

Supplementary Materials

Evaluating Degradation of CO₂ adsorbents in Flue Gas from Bioenergy with Carbon Capture and Storage

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S1. Materials & Synthesis

1) Synthesis of Ni-MOF-74 (Ni₂dobdc)

The synthesis procedure from Dietzel et al. was followed.¹ Nickel (II) acetate tetrahydrate, Ni(CH₃CO₂) (CAS: 6018 89-9), was purchased from Sigma Aldrich, and 2,5-dihydroxyterephthalic acid, H₄(dobdc) (CAS: 610-92-4), was purchased from Alfa Aesar. 0.00500 mol of H₄(dobdc) was added to 17 mL of THF, and 0.010 mol of Ni(CH₃CO₂) was added to 17 mL water. They were mixed inside an autoclave with a Teflon liner. The sealed autoclave was heated at 110 °C in a preheated oven for 72 hrs. After 72 hrs., the reaction mixture was separated via centrifugation. A modified washing procedure was used due to the inability to remove all of the residual linker with only water washes. The solids were washed three times with dimethylformamide (DMF) and subsequently stirred for six days in methanol. Each wash consisted of a one-minute wash on a vortex mixer followed by 30 minutes in the centrifuge. The solids were dried under a 30 mmHg vacuum at 110 °C for 24 hours before use.

2) Synthesis of ZIF-8

The synthesis procedure from Zhang et al. was followed.² Zinc nitrate hexahydrate, Zn(NO₃)₂.6H₂O (CAS: 10196-18-8), was purchased from Alfa Aesar, and 2-methylimidazole (CAS: 693-98-1) was purchased from Sigma Aldrich. 0.00393 mol Zn(NO₃)₂.6H₂O was dissolved in 40 mL of MeOH, and 0.0197 mol of 2-methylimidazole was dissolved in 40 mL of MeOH. The mixture containing 2-methylimidazole was poured into a glass round bottom flask containing the Zn(NO₃)₂.6H₂O and MeOH mixture while stirring. The reaction mixture was stirred for 7 minutes and then separated via centrifugation. The solids were washed three times with MeOH. Each wash consisted of a one-minute vortex mix and 30 minutes of centrifugation. The solids were then dried under a 30 mmHg vacuum at 110 °C for 24 hours.

3) Fabrication of PEI-silica/cellulose acetate fibers

Cellulose acetate (CA, MW 50,000, CAS: 9004-35-7), poly(vinylpyrrolidone) (PVP, MW 55,000, CAS: 9003-39-8), and branched polyethyleneimine (PEI, MW 800, CAS: 25987-06-8) were purchased from Sigma Aldrich. Silica (C32) was obtained from W.R. Grace. Methanol and hexane were purchased from VWR and used without further purification.

The spinning and polyethyleneimine (PEI) infusion procedure from Labreche et al. was followed.³ A prime dope containing 115.5 g n-methyl-2-pyrrolidone (NMP), 15 g deionized (DI) water, 18.3 g cellulose acetate (CA), and 7.4 g polyvinylpyrrolidone (PVP) was prepared. The prime dope was homogenized on a heated roller for over 24 hours. A dispersion solution of 308.4 g NMP and 40.0 g DI water was mixed. Silica (87.4 g total) was added to the dispersion solution in four increments (21.0 g, 22.7 g, 23.0 g, and 20.7 g). A sonication horn and impeller were used to combine the silica and dispersion solution. After adding the silica, the prime dope was added to the silica/NMP/water mixture, and an impeller was used to stir the mixture for 1 hour. Then, PVP (19.5 g) and CA (48.4 g) were added.

The final dope was mixed via an impeller for 4 hours and then continued homogenizing on a heated roller overnight. The dope was loaded into a syringe pump on the custom spinning system and heated at 50 °C under a slight vacuum for 24 hours. The spinning conditions are listed in Table S2.

The fibers were soaked in water for three days, with the water changed each day to exchange the solvent completely. The fibers then underwent two 20-minute methanol solvent exchanges, one four hr. PEI/methanol soak (11% PEI/methanol), and a one hr. hexane solvent exchange. The fibers were then air-dried in a fume hood.

