[Supporting Information]

Selective Adsorption of Carbon Dioxide by Carbonized Porous Aromatic Framework (PAF)

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Prediction of adsorption of binary mixture by IAST theory

The excess adsorption data for pure CO_2, N_2, H_2 and CH_4 measured at 273 K, were first converted to absolute loadings, along with the Peng-Robinson equation of state. In order to perform the IAST calculations, the single-component isotherms should be fitted by a proper model. The dual-site Langmuir-Freundlich (DSLF) adsorption model is adopted to correlate the pure-component equilibrium data and further predict the adsorption of mixtures. The DSLF model is given by

$$N^\circ(f) = \frac{N_1 k_1 f^{n_1}}{1 + k_1 f^{n_1}} + \frac{N_2 k_2 f^{n_2}}{1 + k_2 f^{n_2}}$$

(1)

where f is the fugacity of bulk gas at equilibrium with adsorbed phase, N_i, k_i and n_i are model parameters of maximum adsorption amount at site i (i=1 or 2), the affinity constant, and the deviation from the simple Langmuir equation, respectively.

Based on the above model parameters of pure gas adsorption, we used the IAST model, which was proposed by Myer and Prausnitz in 1965 to predict the multi-component adsorption. Analogous to Raoult's law for vapor-liquid equilibrium, the IAST assumes that the adsorbed solutions are ideal and all activity coefficients in the adsorbed phase are unity. Thus, the adsorption equilibrium between adsorbed and gas phases will lead to the following equation

$$P y_i \phi_i = x_i f_i^\circ(\pi)$$

(2)

where f_i^o is the fugacity of the equilibrium gas phase corresponding to the spreading pressure π for the adsorption of pure gas i, φ_i is the gas fugacity coefficient of component i calculated by PR equation of state (EOS), and x_i and y_i are the molar fraction of component i at the adsorbed and bulk phases, respectively. The binary gas mixing process is carried out at constant spreading pressure π and indicated by

$$\int_0^{f_1^\circ} N_1^\circ(f_1) d\ln f_1 = \int_0^{f_2^\circ} N_2^\circ(f_2) d\ln f_2$$

(3)

where the single-component adsorption amount and selectivity are further obtained from the above equation by numerical integration and root exploration.

To investigate the separation of binary mixtures, the adsorption selectivity is defined by

$$S_{i/j} = \frac{x_i / x_j}{y_i / y_j}$$

(4)

where the selectivity refers to the first component over the second one, and the x_i, x_j and y_i, y_j denote the molar fractions of species i, j in the adsorbed and bulk phases,

respectively.

Table 1. Parameters of Dual-site Langmuir-Freundlich equation by fitting adsorption of pure CO_2, CH_4, H_2 and N_2

