Electronic Supplementary Material for

Preparation of Carbon-Based Solid Acid Catalyst from High-Sulfur Petroleum Coke with Nitric Acid and Ball Milling, and a Computational Evaluation of Inherent Sulfur Conversion Pathways

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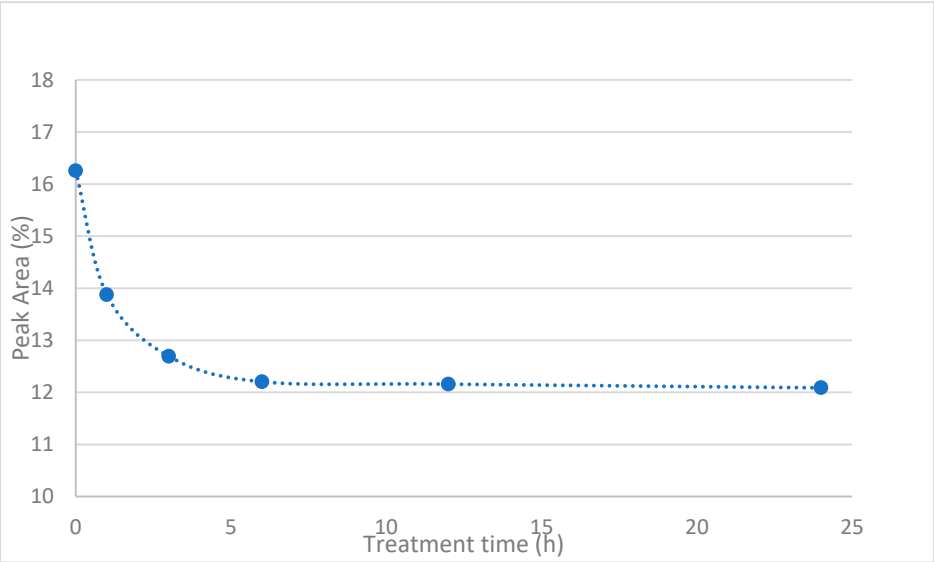

Figure S1. Relative area of the G band in the Raman spectra of acid-treated petcoke in percentage of total area in the 1000-1800 cm^{-1} region.

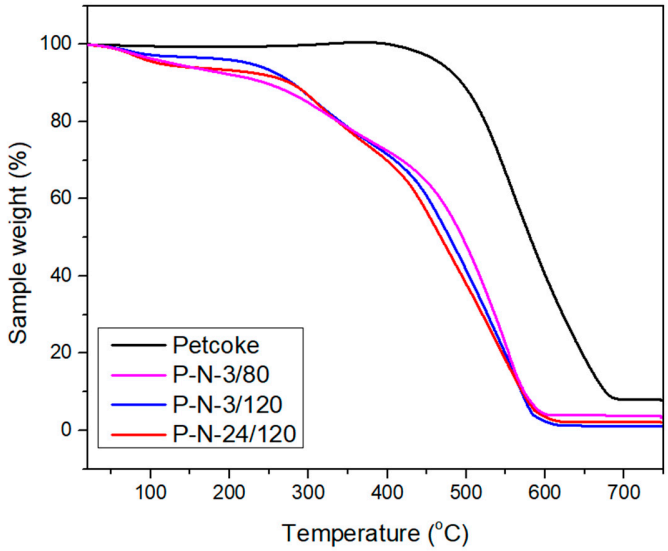

Figure S2. TGA profiles of petcoke and acid-treated petcoke (20 °C/min to 750 °C in a 50 mL/min flow of air).

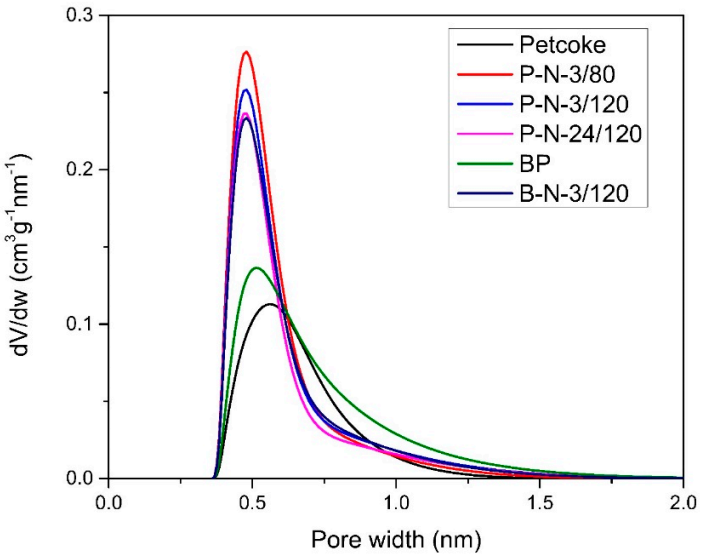

Figure S3. Pore size distributions of petcoke and petcoke-derived samples, as determined by CO_2 adsorption using a 2D-NLDFT-HS model.

