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Supplementary Materials

Nitric Acid Functionalization of Petroleum Coke to Access Inherent Sulfur

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From the CO and CO_2 TPD profiles (Figure S1), HNO_3 and HNO_3/H_2SO_4 treatments generated more O-containing groups than treatment with H_2SO_4. The detected CO_2 molecules below 400 °C are mainly from the decomposition of carboxylic groups, while above 400 °C they are attributed to decomposed carboxylic anhydrides and lactonic groups [1]. Carboxylic anhydride groups simultaneously generate both CO and CO_2 with 1:1 ratio [2]. Hydroxyl and carbonyl groups decomposed to CO at temperatures above 600 °C. Further decomposition of carboxylic groups was confirmed by the corresponding peak of CO_2 at the same temperature [2]. The presence of a significant number of O-containing groups explains the high total acidities of P-N-24 and P-N/S-24.

SEM images of the samples are shown in Figure S2. No major differences exist between the samples. Reaction schemes for the acid treatments are given in Figures S3 and S4.

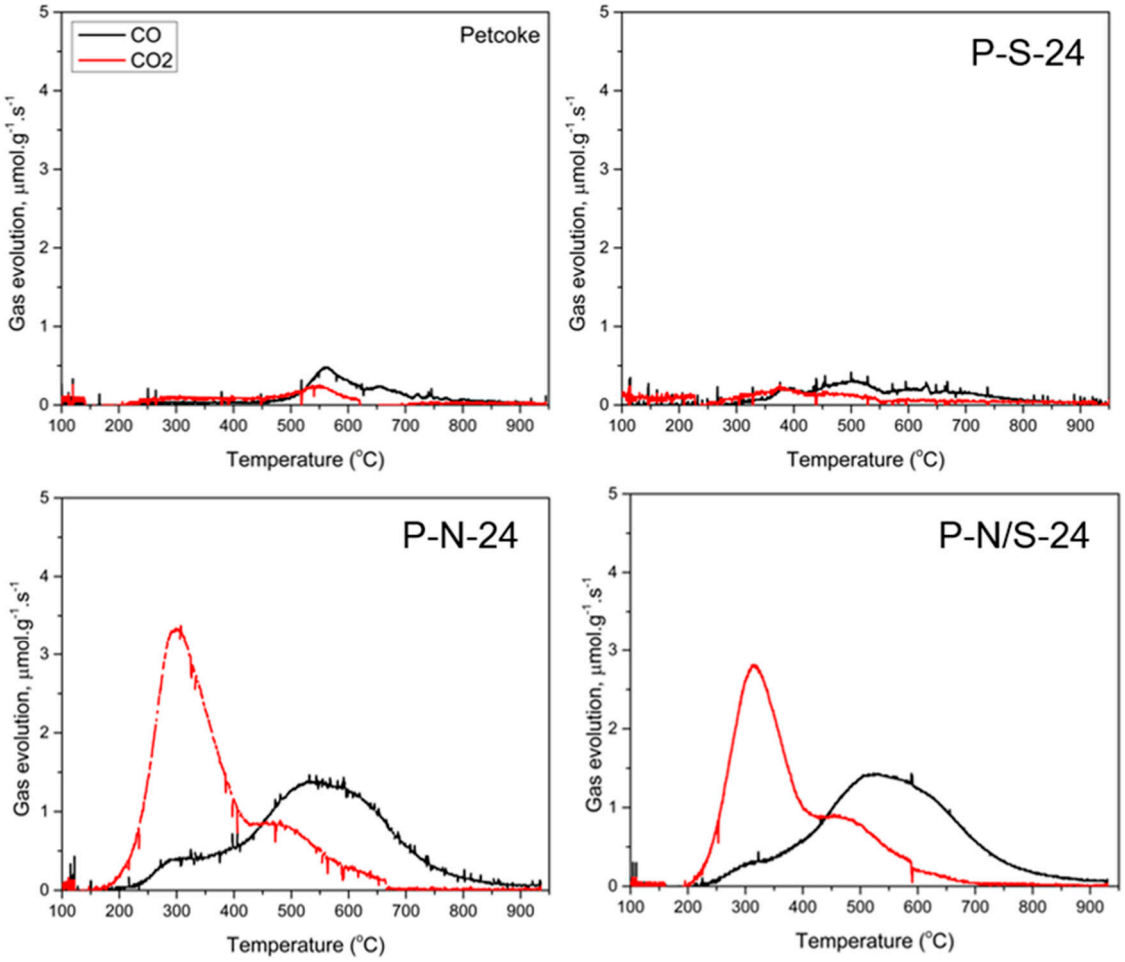

Figure S1. CO and CO_2 temperature-programmed decomposition profiles of petcoke samples before and after acid treatments.

