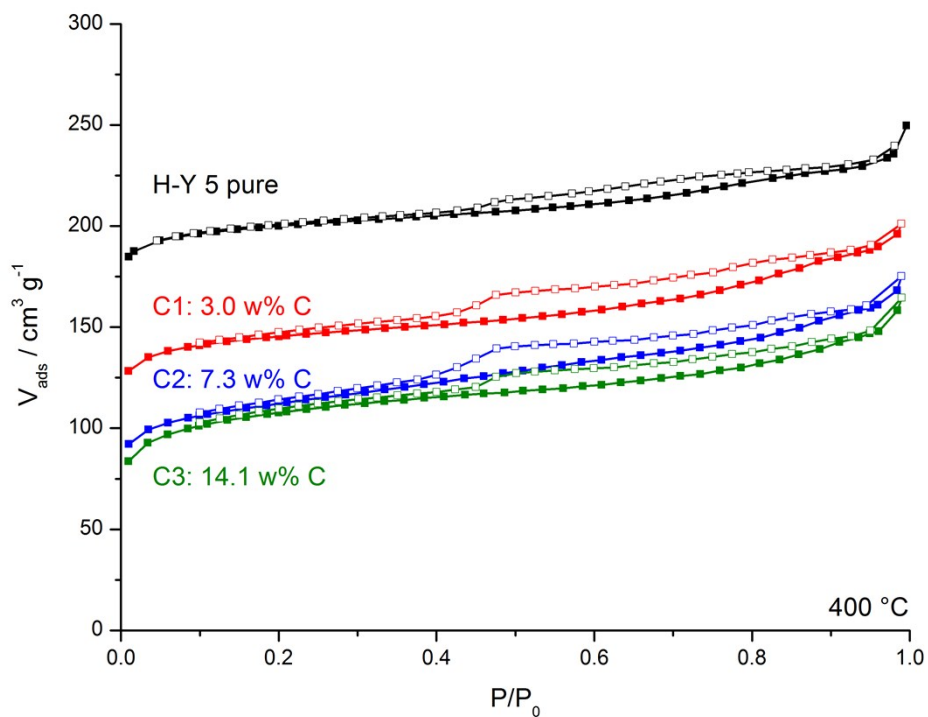


Fig. S5  $N_2$ -adsorption isotherms of parent material and samples with different carbon loadings carbochlorinated at 400 °C

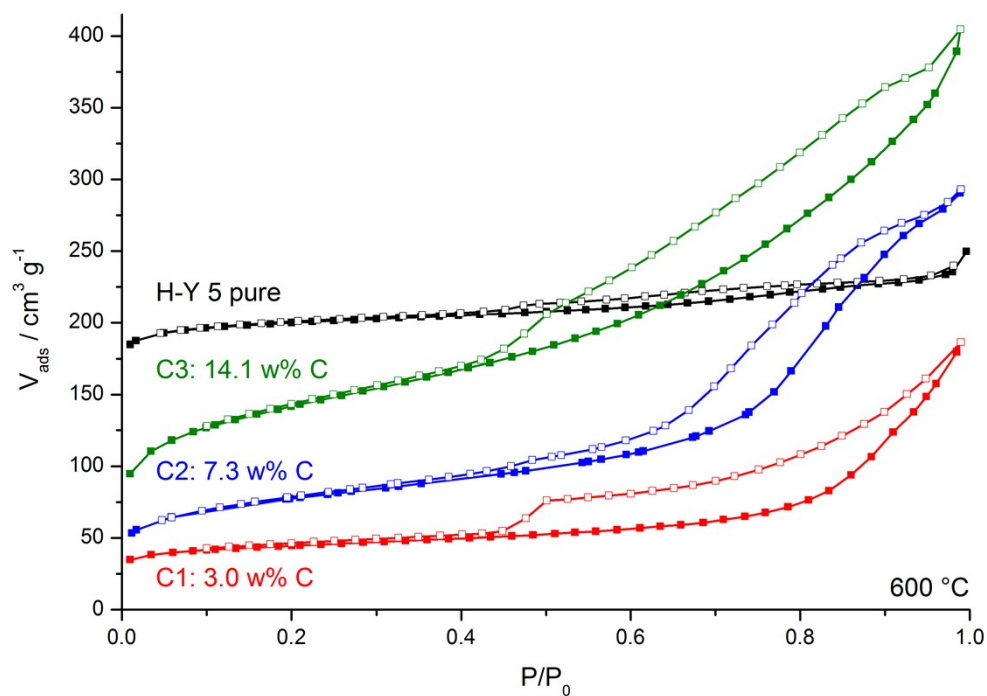


Fig. S6  $N_2$ -adsorption isotherms of parent material and samples with different carbon loadings carbochlorinated at 600 °C