adsorbent	adsorbate	N_1	k_1	n_1	N_2	k_2	n_2
	CH_4	3.6710	0.5954	1.2163	3.8842	4.0428	0.9341
Materials	CO_2	9.4546	3.1707	0.9909	2.7889	23.3745	0.8658
	H_2	0.1900	5.6742	1.3914	0.5664	5.1552	1.4159
	N_2	0.6514	5.6115	0.9427	0.0100	27.9497	13.0573
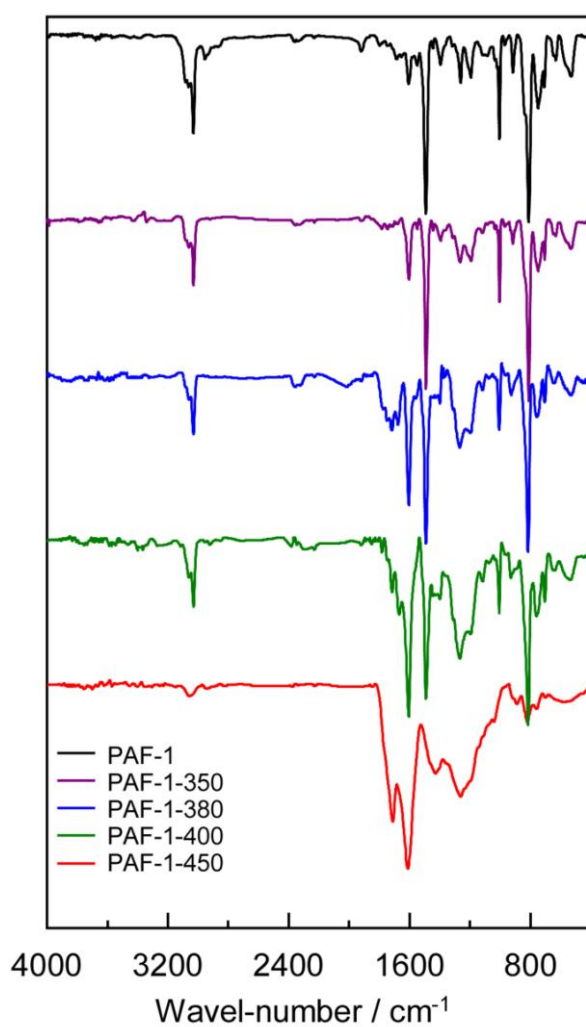
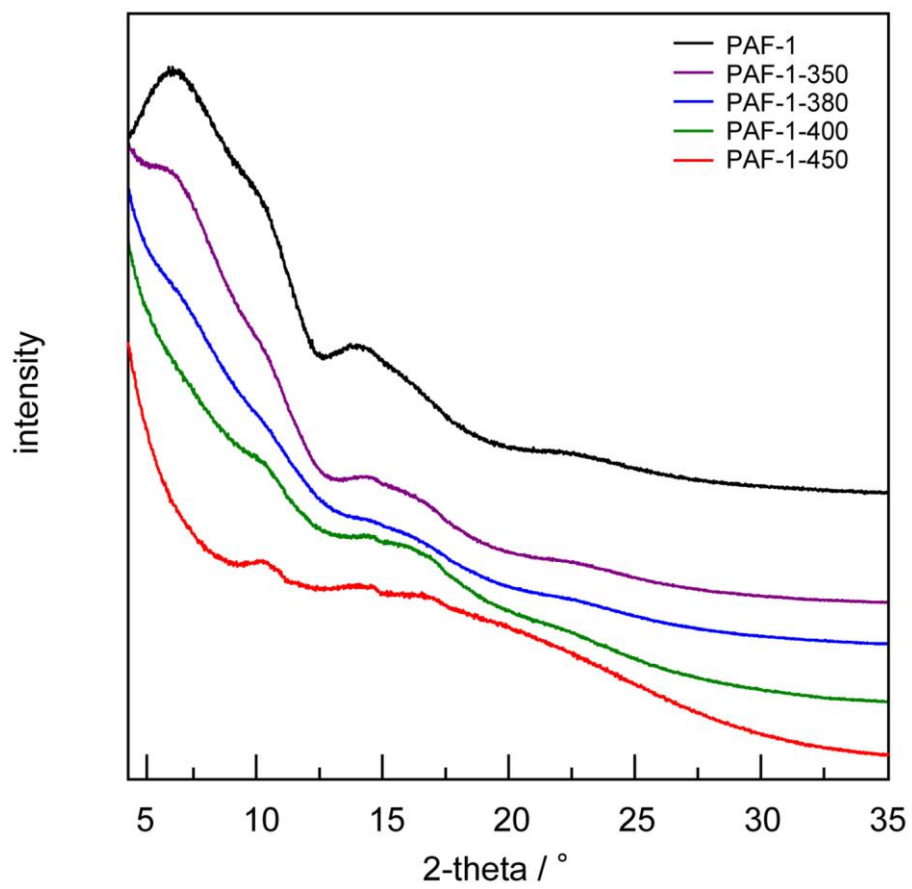***Figure S1.*** FTIR spectra of PAF-1 and the carbonized samples.

