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ARTICLE

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

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The potential degradation of CO₂ adsorbents in Bioenergy with Carbon Capture and Storage (BECCS) was investigated through direct exposure to biomass combustion flue gas. Pre- and post-exposure characterization after 6-12 hours of exposure provided valuable insight into how common adsorbents would realistically perform in the BECCS process. The stability of zeolites and robust ZIFs was confirmed, but some unanticipated degradation mechanisms of less-stable MOFs and amine-based materials were also revealed, including pore fouling and chemical poisoning. The results emphasize the need for stability evaluations of adsorbents in comprehensive flue gas mixtures and suggest relationships between sorbent structure and degradation mechanism and extent.

Introduction

CO₂ capture technologies could mitigate the rising global temperatures associated with increasing atmospheric CO₂ levels. However, even if CO₂ emissions completely stopped today, the effects of atmospheric CO₂ would remain for at least 1,000 years.¹ Negative emission technologies (NETs), which reduce CO₂ already in the atmosphere, are vital for stabilizing the temperature. Indeed, most emissions pathways that can successfully limit global temperature increase employ NETs, and most include Bioenergy with Carbon Capture and Storage (BECCS) to some degree.² BECCS has three main components: (1) biomass that captures atmospheric CO₂ as it grows, (2) combustion of biomass for energy production, and (3) CO₂ capture from the combustion flue gas. BECCS is a subset of Biomass Carbon Removal and Storage (BiCRS), which describes any process that uses biomass to remove CO₂ from the atmosphere and then stores the CO₂.³ The distinction for BECCS is that the biomass is converted to energy, which generates CO₂ emissions that must be captured. It is important that BiCRS feedstocks are grown and harvested in a sustainable way that promotes enhancements in biodiversity.⁴⁻⁶

Current BECCS processes use liquid amine solvents in the CO₂ capture unit, but solid adsorbents could improve the technology by lowering the required regeneration energy and removing the use of corrosive solvents.^{7, 8} While it is likely that some of the many adsorbents already proposed for other post-combustion CO₂ capture processes could be used for BECCS, it is not clear which adsorbents will be stable in the flue gas long

enough to be economically viable. Azarabadi and Lackner determined that solid adsorbents must maintain stability for tens to hundreds of thousands of cycles to be economically viable.⁹ Similarly, we used a techno-economic model of the BECCS process to determine that adsorbents should have a lifetime of at least two years and an exponential half-life of 1.3 years when a degradation-induced capacity loss is considered.¹⁰

It is unknown how sorbents will degrade in the BECCS process because there has been no experimental research evaluating solid adsorbents specifically for BECCS, to the best of our knowledge. There have been numerous publications on the degradation of materials after specific contaminants in the flue gas, such as water, NO_x, and SO_x,¹¹⁻¹⁸ but adsorbents have not been exposed to the flue gas from biomass combustion. BECCS flue gas will contain more and different particulates from coal combustion and higher amounts of NO_x.¹⁹ A wide array of ionic and elemental species are found in wood combustion emissions, including chloride, nitrate, sulfate, ammonium, silicon, sulfur, chlorine, potassium, zinc, calcium, bromine, rubidium, and lead.²⁰ It is unknown how many of these contaminants will affect the CO₂ adsorption performance of materials, especially on the time scales needed for sorbent economic viability. Thus, it is critical that adsorbents be tested not only in the idealized and multi-component separation experiments but also realistic and process streams with all components included.²¹

As a preliminary exploration of the degradation of adsorbents in BECCS flue gas, we directly exposed adsorbents commonly reported in literature to flue gas from biomass combustion. A rocket stove was used to burn hickory wood pellets, and then the resultant flue gas was pumped through a water wash column and then over the adsorbents in parallel for 6 - 12 hours (Fig. S1). Pre- and post-exposure characterization of the adsorbents provides valuable insight into how these materials would realistically perform in a BECCS process.