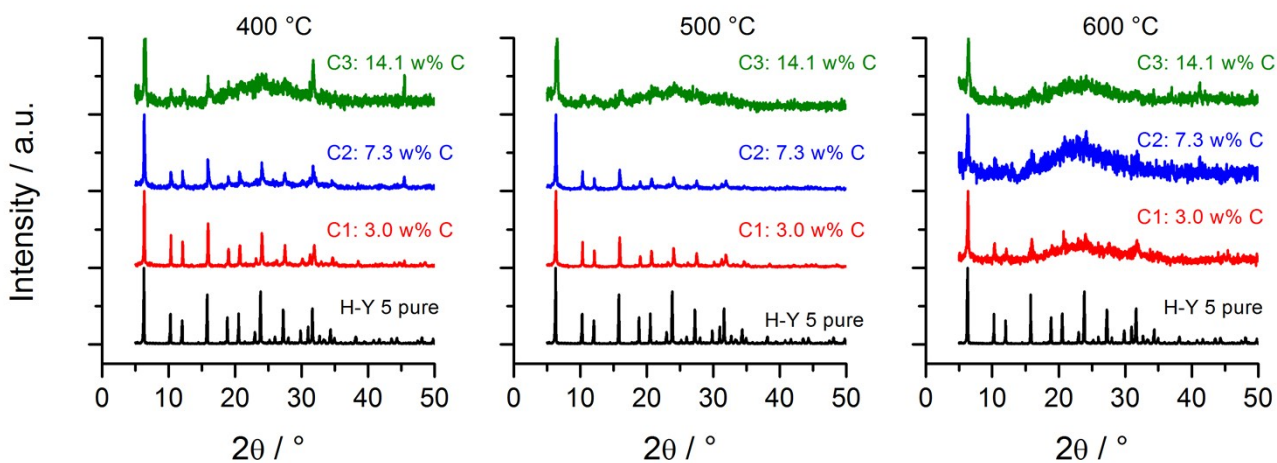


Fig. S7 Powder XRD of carbochlorinated samples with different carbon loadings at 400 °C, 500 °C and 600 °C. Diffractograms are normalized on the main reflex [111] at 6 ° 2θ.

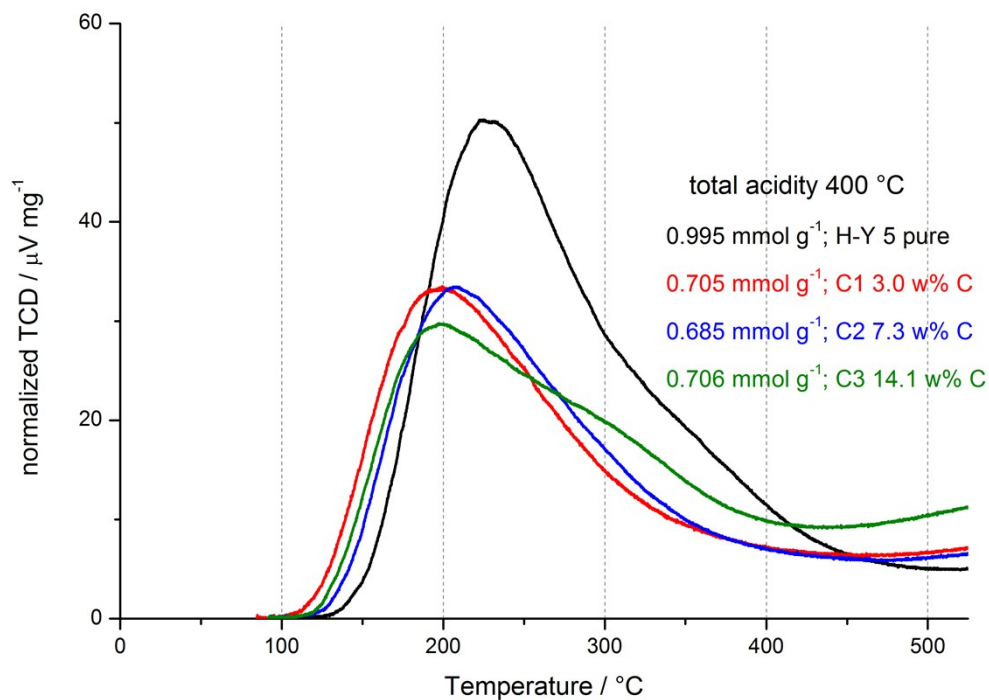


Fig. S8 TPAD of parent material and samples with different carbon loadings carbochlorinated at 400 °C after calcination under air for 6 h at 550 °C.