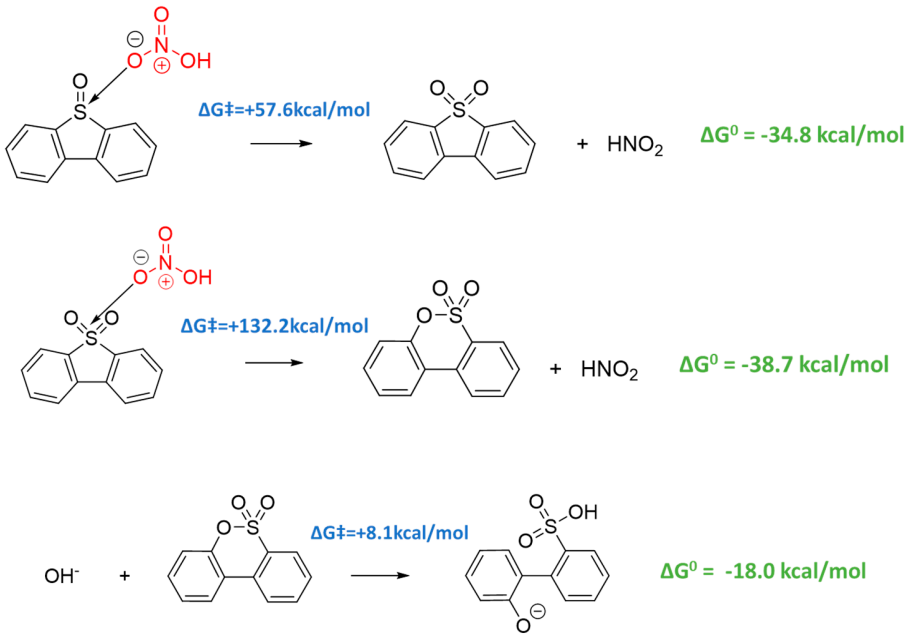

Figure S4. Reaction profile of DBT reacted with nitric acid (HNO_3).

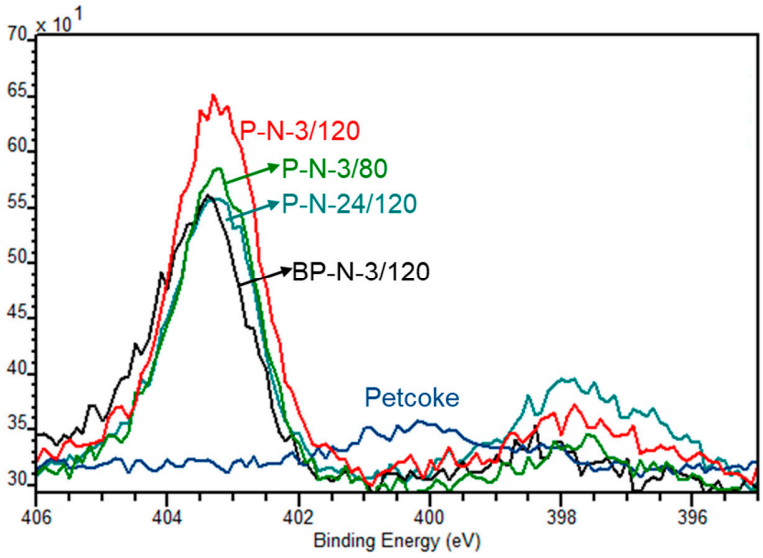

Figure S5. High-resolution XPS spectra of N 1s for petcoke derived solid acid catalysts.