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Experimental

Materials and Synthesis

Nickel (II) acetate tetrahydrate, 2-methylimidazole, cellulose acetate (MW 50,000), and poly(vinylpyrrolidone) (MW 55,000), molecular sieves 13X, and branched polyethyleneimine (PEI, MW 800) were purchased from Sigma Aldrich. Zinc nitrate hexahydrate and 2,5-dihydroxyterephthalic acid were purchased from Alfa Aesar. Silica (C32) was obtained from W.R. Grace. UiO66 was obtained from Inmondo Tech. Dimethylformamide, methanol, and hexane were purchased from VWR and used without further purification.

Detailed synthesis and fabrication procedures are provided in section S1 in the Supplementary Information. Synthesis procedures from Dietzel et al. and Zhang et al. were followed for Ni-MOF-74 and ZIF-8.^{22, 23} The spinning and polyethyleneimine (PEI) infusion procedure from Labreche et al. was followed.²⁴

Biomass Combustion Exposure Experiments

Kingsford 100% Natural Hickory Wood BBQ Smoker Grilling Pellets were purchased from Home Depot, and Pit Boss 100% All-Natural Hickory BBQ grilling pellets were purchased from Walmart. The wood source for both brands was the United States, and the pellets contain no fillers, artificial flavors, binders, dyes, chemical additives, or oils (i.e., 100% hickory wood). A Bruntmor Rocket Stove was used to burn the pellets. A Kingsford quick light fire starter (all-natural hardwood and paraffin) was used to start the fire in the stove, but the adsorbents were not exposed to the smoke until the fire starter was gone and only the hickory pellets remained.

As shown in Figure S1, a coiled 1/8" stainless steel tube was placed above the stove top, and a Thomas vacuum pump (1/10 hp, 12V DC, 22.2 in. Hg) was used to pump smoke from the stove. The flue gas was passed through an Ace Glass impinger (Greenburg-Smith, 500mL bottle, 2.3mm ID orifice impinging plate stem) with pressure gauges on the inlet and outlet. The flue gas temperature was measured with an inline thermometer and was ambient at the point of the adsorbents (between 10 – 25 °C).

The sorbents were packed into ¼" Swagelok particulate filters. The filters were used only as holders; the sorbent was faced toward the flow, so the filter was not removing anything from the flue gas before it touched the sorbents. The sorbents were parallel in the line of flow.

Characterization

SEM Prior to scanning electron microscopy (SEM), materials were applied onto double-sided conductive carbon tape and sputter coated using a Hummer VI Sputter with a gold target, Argon gas, and 25 mA voltage for 1 min. 30 seconds. SEM was performed using a Hitachi SU8230 cold-field-emission scanning electron microscope. An accelerating voltage of 5 kV and emission current between 10 – 15 μ A were used.

PXRD Powder X-ray diffraction (XRD) patterns of samples were collected using a Panalytical X'Pert Pro Alpha-1 diffractometer

at 40 kV and 40 mA (Cu K α source, λ = 1.541 nm). The patterns were collected with a step size of 0.0167° 2 θ and scan time of 19.685 s/step over a 2 θ range of 3–60°.

ATR-FTIR Fourier transform spectroscopy was performed on a Thermo Fischer Scientific Nicolet iS10 IR spectrometer. Spectra were collected with 32 scans at a resolution of 4 cm⁻¹.

Volumetric gas sorption N₂ adsorption measurements were measured at 77 K on a Microtrac Belsorp Max. The equilibrium condition was a pressure change of less than 0.3% for 300 seconds. The activation temperature and time of each material is listed in Table S1. Pore size distribution was evaluated using NLDFT with a slit geometry.

Single-component CO₂ adsorption isotherms were measured at 308K on a Micromeritics ASAP 2020 instrument. The equilibration condition was a pressure change per time interval (first derivative) less than 0.01% of the average pressure, with a time interval of 35 seconds. The activation temperature and time of each material are listed in Table S1.