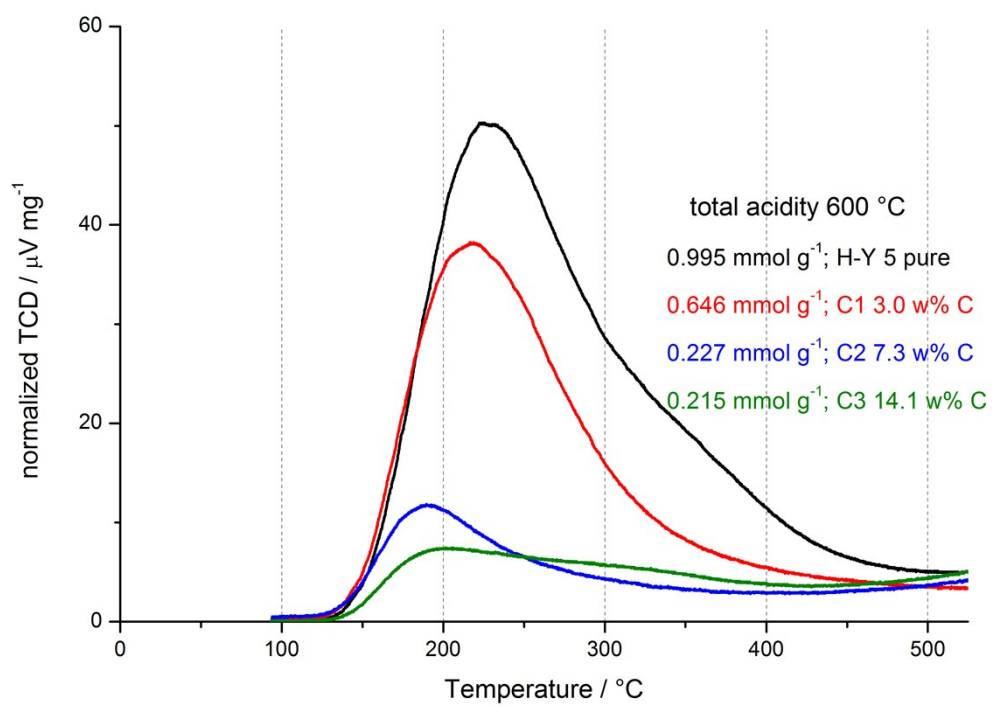


Fig. S9 TPAD of parent material and samples with different carbon loadings carbochlorinated at 600 °C after calcination under air for 6 h at 550 °C.

### S.3 Reaction time

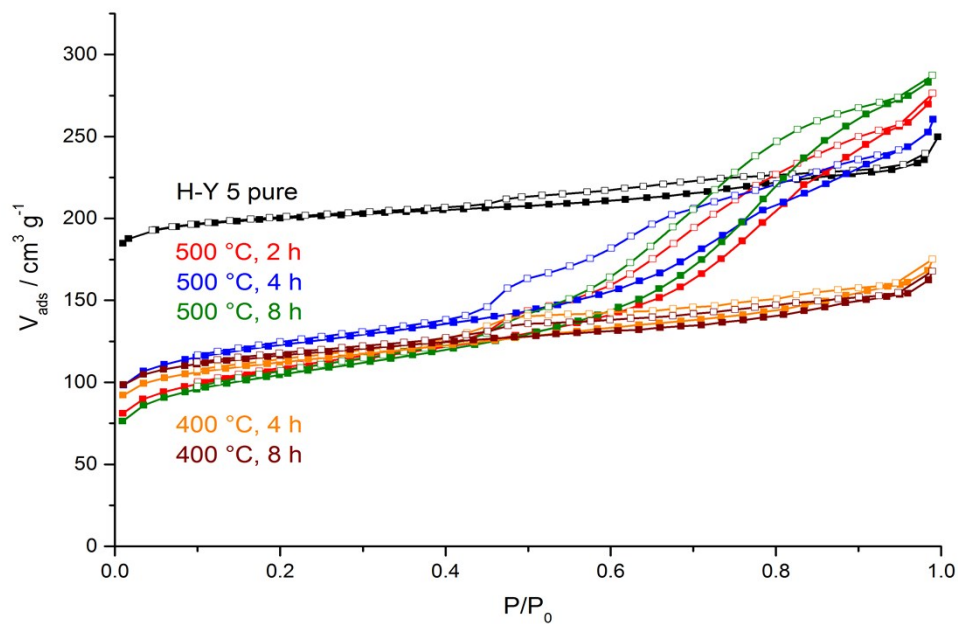


Fig. S10  $\text{N}_2$ -Isotherms at  $-196^\circ\text{C}$  from composite 2 samples at  $400^\circ\text{C}$  and  $500^\circ\text{C}$  with different reaction time