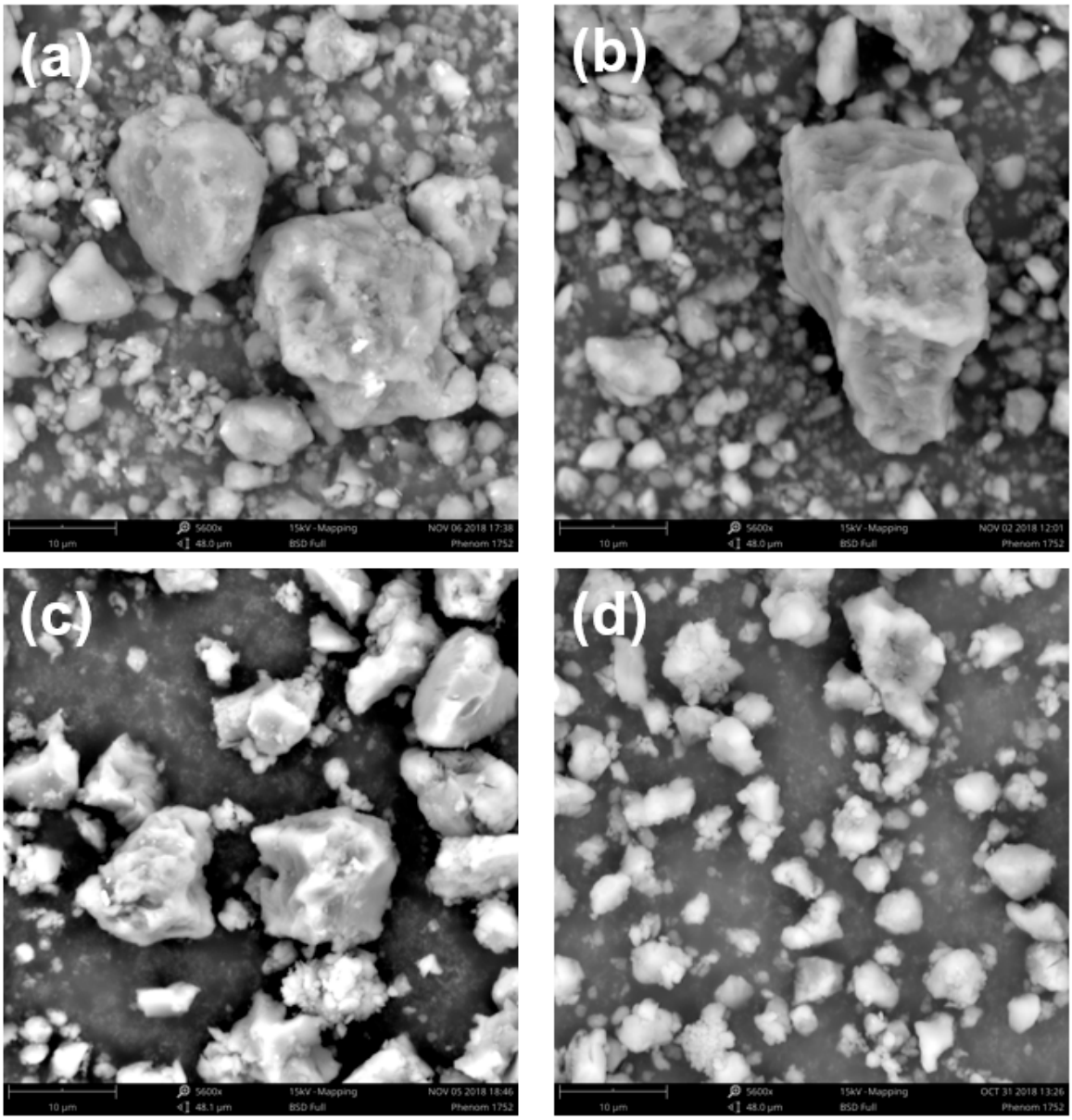

Figure S2. SEM images of (a) Petcoke; (b) P-S-24; (c) P-N-24; (d) P-N/S-24.