4) Preparation of UiO-66 and Zeolite 13X

UiO-66 was obtained from Inmondo Tech (Atlanta, GA, USA). The residual linker was removed with three 24-hour DMF washes followed by three 24-hour methanol washes. The UiO-66 was dried for 24 hours under a 30 mmHg vacuum. The 13X was purchased from Sigma Aldrich, and no modifications were made.

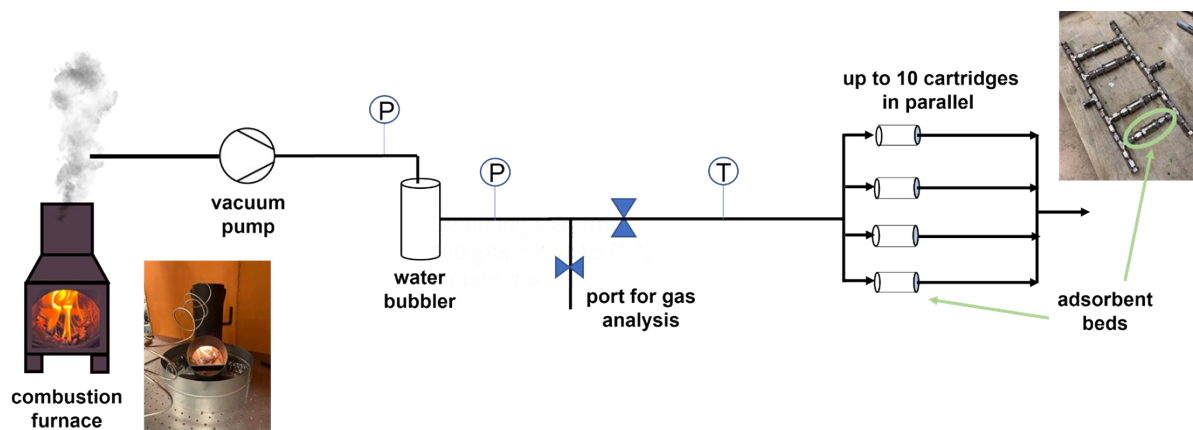


Figure S1. Diagram of experimental setup.