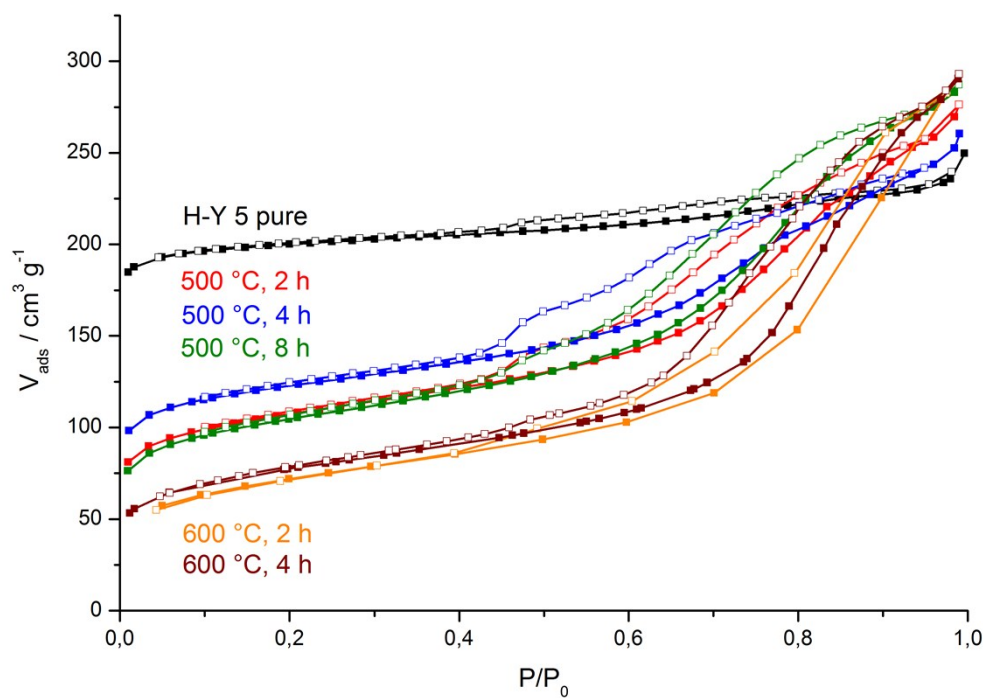


Fig. S11  $\text{N}_2$ -adsorption isotherms of parent material and samples carboclorinated at  $500^\circ\text{C}$  and  $600^\circ\text{C}$  over 2 h, 4 h or 8 h, respectively

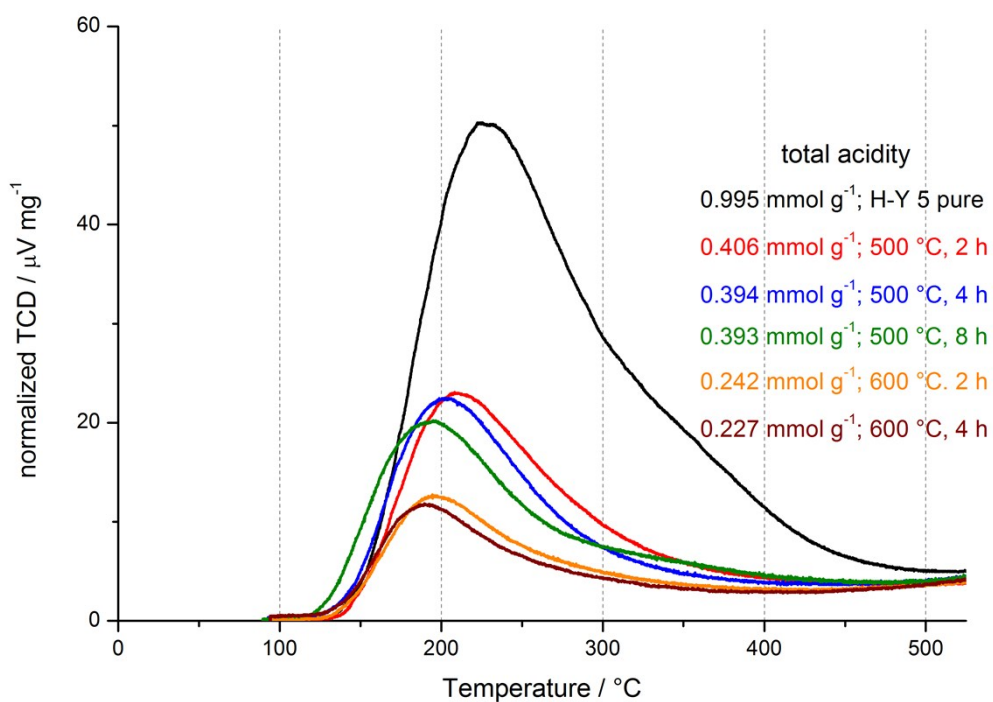


Fig. S12 TPAD of parent material and samples carbobchlorinated at 500°C and 600 °C over 2h, 4 h or 8 h, respectively. Samples were calcinated under air for 6 h at 550 °C.

