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Supporting information for

Solid acid catalysts produced by sulfonation of petroleum coke: dominant role of aromatic hydrogen

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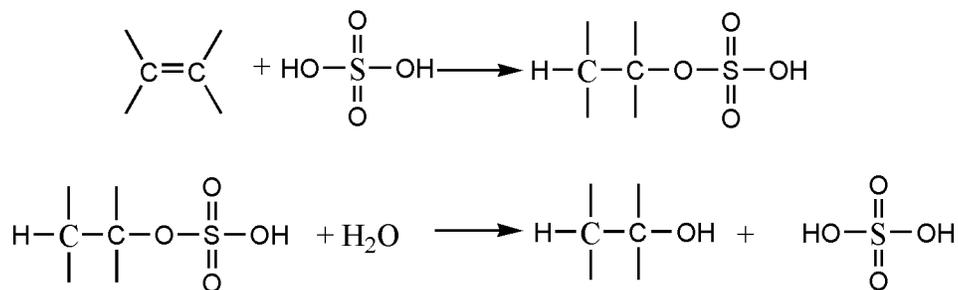
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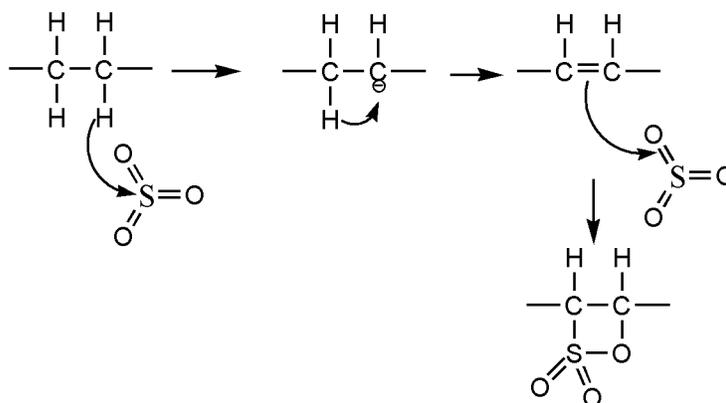
Table S1. The $-\text{SO}_3\text{H}$ acidity of various carbon materials after sulfonation with concentrated H_2SO_4 under different conditions.

Carbon	Sulfur source	Temp (°C)	Time (h)	$-\text{SO}_3\text{H}$ (mmol/g)	Ref
Xylose hydrocarbon after 190 °C hydrothermal carbonization for 24 h	H_2SO_4 (98 %), 1 g: 20 mL	150	15	0.31	[1]
Porous carbon from 800 °C pyrolysis of resorcinol-formaldehyde resin for 1 h	H_2SO_4 , 0.2 g: 10 mL	80	8	0.39	[2]
resorcinol-formaldehyde resin pyrolysis at 800 °C for 2 h	H_2SO_4 (95%), acid/carbon ratio of 47	140	20	0.44 ^a	[3]
Coffee residue activated carbon by ZnCl_2 under CO_2 at 600 for 4 h	H_2SO_4 (98 %), 1 g: 20 mL	200	24	0.45 ^a	[4]
Activated carbon	H_2SO_4 (>98 %), 7 g: 100 mL	150	12	0.544	[5]
Activated carbon	H_2SO_4 , 1 g: 10 mL	180	24	0.56 ^a	[6]
Coffee residue activated carbon by ZnCl_2 under CO_2 at 600 for 4 h	H_2SO_4 (98 %), 1 g: 20 mL	180	24	0.57 ^a	[4]
Mesoporous silica - carbon composite	H_2SO_4 , 1 g: 20 mL	150	15	0.57	[7]
Rubber char from charring at 520 °C for 2 h	H_2SO_4 (98.3%), 10 g: 100 mL	120	5	0.64 ^a	[8]
Coffee residue activated carbon by ZnCl_2 under CO_2 at 600 for 4 h	H_2SO_4 (98 %), 1 g: 20 mL	160	24	0.66 ^a	[4]
Wood powder char obtained from 400 °C charring for 80 min	H_2SO_4 (95-98 %), 10 g: 100 mL	80	3	0.67 ^a	[9]
D-glucose or sucrose char	H_2SO_4 (> 96%), <20 g: 200 mL	150	15	0.7	[10]
Coffee residue activated carbon by ZnCl_2 under CO_2 at 600 for 4 h	H_2SO_4 (98 %), 1 g: 20 mL	140	24	0.72 ^a	[4]
resorcinol-formaldehyde resin activated by ZnCl_2 at 400 °C	H_2SO_4 , 1 g: 10 mL	150	8	0.94	[11]
Coal after carbonization at 350 °C for 2 h	H_2SO_4	135	4	1.09	[12]
Porous carbon from 800 °C pyrolysis of resorcinol-formaldehyde resin for 1 h	H_2SO_4 (98 %), 0.2 g: 10 mL	80	8	1.10	[13]
Sugar-derived carbon spheres pyrolysis at 850 °C for 1 h	H_2SO_4 (95%), acid/carbon ratio of 47	140	20	1.34 ^a	[3]
Mesoporous polydivinylbenzene polymer	H_2SO_4 , 1.5 g: 70 mL (30 mL dichloromethane, and 20 mg Ag_2SO_4 as catalyst)	80	24	2.1 ^a	[14]

