SUPPLEMANTARY INFORMATION

Catalytic oxidative desulfurization of 4,6-DMDBT containing model fuel by metal-free activated carbons: the key role of the surface chemistry

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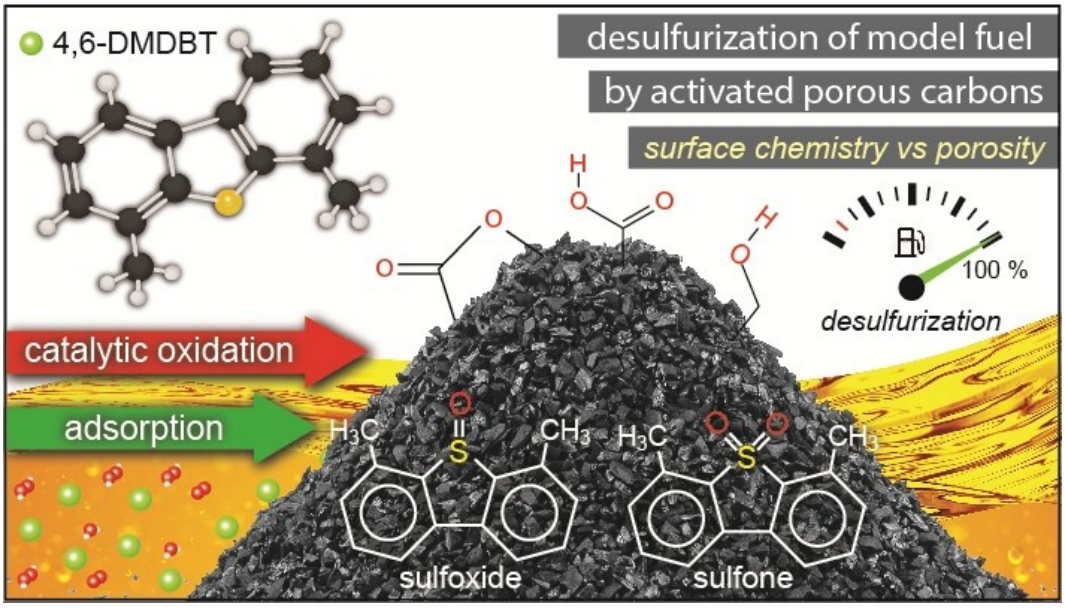
Graphical abstract



Supplementary Figures and Tables

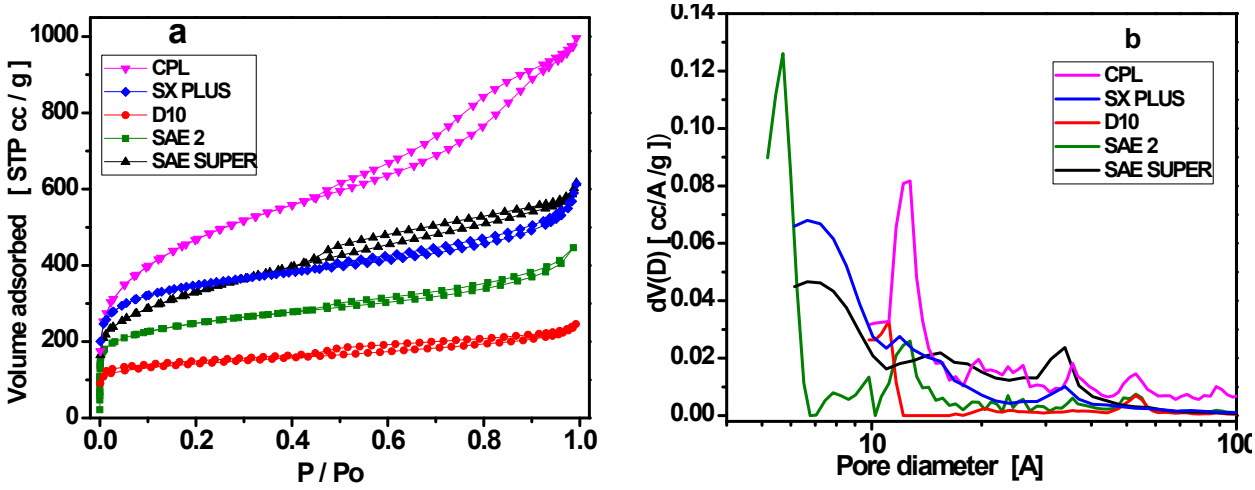


Figure s1. Nitrogen adsorption/desorption isotherms and pore size distribution (DFT analysis).