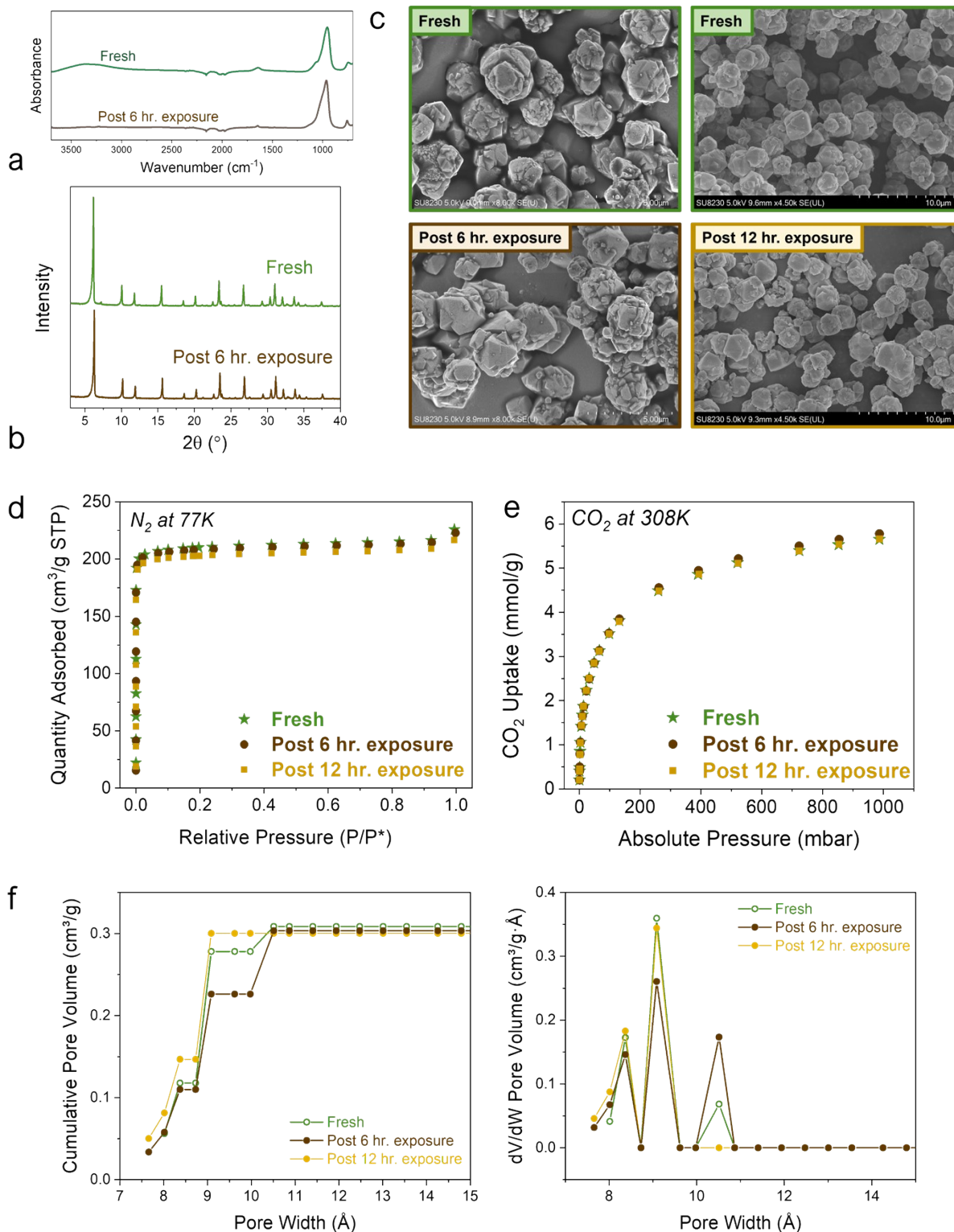


Figure S2. Zeolite 13X (a) ATR-FTIR spectra, (b) XRD spectra, (c) SEM images, (d) N_2 isotherm (77 K), (e) CO_2 isotherm (308 K), and (f) pore size distribution before and after 6-12 hrs. of exposure to biomass combustion flue gas. The minor reflection in the fresh data at a 2θ of 7.22° has been reported previously for commercial 13X, and it has also been observed to disappear after adsorption.[4-6]