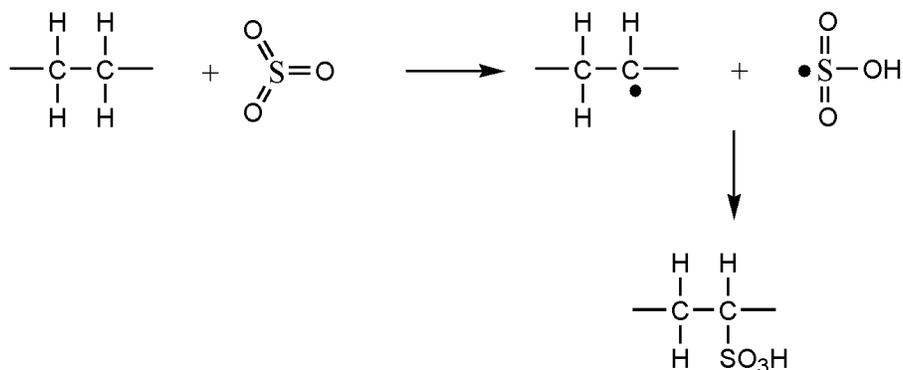
Note: ^a estimated from the sulfur content.



Scheme S1. Addition of sulfuric acid to alkenes and the following hydrolysis of the obtained alkyl hydrogen sulfate [15].



Scheme S2. Sulfonation of alkanes to generate sultone [16].



Scheme S3. Sulfonation of alkanes to generated sulfonic acid [17].

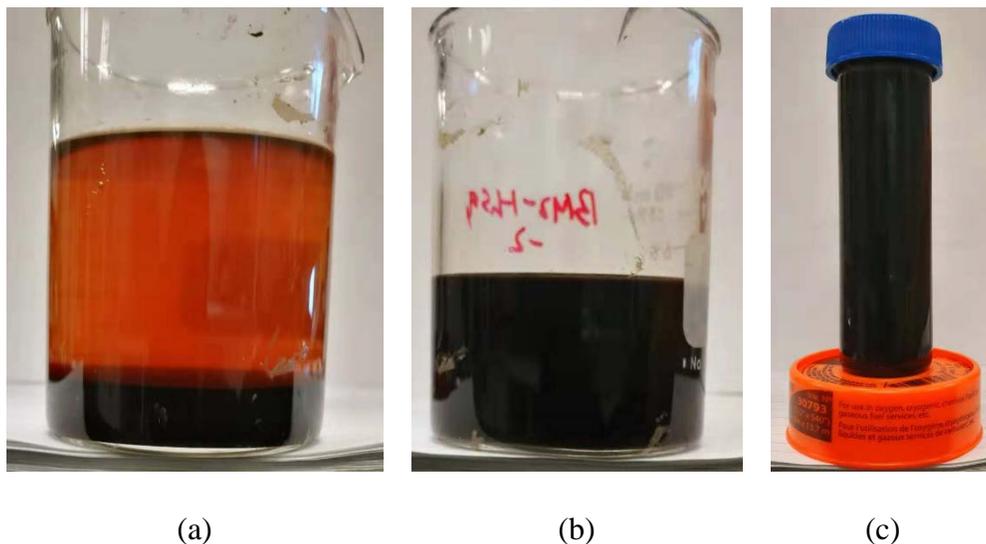


Figure S1. Washing solutions during the preparation of sulfonated petcoke. (a) First three washes with deionized water ($\text{pH} < \sim 2$), (b) fourth wash with deionized water ($\text{pH} > \sim 4$) showing the suspension of the carbon particles that could not be broken even with centrifuging at 6000 rpm for 5 min as shown in (c).