Table s1. Textural parameters of the commercial activated carbons.

Activated Carbons	S_{BET} m^2/g	V_{tot} cm^3/g	V_{mic} cm^3/g	V_{mes} cm^3/g	V_{mes}/V_{tot}
CPL	1702	1.54	0.16	1.38	0.90
SX PLUS	1280	0.95	0.35	0.60	0.63
D10	515	0.38	0.13	0.26	0.67
SAE SUPER	1182	0.95	0.14	0.81	0.85
SAE 2	896	0.69	0.24	0.45	0.66

Table s2. Surface chemistry analysis of the commercial activated carbons.

Activated Carbons	Surface pH	Carboxyls (mmol/g)	Lactones (mmol/g)	Phenols (mmol/g)	Acidic groups (mmol/g)	Acidic density (µmol/m²)	Basic groups (mmol/g)	Basic density (µmol/m²)	Total groups (mmol/g)	Total density (µmol/m²)	Acidic to Basic ratio
CPL	5.3	0.000	0.062	0.450	0.512	0.332	0.000	0.000	0.612	0.360	1.00
SX PLUS	6.8	0.000	0.151	0.037	0.188	0.147	0.269	0.210	0.457	0.357	0.70
D10	7.9	0.000	0.106	0.081	0.187	0.363	0.887	1.722	1.074	2.085	0.21
SAE SUPER	9.3	0.000	0.062	0.039	0.101	0.085	1.320	1.117	1.421	1.202	0.08
SAE 2	9.8	0.000	0.081	0.144	0.225	0.251	1.731	1.932	1.956	2.183	0.13

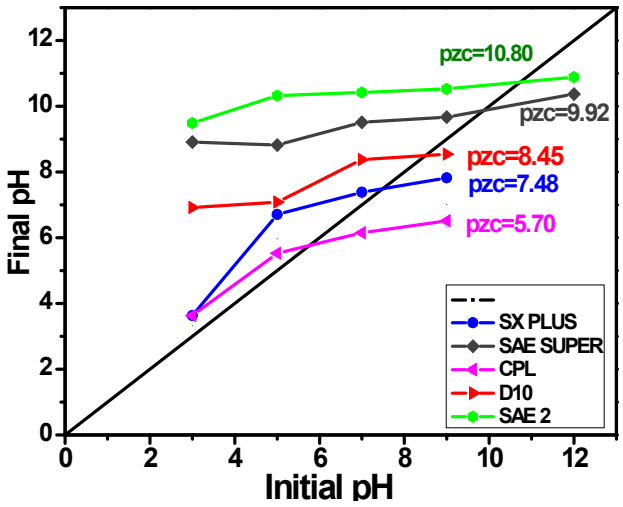


Figure s2. Point of zero charge (pzc) of the activated carbons.

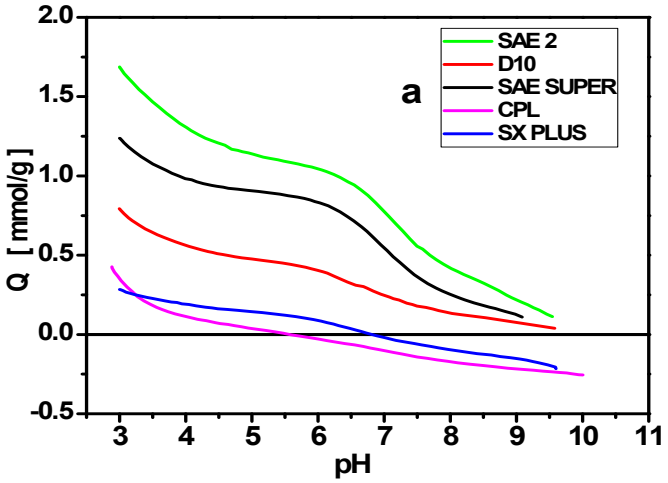


Figure s3. Proton binding curves of the activated carbons obtained by potentiometric titration.