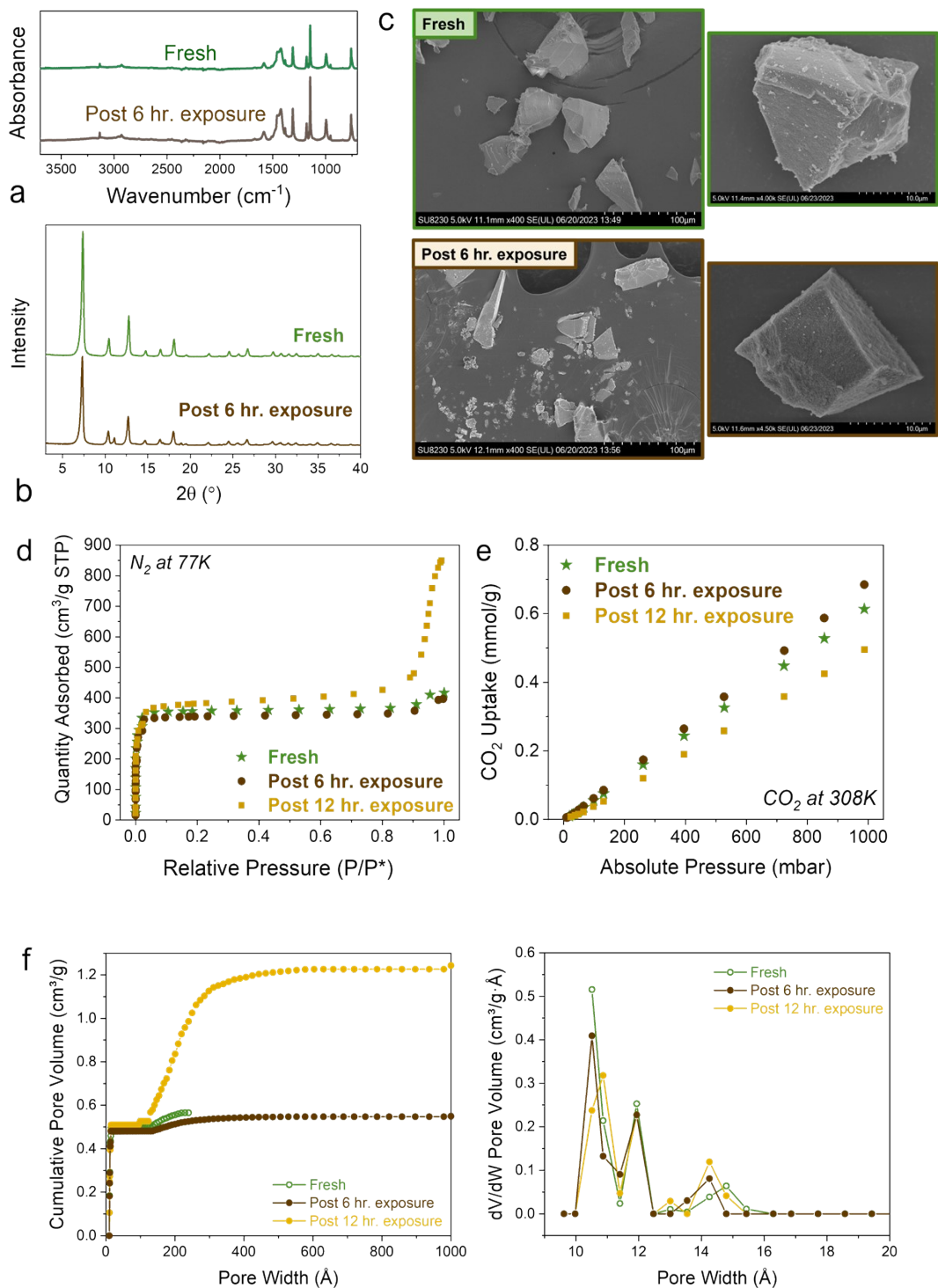


Figure S3. ZIF-8 (a) ATR-FTIR spectra, (b) XRD spectra, (c) SEM images, (d) N_2 isotherm (77 K), (e) CO_2 isotherm (308 K), and (f) pore size distribution before and after 6-12 hrs. of exposure to biomass combustion flue gas.