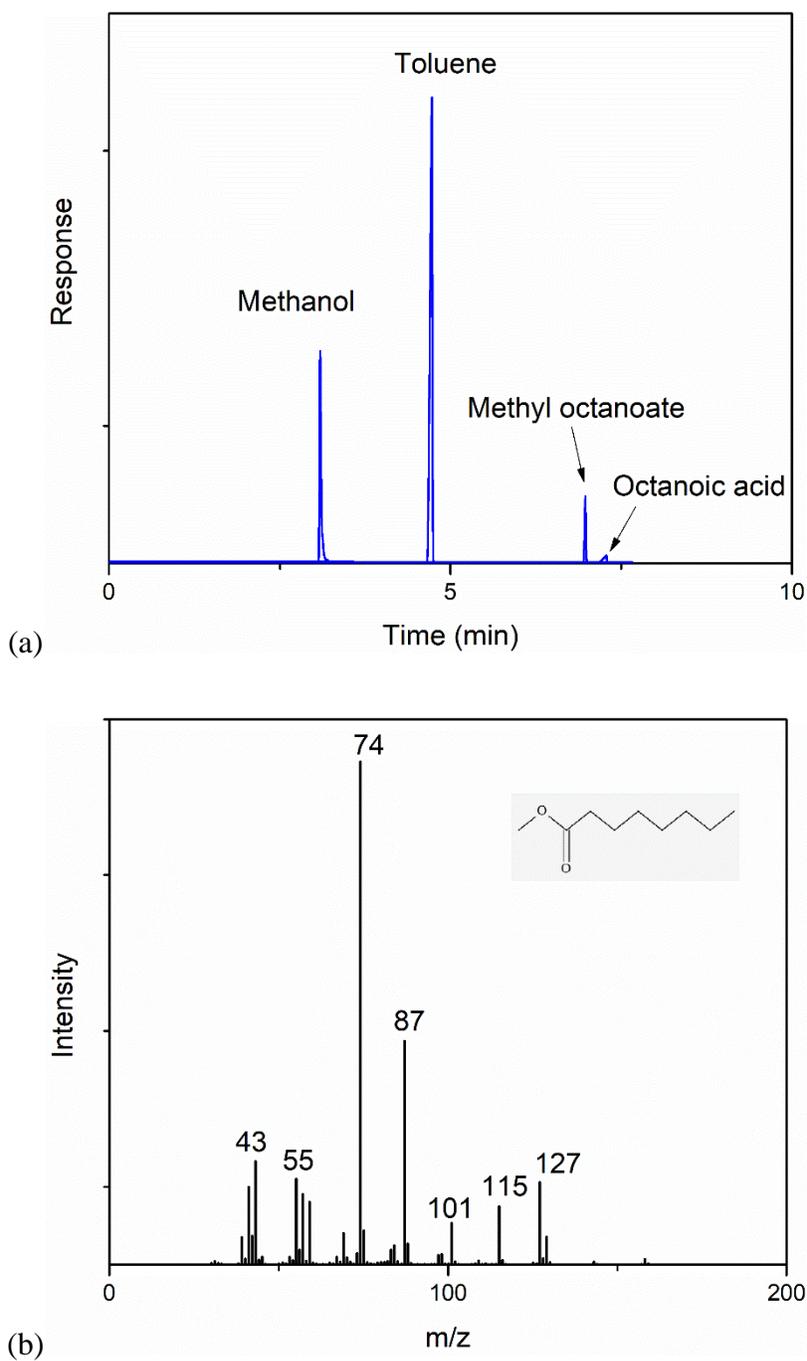


Figure S2. (a) GC analysis of the products after esterification of octanoic acid with methanol, and (b) Mass spectrum of methyl octanoate produced by the esterification reaction.