N1s: before acid functionalization, there is little nitrogen on petcoke surface. The nitric acid resulted in the increase of nitrogen content and from the N1s spectra that -NO_2 groups are the dominated nitrogen-containing groups, which the binding energy is at 405.6 eV. The peaks centered at ~400 eV were reported as N-O, pyrrolic or pyridinic structures.[1] However, it could be a result of conversion of the -NO_2 into -NH_2 by exposing to X-ray irradiation during the XPS measurement.[2]

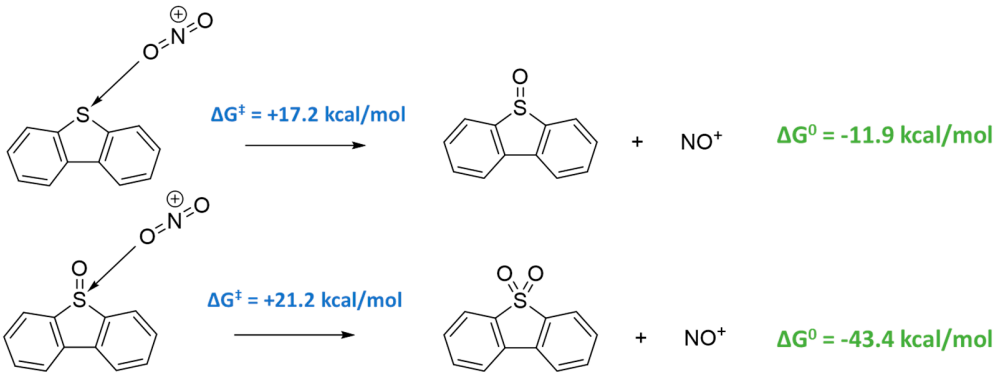

Figure S6. Reaction profile of DBT reacted with nitronium ion (NO_2^+).

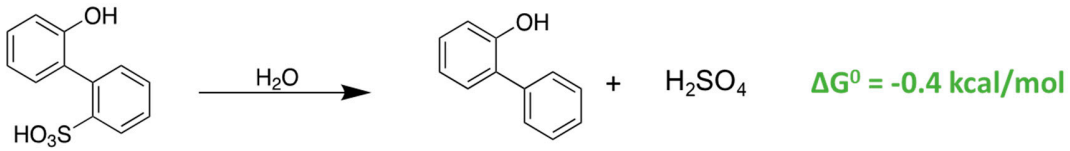

Figure S7. A spontaneous desulfurization reaction.

Table S1. Esterification of octanoic acid with methanol over different acid catalysts.

No.	Reactants	Catalyst (concentration of catalytic acid sites)	Reaction Conditions	Estimated TOF (h^{-1})	Productivity[3] ($g \cdot g^{-1} \cdot h^{-1}$)	Ref.
1	OA[1]+ MeOH[2]	H_2SO_4	60 °C, OA/MeOH = 1/40 (molar ratio)	87	52.5	3
2	OA+ MeOH	Silica Ball milled sulfonated petcoke (3.73 mmol/g)	60 °C, OA/MeOH = 1/40 (molar ratio)	85	10.3	3
3	OA+ MeOH	Ball milled sulfonated petcoke (1.58 mmol/g)	60 °C, OA/MeOH = 1/40 (molar ratio)	52	7.1	3
4	OA+ MeOH	Sulfonated petcoke (1.25 mmol/g)	60 °C, OA/MeOH = 1/40 (molar ratio)	48	5.6	3
5	OA+ MeOH	Sulfonated activated carbon from coffee residue (0.45-0.72 mmol/g)	60 °C, OA/MeOH = 1/3 (molar ratio)	25-47	4.0-6.0	4
6	OA+ MeOH	Amberlyst-15 (4.7 mmol/g)	60 °C, OA/MeOH = 1/3 (molar ratio)	4	3.9	4
7	OA + MeOH	Hollow sulfonated mesoporous carbon spheres (1.43 mmol/g)	75 °C, OA/MeOH =1/30 (molar ratio)	21.7	3.7	5
8	OA+ MeOH	Amberlyst-15 (4.7 mmol/g)	60 °C, OA/MeOH = 1/20 (molar ratio)	6	2.8	This work
9	OA+ MeOH	Ball milled nitric acid oxidized high sulfur petroleum coke (0.12 mmol/g)	60 °C, OA/MeOH = 1/20 (molar ratio)	143	1.9	This work
10	OA+ MeOH	Sulfonated chitosan (3.17 mmol/g)	60 °C, OA/MeOH = 1/95 (molar ratio)	114	1.3	6
11	Oleic acid +MeOH	Carbonized and sulfonated spent coffee grounds (3.36 mmol/g)	80 °C, oleic acid/MeOH = 1/10 (molar ratio)	-	1.3	7
12	OA+ MeOH	Nitric acid oxidized high sulfur petroleum coke (0.08 mmol/g)	60 °C, OA/MeOH = 1/20 (molar ratio)	114	1.1	This work
13	OA+ MeOH	Acid-activated clay (smectite) (0.57 mmol/g)	100 °C, OA/MeOH = 1/3 (molar ratio)	12	0.7	8

[1.] OA, octanoic acid; [2.] MeOH, methanol; [3.] gram of product per gram of catalyst and per hour.

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