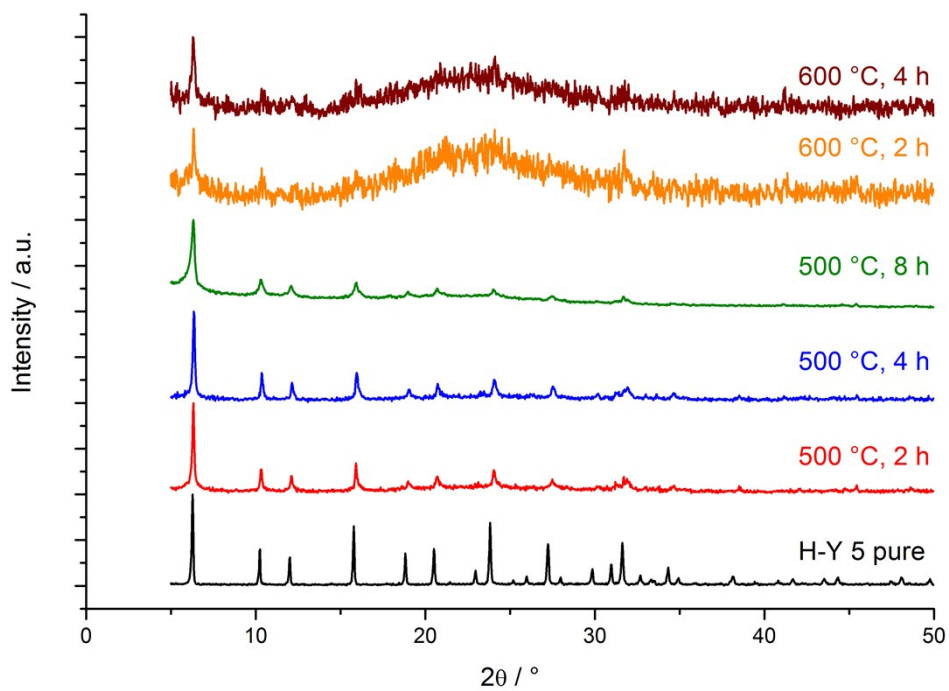


Fig. S13 Powder XRD of parent material and samples carbobchlorinated at 500°C and 600 °C over 2h, 4 h or 8 h, respectively. Diffractograms are normalized on the main reflex [111] at 6 ° 2θ.



## S.4 Chlorine concentration

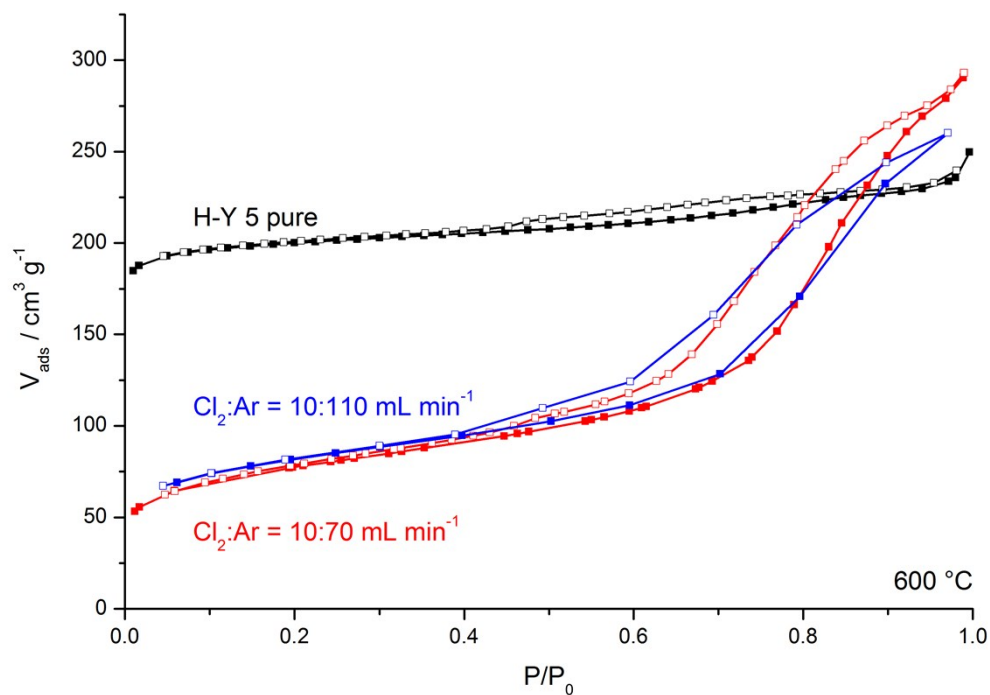


Fig. S14 N<sub>2</sub>-adsorption isotherms of parent material and samples carbochlorinated at 600 °C for 4 h with different chlorine concentrations.