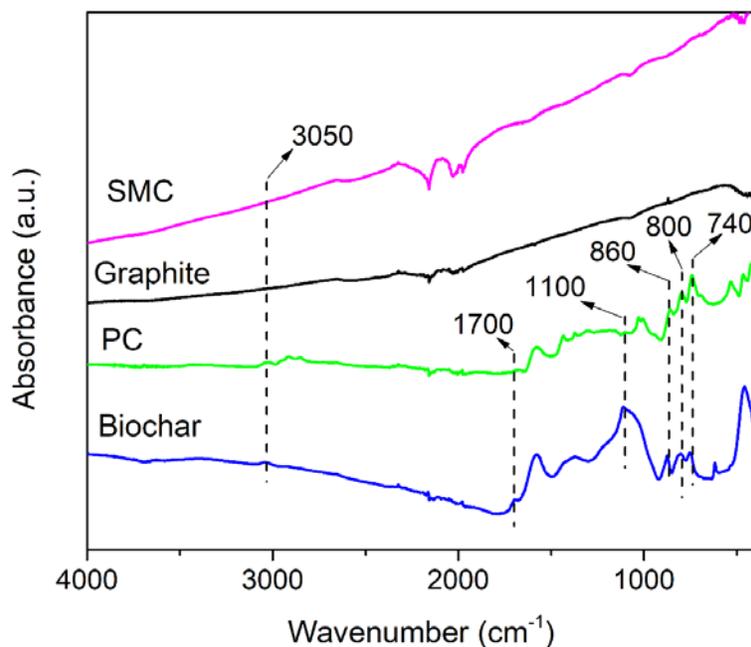


Figure S3. FTIR spectra of different carbon materials before sulfonation. The downward peaks around $\sim 2200 \text{ cm}^{-1}$ in the SMC spectrum were related to the atmospheric CO_2 .

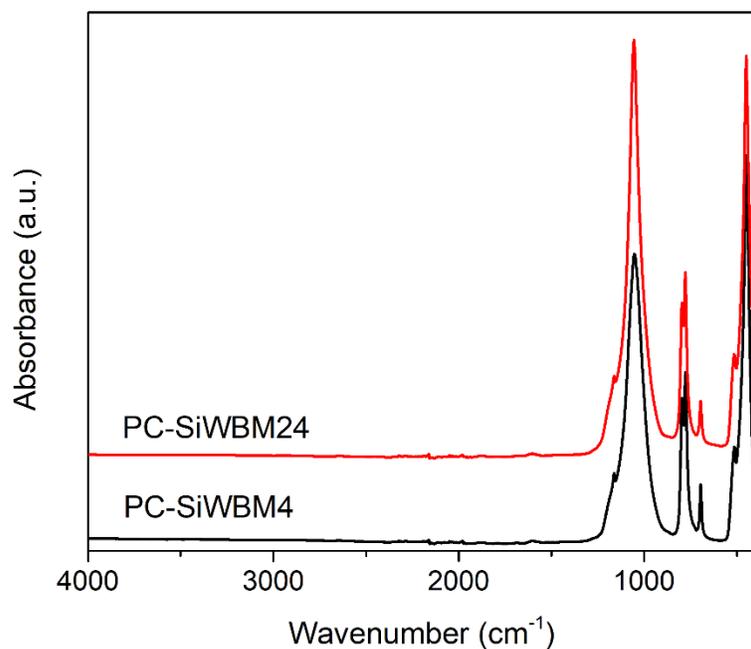


Figure S4. The FTIR spectrum of PC-SiWBM4 and PC-SiWBM24. The large peaks from $\sim 1300 \text{ cm}^{-1}$ to 400 cm^{-1} were associated with the silica in the samples because silica was not separated from the sample after ball milling.