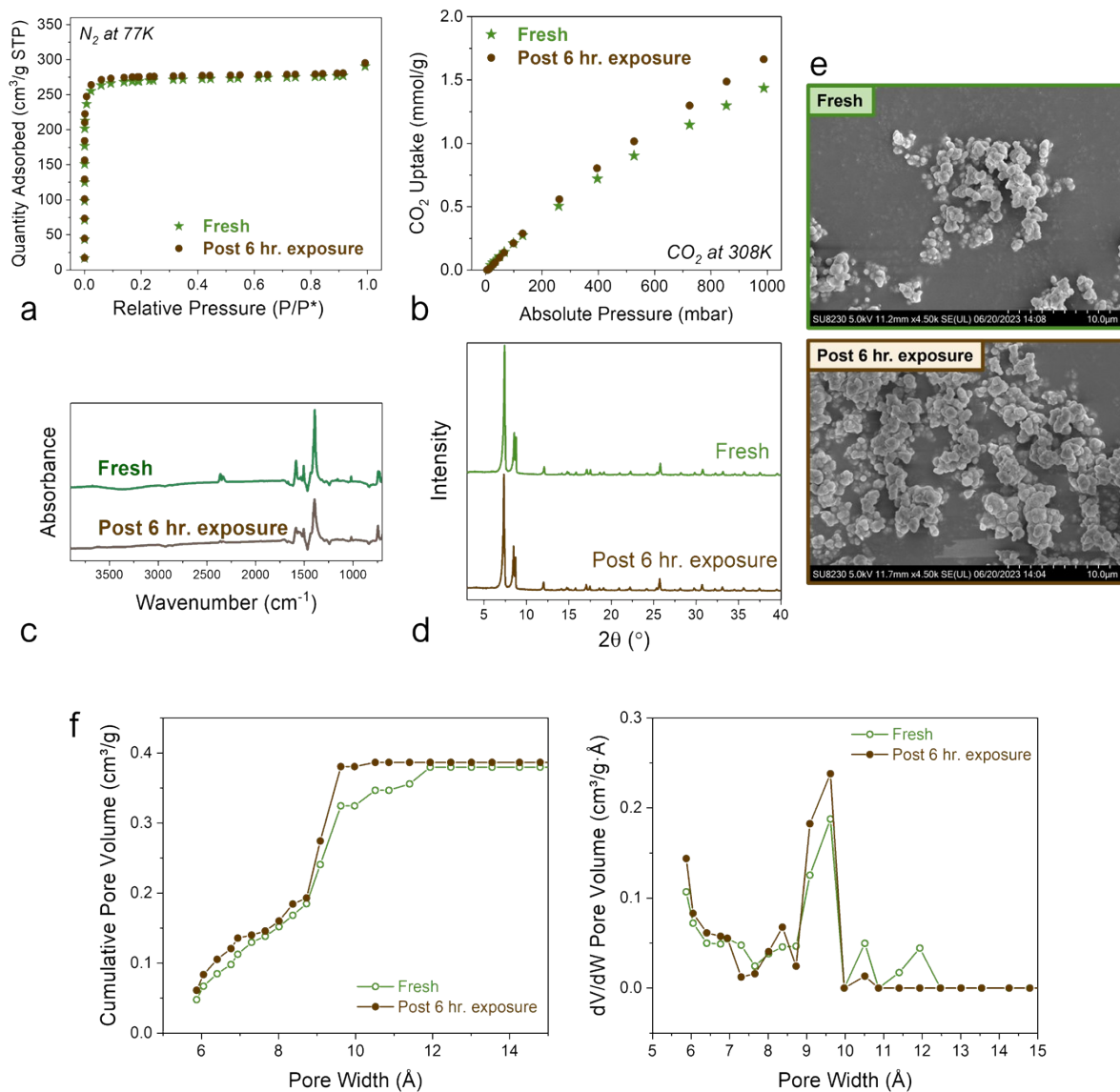


Figure S4. UiO-66 (a) N_2 isotherm (77 K), (b) CO_2 isotherm (308 K), (c) ATR-FTIR spectra, (d) XRD spectra, (e) SEM images, and (f) pore size distribution before and after 6 hrs. of exposure to biomass combustion flue gas.