TGA-MS Thermogravimetric analysis was performed on a TA Instruments TGA Q500. The outlet of the TGA furnace was connected to a Pfeiffer Omnistar GSD 320 mass spectrometer via a heated (100°C), 1/8" stainless steel tube. The purge gas was N₂, with a mass flow of 90 mL/min and balance flow of 10 mL/min. The furnace and lines were purged for 4 hours before the sample was loaded, and then an additional 30 minutes after the sample was loaded. The temperature was increased to 100 °C at 10 °C/min and then held isothermally for 60 min. The mass flow was then reduced to 25 mL/min, and the temperature was ramped to 250 °C at 10 °C/min. The temperature was held isothermally for 30 min.

TGA-DSC Heats of adsorption were measured with a thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC) system (STA 449 F3 Jupiter/NETZSCH).

Results & Discussion

A suite of characterization techniques was utilized to test for various degradation mechanisms, including N₂ and CO₂ isotherm measurements (volumetric), attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, scanning electron microscopy (SEM), and x-ray diffraction (XRD). The combination of these techniques enables insight into each material's structure, porosity, active sites, and bonding before and after flue gas exposure. The adsorbents were chosen to include both physisorbents and chemisorbents to evaluate the effects of degradation on both types of adsorption.

Upon exposing adsorbents to BECCS flue gas, varying levels and types of degradation were observed. The degradation can be classified into subsets based on terminology borrowed from catalysis, including (1) no degradation, (2) chemical degradation (i.e., poisoning, reaction, loss of active site), and (3) mechanical degradation (i.e., fouling, attrition).²⁵ The results highlight the range of degradation mechanisms in BECCS based on structural and compositional differences between adsorbents.

Three adsorbents tested, zeolite 13X, ZIF-8, and UiO-66, showed minimal to no degradation after six hours of flue gas exposure. The N₂ and CO₂ isotherms of 13X and ZIF-8 are shown

in Figure 1. The cryogenic N_2 isotherm probes changes in porosity, while the CO_2 isotherm probes both active sites and porosity. For 13X, there is no evidence of degradation in either isotherm or any of our other analyses even when challenged for an additional 6 hours (Fig. S2), highlighting the stability of zeolite 13X under these conditions. Indeed, the stability of 13X is expected as it has been well-documented in both dry and humid gas mixtures.^{26, 27} Moreover, Hu et al. observed minimal loss of CO_2 capacity after a 24-hr. exposure to simulated flue gas, with little change after an additional 36 hours.²⁸ Our results show that the additional contaminants found in the complex BECCS flue gas mixture do not reduce the stability of 13X on these time scales. However, despite its stability, the CO_2 capacity of 13X is reduced in humid feeds (Table S7), and therefore, it would not be suitable for humid BECCS feeds without significant and costly pre-treatment.^{27, 29-31} This emphasizes that stability is just one metric and cannot be used alone to predict the economic feasibility of a sorbent.

Both ZIF-8 and UiO-66 are also considered stable in humid conditions but have some loss of capacity in humid feeds as well (Table S7).³²⁻³⁵ Specifically, ZIF-8 is stable in humid environments due to its hydrophobic pore and strong metal-linker bonding.^{36, 37} However, 5-10 days of exposure to humid 10-20 ppm SO_2 can lead to structural degradation of ZIF-8 through H_2SO_4 binding to the Zn.³⁸⁻⁴⁰ Some porosity loss has also been observed after 3 days of humid CO_2 exposure.⁴¹ Despite the presence of SO_2 , CO_2 , and humidity in biomass combustion flue gas, the characteristic loss of pore volume and surface area was not observed for ZIF-8 after 6 hours, likely due to a much shorter exposure time. Using the porosity loss model developed by Bhattacharyya et al.⁴¹, the predicted porosity loss of ZIF-8 after 6 hours of exposure to approx. 10 ppm SO_2 is 4-5%, consistent with the slight decrease observed in N_2 physisorption (Fig. 1c). This result suggests that their model developed in a multi-component system does indeed translate to a complex process stream. We observed an additional reflection at 11° in