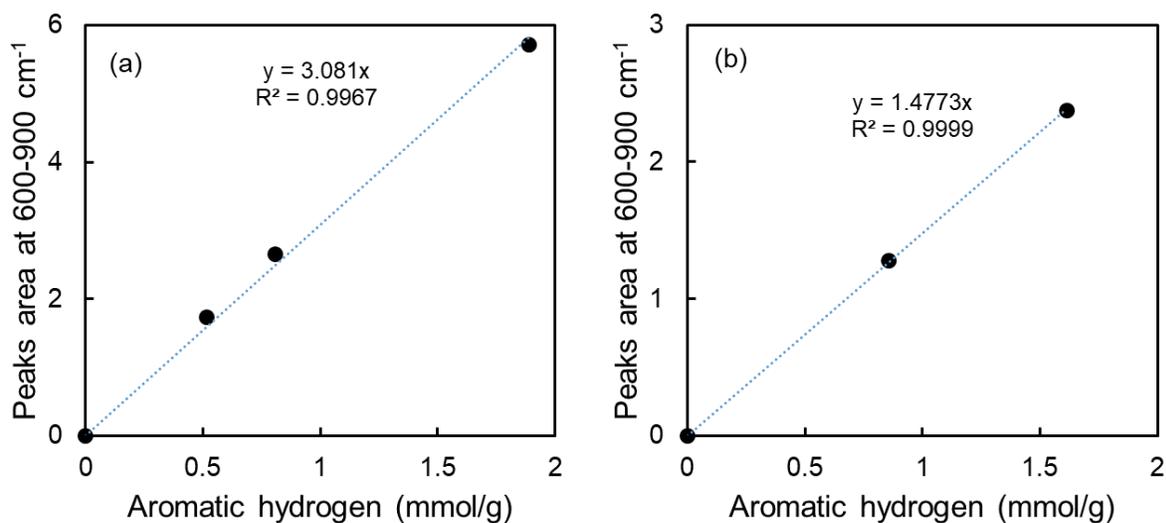


Figure S5. The relationship between FTIR peak area at 600-900 cm^{-1} and aromatic hydrogen concentration of (a) salicylic acid and (b) dibenzothiophene.