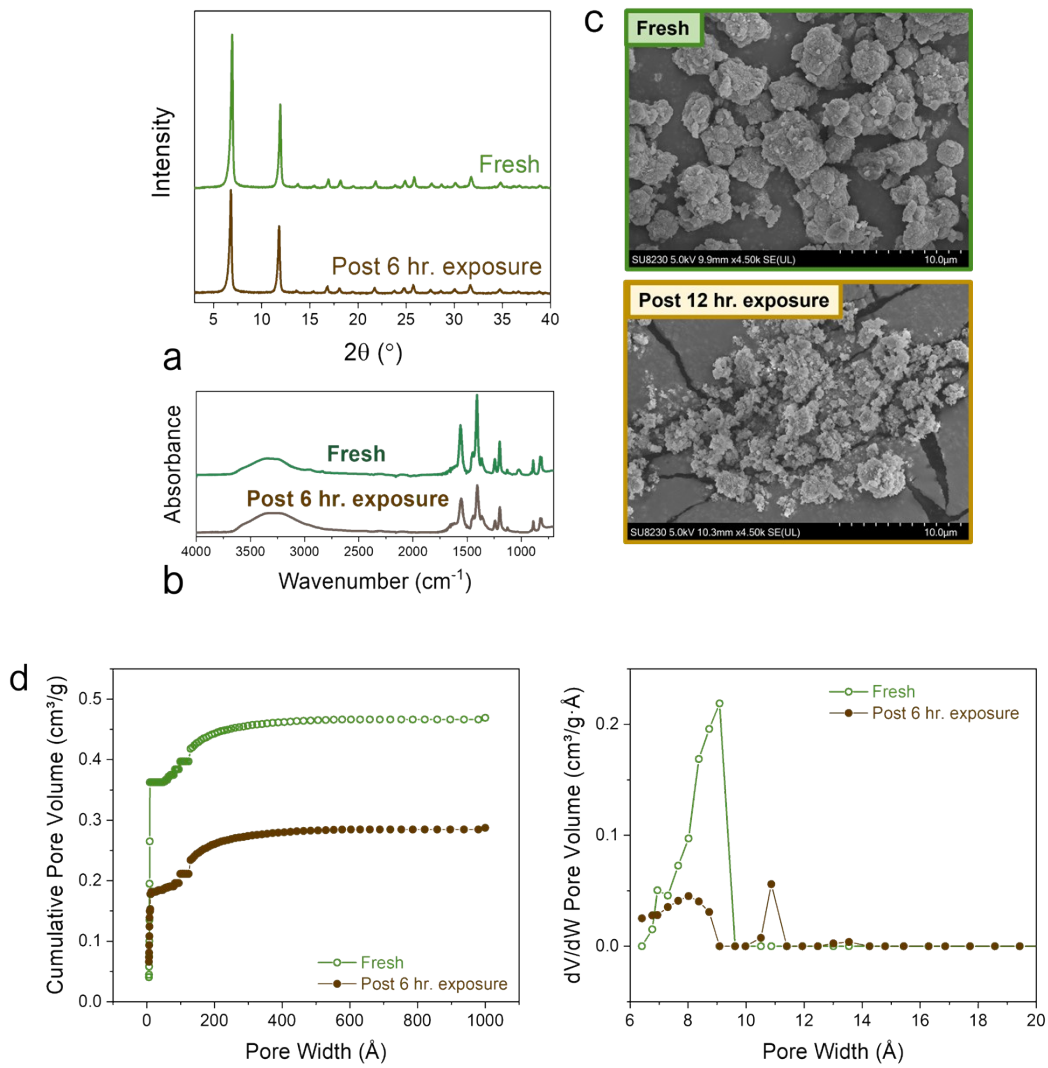


Figure S5. Ni MOF-74 (a) XRD spectra, (b) ATR-FTIR spectra, (c) SEM images, and (d) pore size distribution before and after 6-12 hrs. of exposure to biomass combustion flue gas.