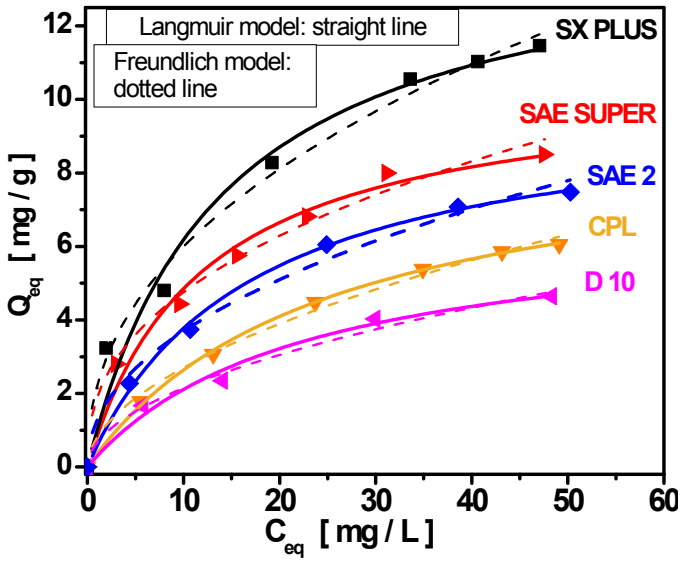


Figure s4. Langmuir isotherms for the desulfurization of 4,6-DMDBT for all the commercial carbons (hexadecane solvent, 25 °C).

Table s3. The adsorption parameters of Langmuir and Freundlich models for the commercial carbons.

	Langmuir model			Freundlich model		
	Q_{max} (mg/g)	K_L (L/mg)	R^2	K_F (mg $^{1-1/n}$ L $^{1/n}$/g)	1/n	R^2
SAE 2	7.6	0.0605	0.9962	1.2723	0.4632	0.9816
SAE SUPER	8.2	0.0849	0.9684	1.8826	0.4026	0.9785
D10	6.8	0.0452	0.9712	0.6680	0.5067	0.9757
CPL	6.1	0.0401	0.9977	0.7973	0.5294	0.9867
SX PLUS	11.3	0.0726	0.9591	2.2019	0.4352	0.9862

Table s4. The surface chemistry analysis results of SX PLUS and its oxidized counterparts.

Activated Carbons	Surface pH	Acidic groups (mmol/g)	Acidic density (mmol/m^2 x 10^{-3})	Basic groups (mmol/g)	Basic density (mmol/m^2 x 10^{-3})	Total groups (mmol/g)	Total density (mmol/m^2 x 10^{-3})
SX PLUS	6.8	0.188	0.147	0.269	0.210	0.457	0.357
SX PLUS-Nox	4.6	0.717	0.772	0.144	0.155	0.861	0.927
SX PLUS-Sox	5.2	0.288	0.285	0.058	0.057	0.346	0.342