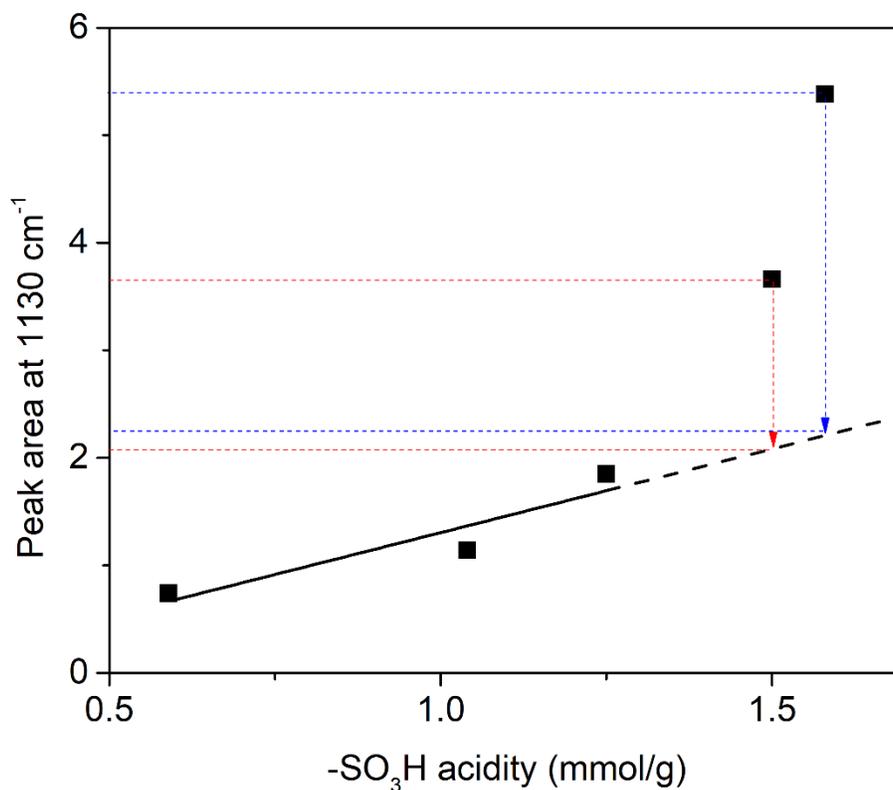
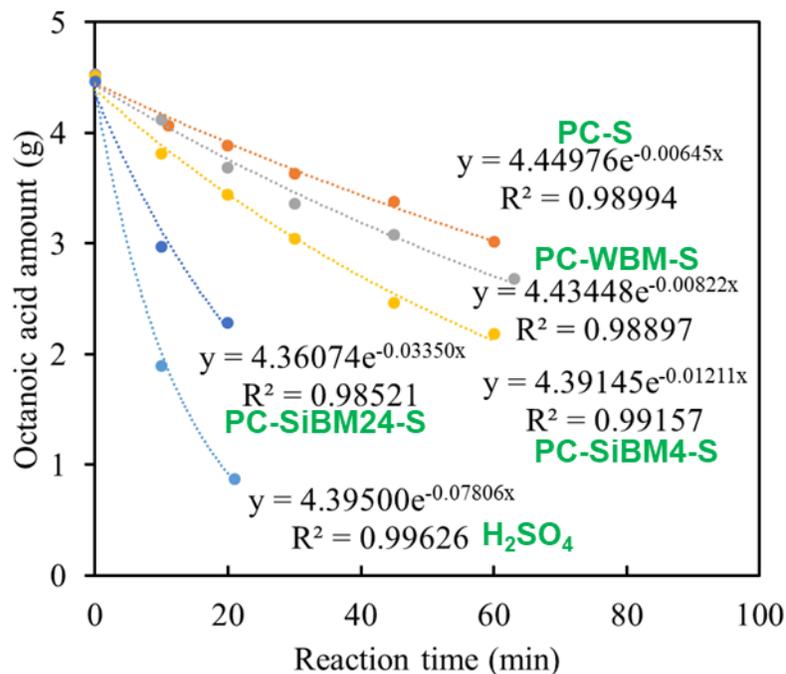
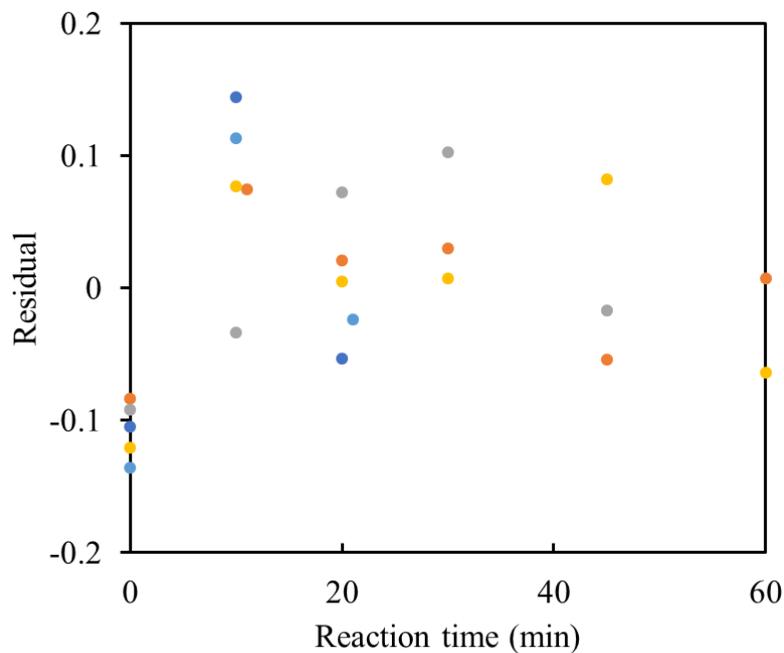


Figure S6. Relationship between peak area at 1130 cm^{-1} and $-\text{SO}_3\text{H}$ acidity of the sulfonated petcoke samples. The arrows show the correction of peak area for the ball-milled samples based on the assumption that the peak area was linearly correlated to the $-\text{SO}_3\text{H}$ acidity, as seen in the calibration curves for salicylic acid and dibenzothiophene (Figure S5).



(a)



(b)

Figure S6. Conversion of octanoic acid over different catalysts with lines of best fit (a) and residuals associated with the fits (b).