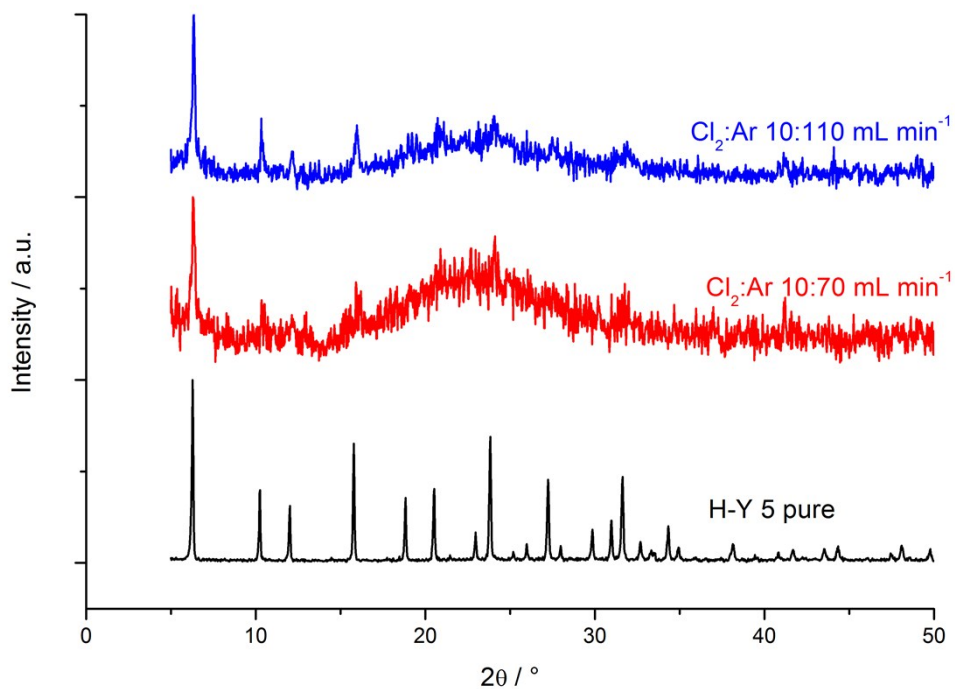
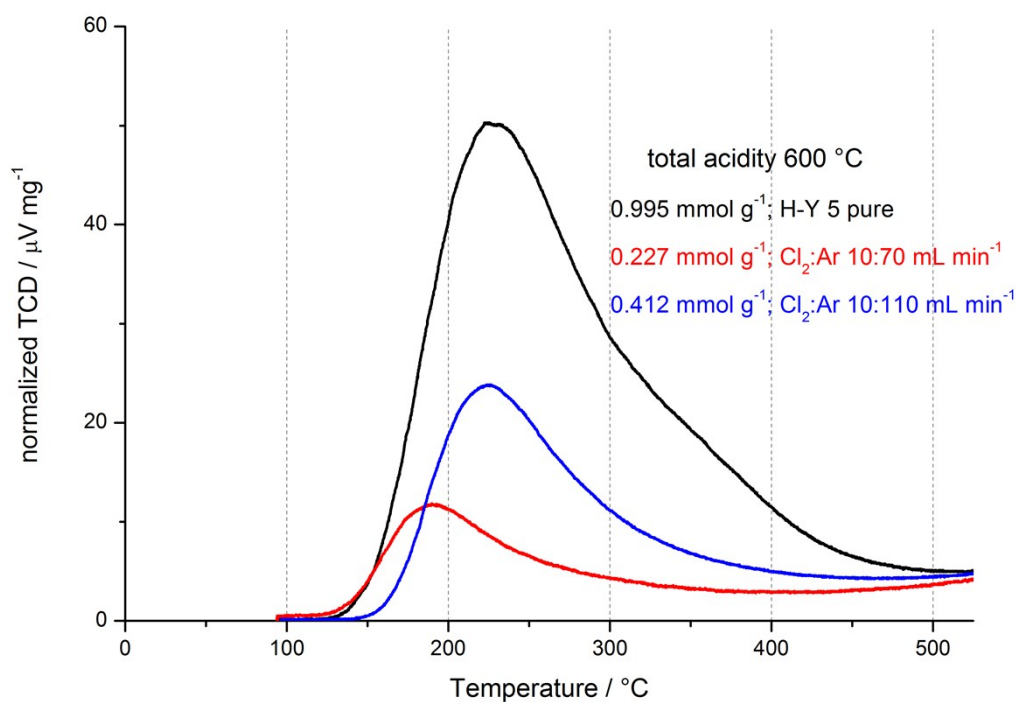


Fig. S15 Powder XRD of parent material and samples carbochlorinated at 600 °C for 4 h with different chlorine concentrations. Diffractograms are normalized on the main reflex [111] at  $6^\circ 2\theta$ .



**Fig. S16** TPAD of parent material and samples carbochlorinated at 600 °C for 4 h with different chlorine concentrations. Samples were calcinated under air for 6 h at 550 °C.

**Table S1** characterization data of samples synthesized at 600 °C for different chlorine concentrations. Physisorption data derived from N<sub>2</sub>-isotherms measured at -196 °C.

Sample <sup>a</sup>	Si/Al <sup>b</sup> / mol mol <sup>-1</sup>	SSA <sub>BET</sub> <sup>c</sup> / m <sup>2</sup> g <sup>-1</sup>	PV <sub>total</sub> <sup>d</sup> / m <sup>3</sup> g <sup>-1</sup>	PV <sub>micro</sub> <sup>e</sup> / m <sup>3</sup> g <sup>-1</sup>	PV <sub>meso</sub> <sup>f</sup> / m <sup>3</sup> g <sup>-1</sup>	HF <sup>g</sup>	C <sub>XRD</sub> <sup>h</sup> / %	Total acidity <sup>i</sup> / mmol g <sup>-1</sup>	C <sub>res</sub> <sup>j</sup> / w%	Yield <sup>k</sup> / w%
H-Y 5 pure	3.0	751	0.43	0.29	0.12	0.08	100	0.995	-	-
C2-600-4-10/110	16.0	287	0.40	0.06	0.34	0.08	28	0.412	1.09	70.6
C2-600-4-10/70	18.3	275	0.42	0.05	0.37	0.07	26	0.227	0.71	72.2

a sample description given in experimental section

b ICP-OES elemental analysis

c Multi-point BET-method

d Total pore volume at p/p<sub>0</sub> = 0.95

e t-plot method p/p<sub>0</sub> from 0.2 to 0.5

f PV<sub>meso</sub> = PV<sub>total</sub> - PV<sub>micro</sub>

g hierarchy factor HF = (PV<sub>micro</sub>/PV<sub>total</sub>) (S<sub>ext</sub>/SSA<sub>BET</sub>)<sup>70</sup>

h % XRD intensity/HY after ASTM 3906-03<sup>69</sup>

i total acidity determined by TPAD

j residual carbon (C<sub>res</sub>) analyzed by TG; C<sub>res</sub> = C<sub>sample</sub> - C<sub>H-Y 5 pure</sub>