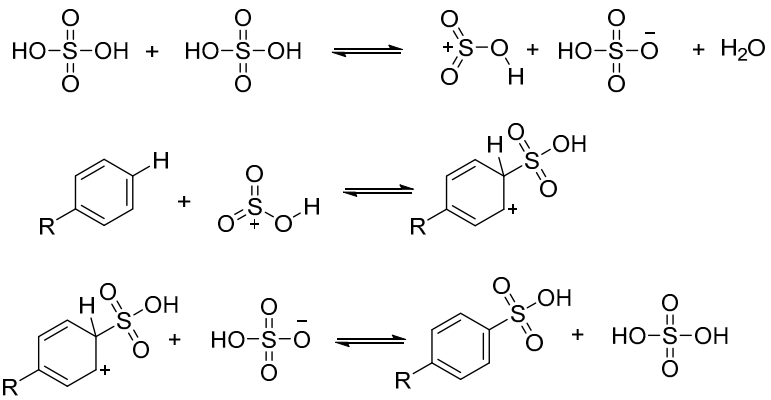

Figure S3. Scheme of aromatic sulfonation with sulfuric acid treatment.

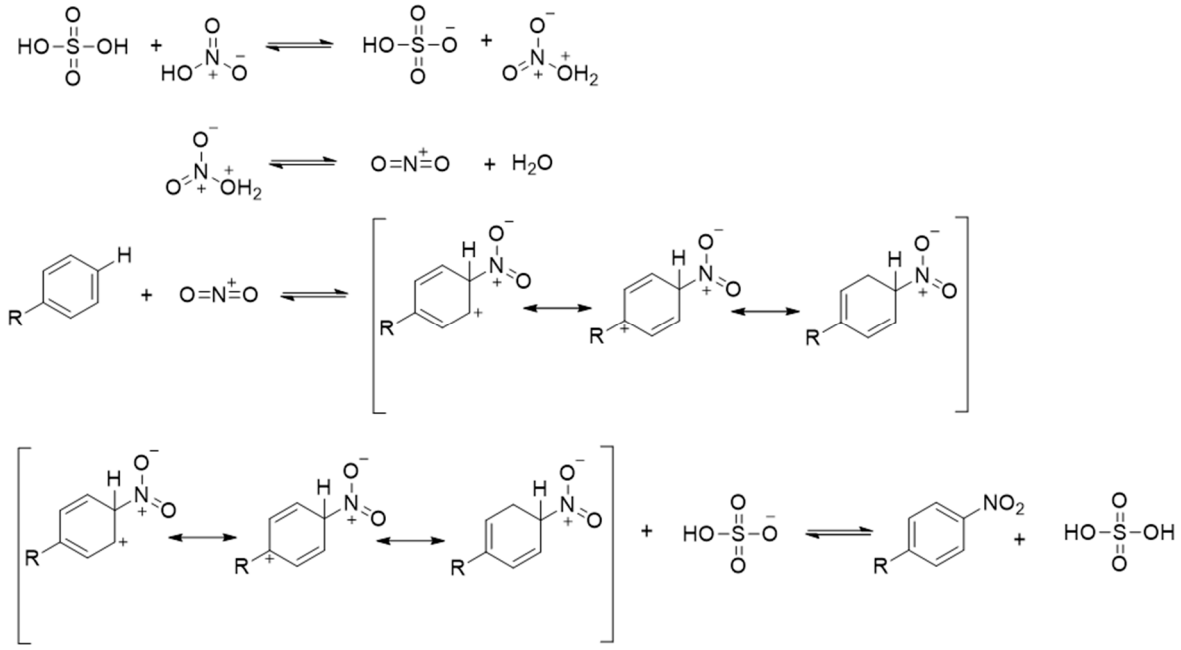

Figure S4. Scheme of aromatic nitration with nitric acid treatment.

References

1. Gorgulho, H.F.; Mesquita, J.P.; Gonçalves, F.; Pereira, M.F.R.; Figueiredo, J.L. Characterization of the surface chemistry of carbon materials by potentiometric titrations and temperature-programmed desorption. *Carbon N. Y.* **2008**, *46*, 1544–1555.
2. Li, N.; Ma, X.; Zha, Q.; Kim, K.; Chen, Y.; Song, C. Maximizing the number of oxygen-containing functional groups on activated carbon by using ammonium persulfate and improving the temperature-programmed desorption characterization of carbon surface chemistry. *Carbon N. Y.* **2011**, *49*, 5002–5013.