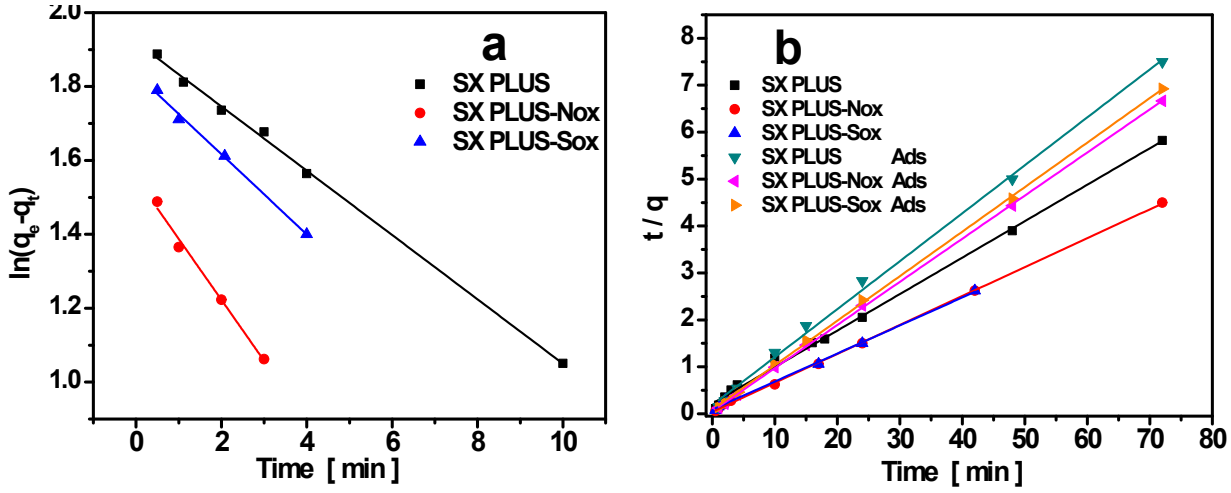


Figure s5. Pseudo-first order (a) and pseudo-second order (b) plots for parent and oxidized SX PLUS activated carbons at initial concentration 20 ppm of sulfur.

Table s5. Pseudo-first and pseudo-second order kinetic parameters for the catalytic oxidation (Cat) and adsorption (Ads) process for the parent and oxidized SX PLUS activated carbons.

Activated carbons			Pseudo-first order			Pseudo-second order		
		q_e (Langmuir)	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g/mg min)	q_e (mg/g)	R^2
SX PLUS	Cat	-	0.087	6.82	0.997	0.027	12.98	0.986
SX PLUS-Nox	Cat	-	0.165	4.71	0.997	0.084	16.39	0.979
SX PLUS-Sox	Cat	-	0.108	6.23	0.994	0.038	16.95	0.977
SX PLUS	Ads	11.3	-	-	-	0.056	9.80	0.997
SX PLUS-Nox	Ads	13.0	-	-	-	0.153	10.98	0.999
SX PLUS-Sox	Ads	12.2	-	-	-	0.104	10.63	0.999

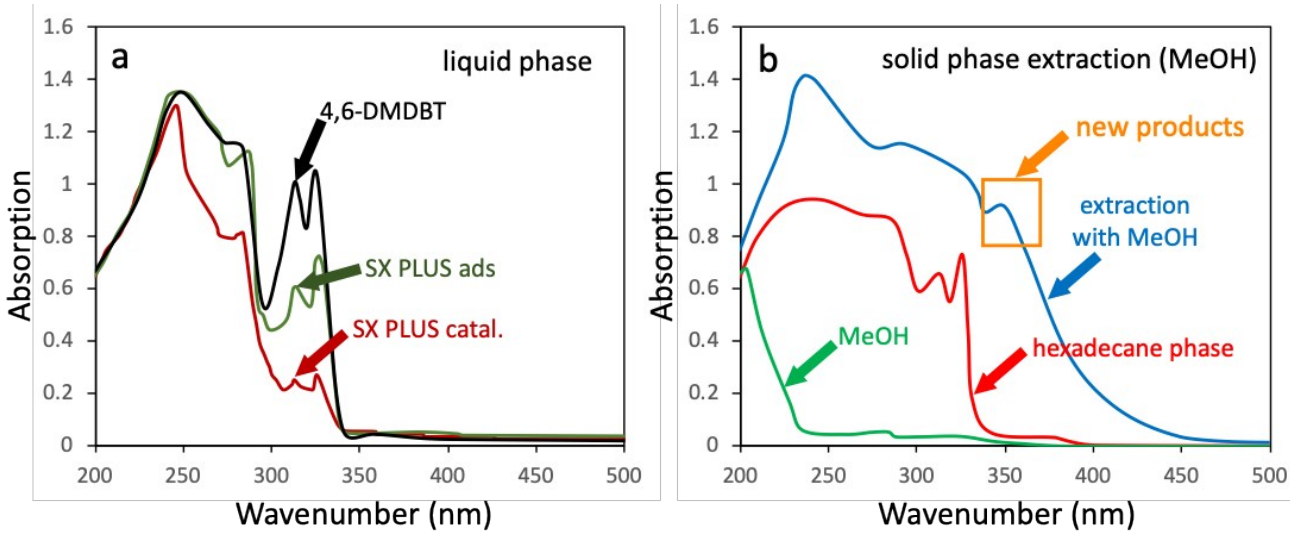


Figure s6. UV-Vis spectra of 4,6-DMDBT and of the product solution from adsorption or catalytic oxidation tests with SX PLUS (a) and UV-Vis spectrum of the solution derived by extraction of the used SX PLUS carbon with MeOH (b).