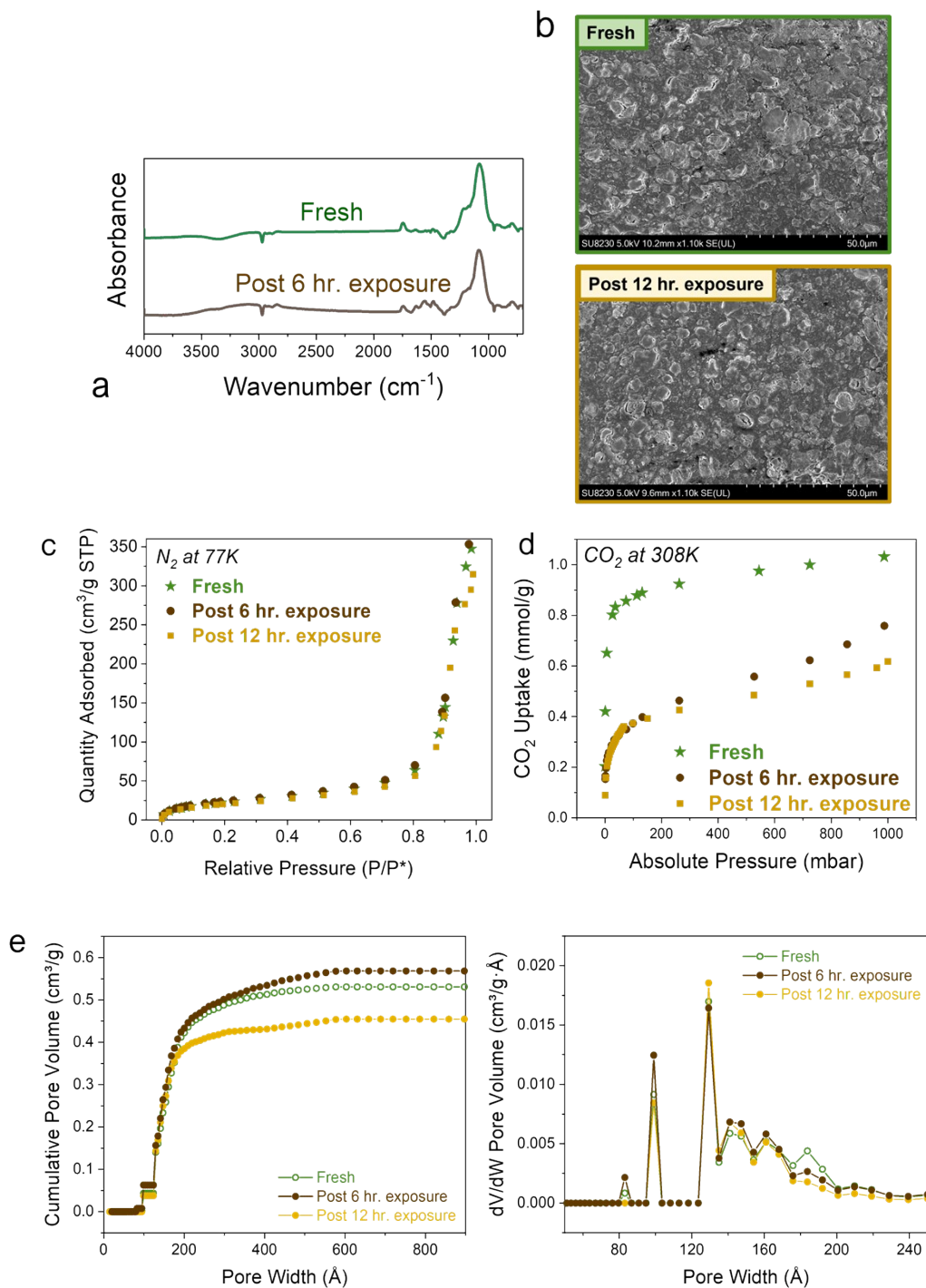


Figure S6. Polyethylenimine-infused silica/cellulose acetate fibers (a) ATR-FTIR spectra, (b) SEM images, (c) N_2 isotherm (77 K), (d) CO_2 isotherm (308 K), and (e) pore size distribution before and after 6-12 hrs. of exposure to biomass combustion flue gas.

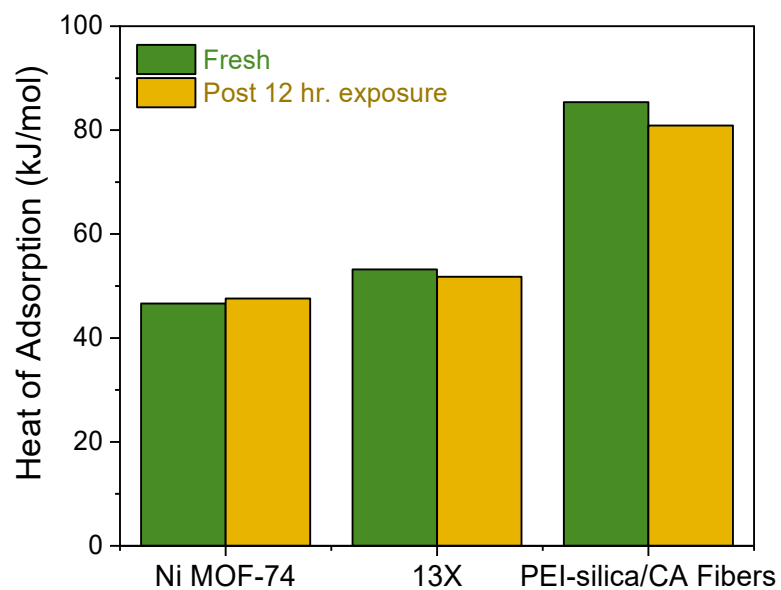


Figure S7. Heats of adsorption measured via TGA-DSC for Ni MOF-74, 13X, and PEI-silica/CA fibers before and after 12 hrs. of exposure to biomass combustion flue gas.