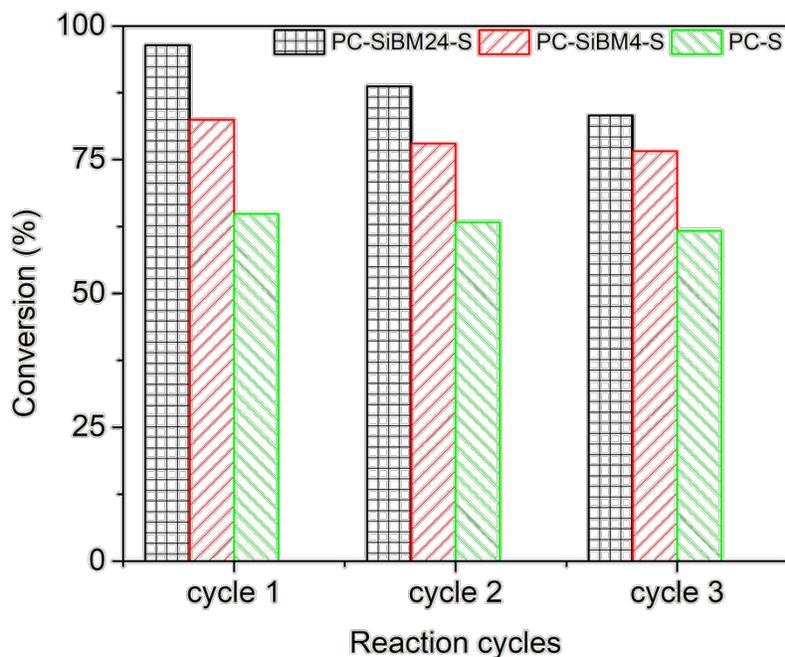


Figure S7. The reusability of the sulfonated petcoke as solid acid catalyst for octanoic acid esterification. Reaction conditions: methanol: octanoic acid = 40:1 molar ratio, 60 °C, 500 rpm.

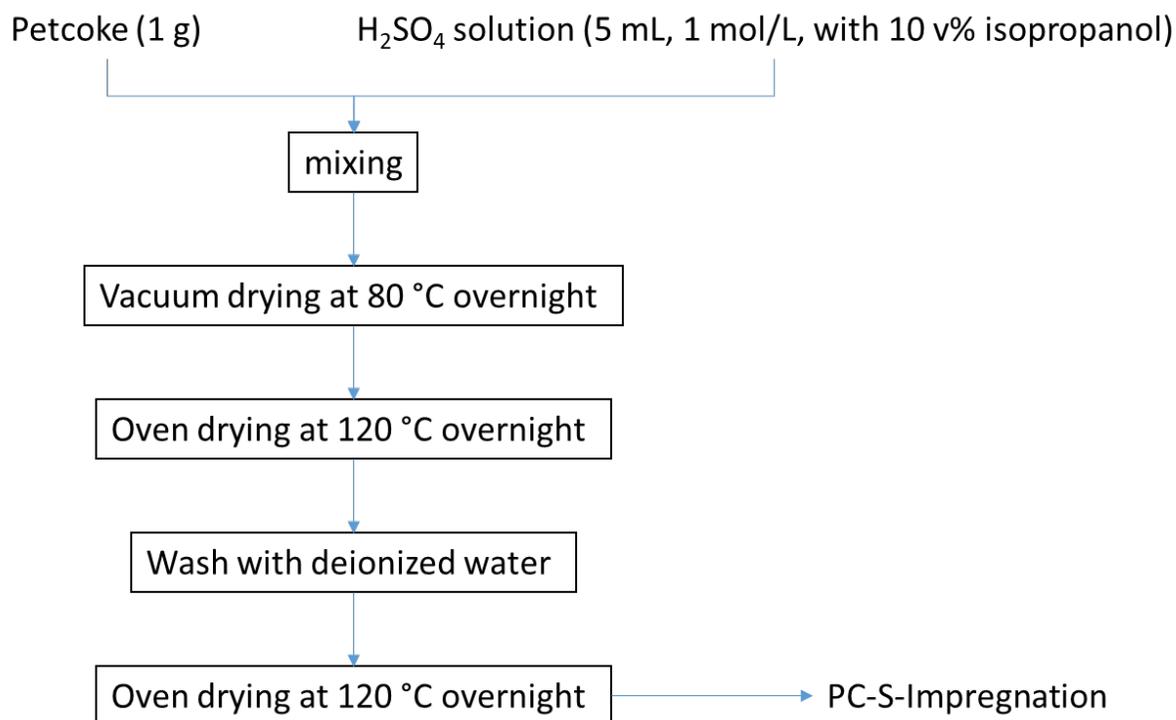


Figure S8. Preparation of sulfonated petcoke with impregnation method.

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