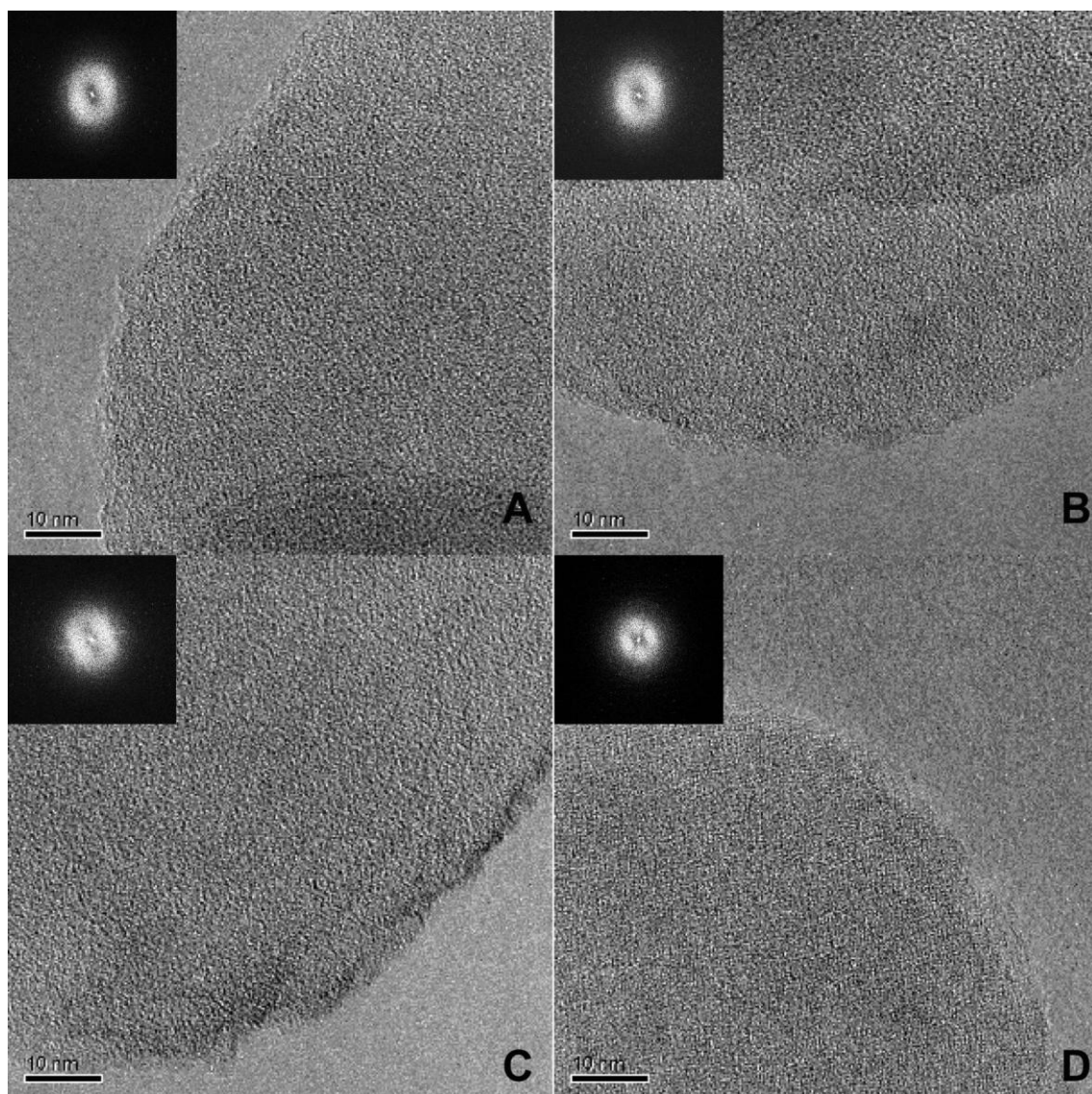***Figure S2.*** PXRD patterns of PAF-1 and the carbonized samples.