Table S1. Activation conditions prior to volumetric adsorption experiments.

Sample	Temp. (°C)	Time (hrs.)
PEI-silica/CA fibers	110	12
ZIF-8	150	12
Ni MOF-74	150	12
Zeolite 13X	300	12
UiO-66	180	12

Table S2. Spinning conditions for PEI-silica/CA fibers.

Parameter	Value
Bath temperature	40 °C
Line temperature	50 °C
Spinneret temperature	50 °C
Pump temperature	50 °C
Axis speed	50 mm/min
Drum speed	20,000 mm/min
Dope flow rate	200 mL/min

Table S3. Compositions of zeolite 13X from XPS before and after 12 hr. exposure.

Zeolite 13X		
Element	Atomic %	
	Fresh	Post 12 hr. exposure
O (1s)	54.95 ± 0.34	56.56 ± 0.30
Si (2p)	17.01 ± 0.14	17.05 ± 0.21
Al (2p)	11.90 ± 0.27	12.11 ± 0.04
Na (1s)	10.55 ± 0.05	11.36 ± 0.16
C (1s)	5.02 ± 0.35	2.29 ± 0.40
Cl (2p)	0.57 ± 0.05	0.63 ± 0.00

Table S4. Compositions of ZIF-8 from XPS before and after 12 hr. exposure.

ZIF-8		
Element	Atomic %	
	Fresh	Post 12 hr. exposure
C (1s)	61.44 ± 1.47	58.41 ± 0.20
N (1s)	25.48 ± 1.31	29.02 ± 0.82
Zn (2p3)	8.31 ± 0.24	7.56 ± 0.08
O (1s)	4.77 ± 0.25	5.01 ± 0.55

Table S5. Compositions of Ni MOF-74 from XPS before and after 12 hr. exposure.

Ni MOF-74		
Element	Atomic %	
	Fresh	Post 12 hr. exposure
C (1s)	57.95 ± 0.09	56.89 ± 0.52
O (1s)	30.11 ± 0.18	31.46 ± 0.46
Ni (2p3)	7.37 ± 0.16	7.47 ± 0.38
N (1s)	4.57 ± 0.28	4.20 ± 0.32

Table S6. Compositions of PEI-silica/CA fibers from XPS before and after 12 hr. exposure.

PEI-silica/CA fibers		
Element	Atomic %	
	Fresh	Post 12 hr. exposure
C (1s)	49.78 ± 1.30	51.54 ± 0.52
O (1s)	29.37 ± 0.44	33.75 ± 2.12
Si (2p)	7.55 ± 1.26	6.86 ± 0.67
N (1s)	13.30 ± 0.38	6.39 ± 0.14
F (1s)	Not detected	1.09 ± 0.54
Ca (2p)	Not detected	0.38 ± 0.54

Table S7. Literature values for dry and humid CO₂ uptakes of sorbents.

Sorbent	CO ₂ conc.	Temp.	CO ₂ uptake (dry)	Humidity	CO ₂ uptake (humid)	Ref.
13X	15%	50°C	1.18 mmol/g	20.5% RH (1.38%)	1.04 mmol/g	7
				40.9% RH (2.75%)	0.96 mmol/g	
61.7% RH (4.13%)	0.95 mmol/g					
81.9% RH (5.51%)	0.91 mmol/g					
99.9% RH (6.89%)	0.88 mmol/g					
	12%	30°C	0.29 kg/hr/kg	95% RH (3.4%)	0.23 kg/hr/kg	8
ZIF-8	10%	35°C	0.1 mmol/g	50% RH	0.1 mmol/g	9
	100%	25°C	0.75 mmol/g	50% RH	0.43 mmol/g	10
UiO-66	100%	27°C	1.7 mmol/g	1-4 wt.%	2.0 mmol/g	11
				7 wt.%	1.6 mmol/g	
Ni MOF-74	16.7%	25°C	2.85 mmol/g	70% RH	1.74 mmol/g	12
PEI-silica/CA fibers	10%	35°C	1.1 mmol/g	100% RH	>0.9 mmol/g	3

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