k calculated by weighing before and after carbochlorination

## S.5 Si/Al ratio

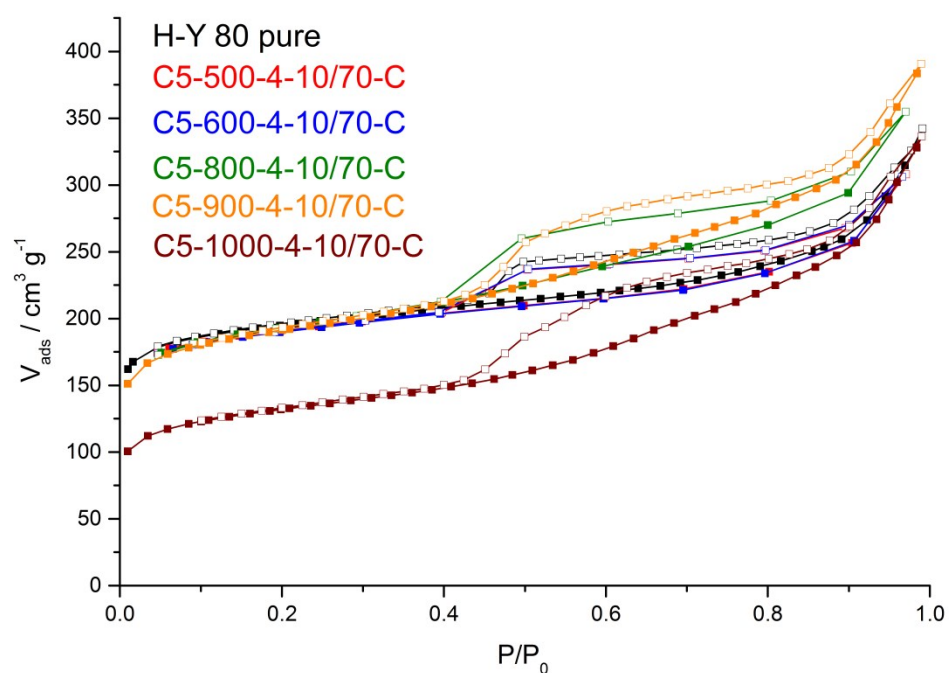


Fig. S17 N<sub>2</sub>-adsorption isotherms of parent material and composite 5 carbochlorinated at different temperatures for 4 h respectively

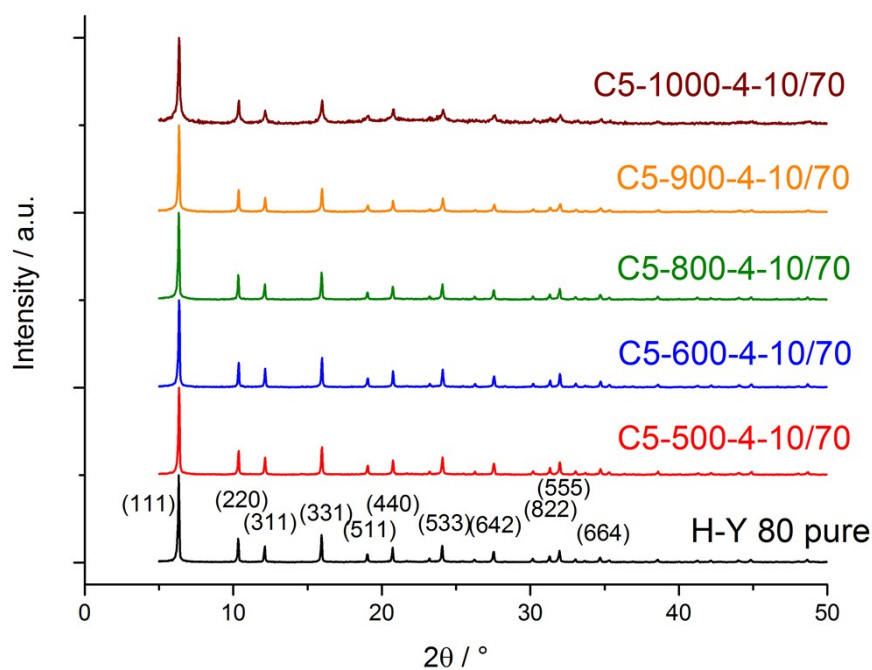


Fig. S18 XRD from composite 5 samples carbochlorinated at different temperatures. Diffractograms are normalized on the main reflex [111] at 6° 2θ.