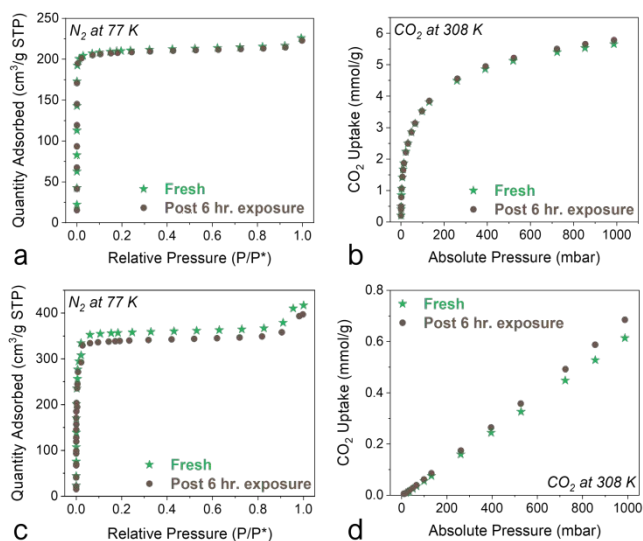


Fig. 1 (a) Zeolite 13X N_2 isotherm (77 K), (b) Zeolite 13X CO_2 isotherm (308 K), (c) ZIF-8 N_2 isotherm (77 K), and (d) ZIF-8 CO_2 isotherm (308 K) before ("fresh", green stars) and after 6-hour exposure to biomass combustion flue gas ("post 6 hr. exposure", brown circles).

the PXRD pattern (Fig. S3b) after exposure, which was also reported after the three-day humid CO_2 exposure, further indicating degradation could be starting at 6 hrs. of exposure. Interestingly, the CO_2 uptake after exposure is slightly higher for both ZIF-8 (Fig. 1d) and UiO-66 (Fig. S4b) after the 6-hour exposure. The increased uptake could result from missing linker defects, which have been shown to increase porosity and CO_2 uptake for some MOFs.⁴²⁻⁴⁷ However, defects can also increase the adsorption of contaminants and overall instability.^{47, 48} An additional 6 hours of exposure led to reduced CO_2 uptake (Fig. S3e).

Several adsorbents showed signs of mechanical degradation. One form of mechanical degradation was fouling, i.e., species filling the pores of the adsorbent media. Since the samples are activated before N_2 or CO_2 adsorption measurements, only irreversible fouling is considered, i.e., not mitigated by regeneration under normal conditions. Ni-MOF-74 was one example of an adsorbent with suspected fouling. In Fig. 2a, a significant loss of pore volume (almost 50%) is observed via N_2 physisorption. In Fig. 2b, while the CO_2 capacities at low partial pressures are unchanged, the CO_2 capacity at high partial pressures is reduced. The adsorption at lower partial pressures can be attributed to chemisorption of CO_2 on the metal sites, and the adsorption at higher partial pressures is a combination of both physisorption and chemisorption. Thus, CO_2 physisorption is reduced due to the loss of pore volume based on the observed differences in the isotherm.

Moreover, there were no changes in the XRD patterns of Ni-MOF-74 after the 6-hour biomass flue gas exposure (Fig. S5a), which suggests that the MOF crystal structure was still intact. Additionally, FTIR showed no signs of degradation (Fig. S5b), supporting the hypothesis that the chemical adsorption sites (metal sites) and binding modes were not irreversibly affected by the exposure and explaining the consistent capacity at low