Figure S3. TEM images of PAF-1-350 (A), PAF-1-380 (B), PAF-1-400 (C) and PAF-1-450 (D). The inserts are the corresponding Fourier transforms of the TEM images.
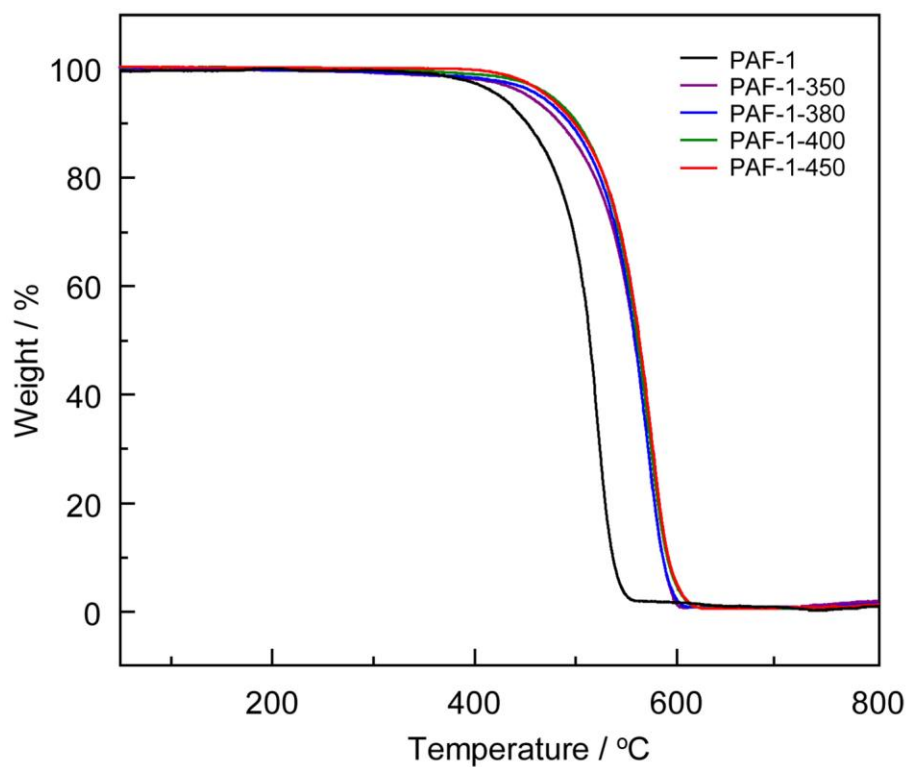
Figure S4. TGA plots of PAF-1 and carbonized samples at air condition with a ramp rate of 10 ^{o}C min^{-1}.
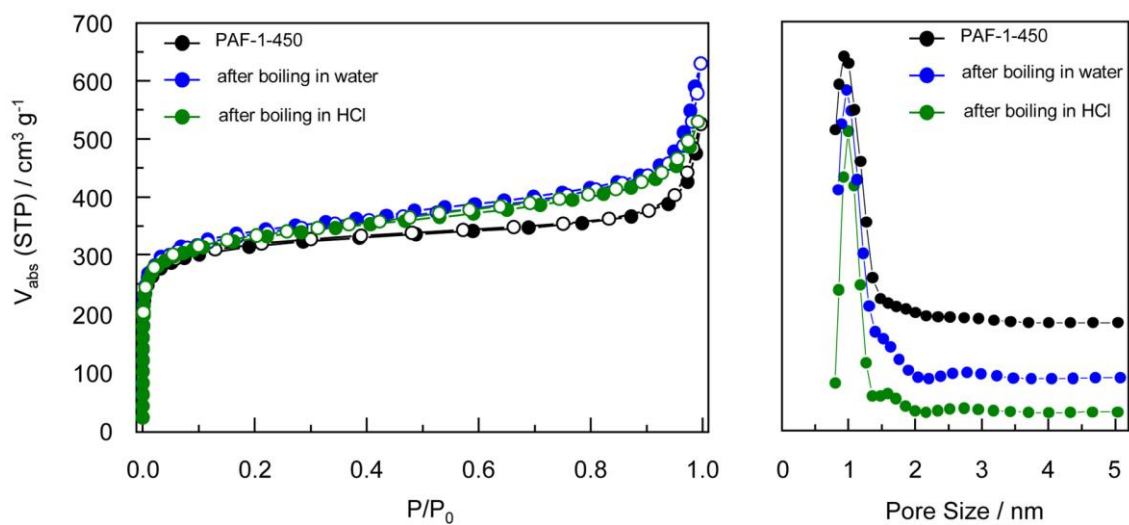
Figure S5. N_2 sorption isotherms and pore size distributions of PAF-1-450 after boiling in water (blue) and 1N HCl (olive) for seven days.
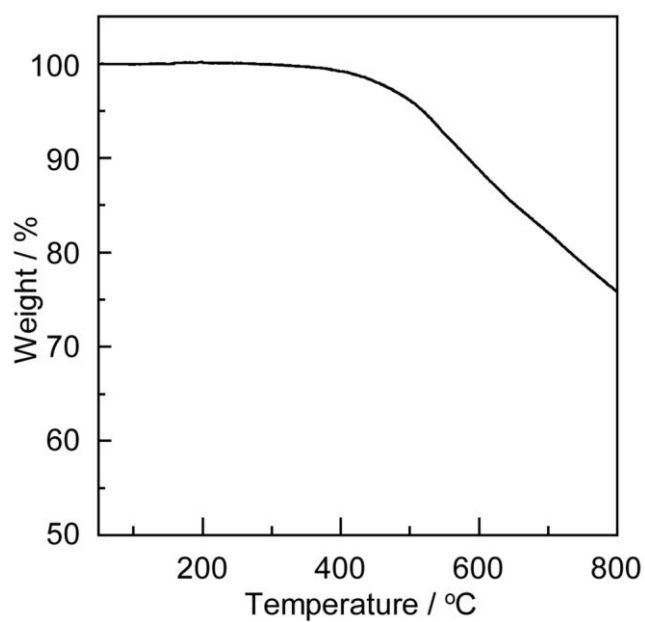

Figure S6. TGA analysis of PAF-1 in 99.999% N_2 with a ramp rate of 10 ^{o}C min^{-1}.