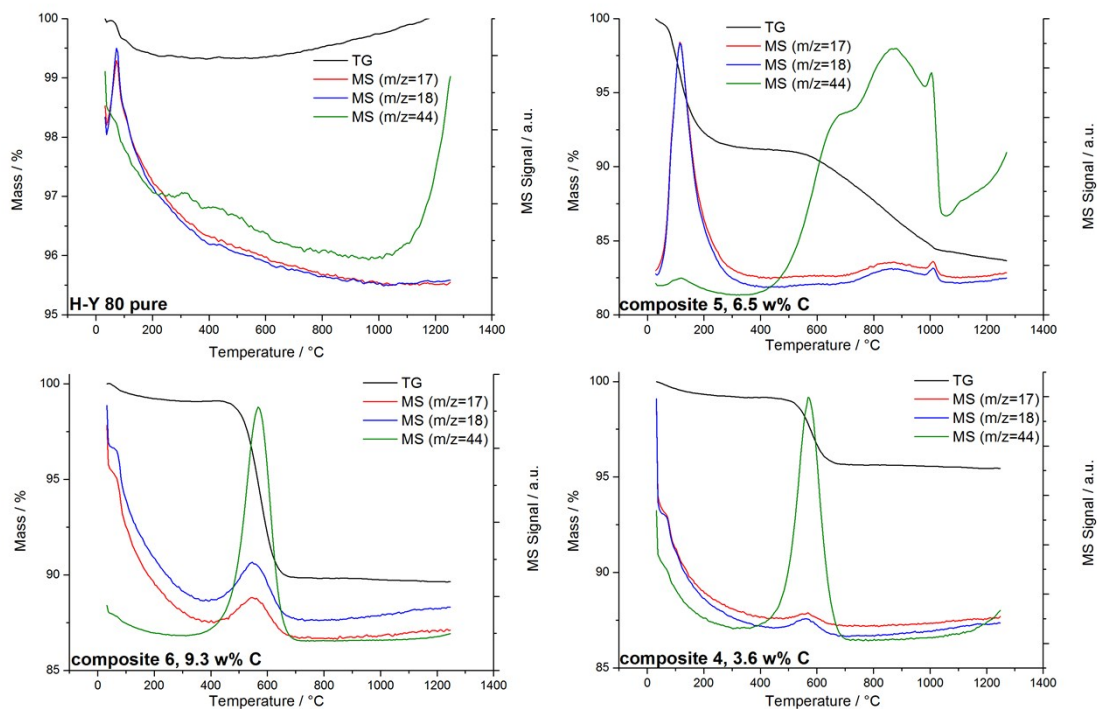


Fig. S19 TG/MS of parent material and all 3 composites with different carbon loadings under synthetic air from 25 to 1250 °C (heating rate 5 K min<sup>-1</sup>)

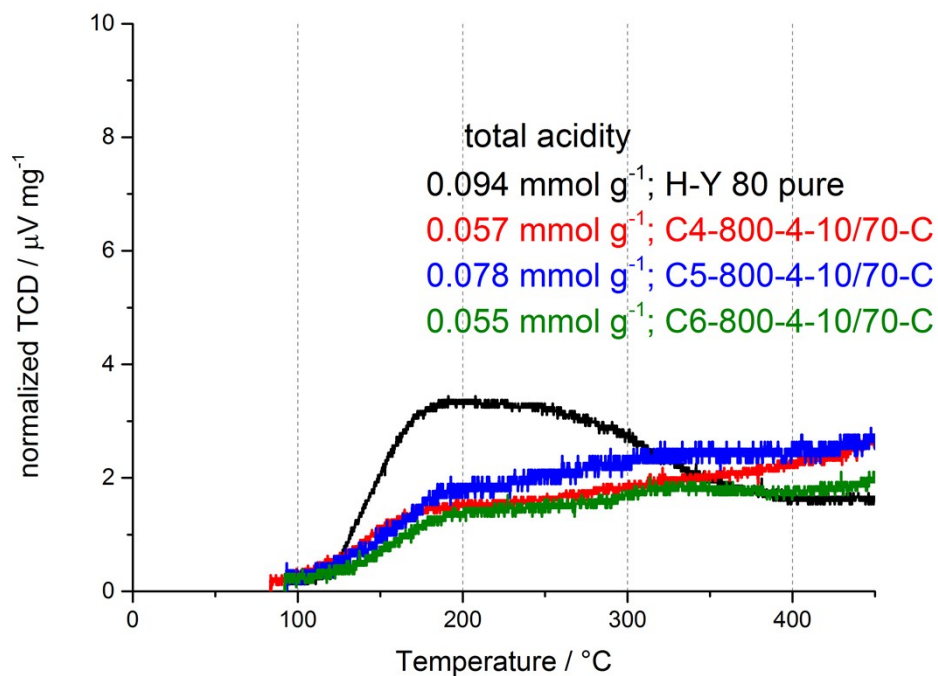


Fig. S20 TPAD of parent material and samples with different carbon loadings carbochlorinated at 800 °C after calcination under air for 6 h at 550 °C.

## S.6 References

[S1] Jiao, J., Wang, W., Sulikowski, B., Weitkamp, J., & Hunger, M. (2006).  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR characterization of non-hydrated zeolites Y upon adsorption of ammonia. *Microporous and mesoporous materials*, 90(1), 246-250.

[S2] Van Bokhoven, J. A., Roest, A. L., Koningsberger, D. C., Miller, J. T., Nachtegaal, G. H., & Kentgens, A. P. M. (2000). Changes in structural and electronic properties of the zeolite framework induced by extraframework Al and La in H-USY and La (x) NaY: A  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR and  $^{27}\text{Al}$  MQ MAS NMR study. *The Journal of Physical Chemistry B*, 104(29), 6743-6754.