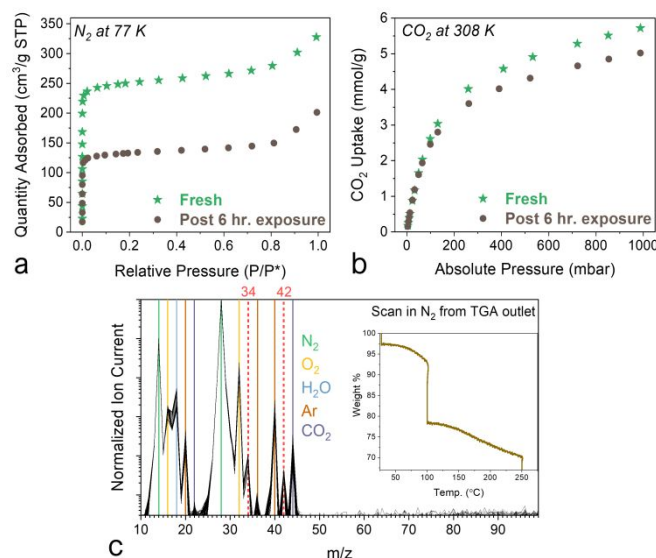


Fig. 2 Ni-MOF-74 (a) N_2 isotherm at 77 K and (b) CO_2 isotherm at 308 K before ("fresh", green stars) and after 6-hour exposure to biomass combustion flue gas ("post 6 hr. exposure", brown circles). (c) Mass spectrum measured from TGA outlet during heating of Ni-MOF-74 to 250 °C under N_2 . Weight % as a function of temperature is shown in inset.

partial pressures. However, it is likely that contaminants (such as SO_x and NO_x) did adsorb to the metal sites during the exposure but were removed during the regeneration before characterization.⁴⁹⁻⁵¹ While contaminant adsorption did not significantly affect the MOF's stability, it will affect its selectivity and overall feasibility in BECCS.

Ni-MOF-74 was chosen because of its increased stability in humid conditions compared to other metals in the series (e.g., Co and Mg).^{28, 52} However, this stability decreases rapidly as exposure time increases past three days.⁵³ The deactivation is significantly accelerated when humidity is combined with CO_2 resulting in an acidic environment.²⁸ Our flue gas was 100% RH when contacted with the adsorbents, but the XRD and FTIR spectra after exposure did not show evidence of structural decomposition caused by humidity. The exposure time was short enough to prevent decomposition by water; however, the humidity will likely play a more prominent role for this adsorbent during longer-term utilization in BECCS processes. MOFs with demonstrated instability in humidity (such as HKUST-1, MOF-5, DMOF-1, and Mg-MOF-74) will struggle in humid CO_2 streams without modification to the material or feed stream.^{32, 54-61}

To probe what species could be filling the Ni-MOF-74 pores, TGA-mass spectrometry (TGA-MS) was utilized (Fig. 2c). In TGA-MS, the temperature was slowly ramped under N_2 flow while the outlet gas was fed into the mass spectrometer for identification. The TGA simultaneously measured the decreasing sample weight. The decreasing sample weight between 100 and 250 °C (below the decomposition temperature of Ni-MOF-74) corresponds to additional desorption, and two m/z ratios were observed that could not be assigned to expected air or adsorption species (i.e., N_2 , Ar, CO_2 , H_2O , O_2), specifically 34 (minor) and 42. The m/z of 42 is likely C_3H_6 , a known component of wood combustion emissions.⁶² The m/z of 34 is tentatively assigned to H_2S ; while not an expected combustion product, it has been observed previously in raw tree wood and palm frond combustion emissions.⁶³

Chemical degradation was observed in some of the materials in the form of poisoning, or irreversible binding of species to the active sites. Polyethylenimine (PEI)-infused silica/cellulose acetate fibers are one example of an adsorbent with poisoning after the flue gas exposure. There was no noticeable reduction in the internal surface area of the fibers after the 6- or 12-hr. exposures (Fig. 3a, Fig. 6c). However, there

was a significant impact on the CO_2 uptake, with over 60% loss at lower partial pressures (Fig. 3b). In contrast to the Ni-MOF-74 example, the greater extent of capacity loss at lower partial pressures indicates that the binding sites for chemisorption were affected rather than physisorption in the pore volume. Thermogravimetric analysis showed no amine loss, further suggesting the amines were poisoned rather than volatilized, and a slight reduction in the heat of adsorption was observed after the 12-hr. exposure (Fig. S7).

Indeed, many reports in the literature indicate the impact of SO_x and NO_x poisoning of amine-based sorbents in post-combustion flue gas.^{13, 14, 16, 17, 64, 65} Amine-based sorbents rapidly lose most of their CO_2 capacity in SO_2 -containing flue gas due to the largely irreversible binding of SO_2 to active sites. These results can likely be extended to other branched polyamines and, more broadly, to all amine-based sorbents. One benefit of amine-functionalized supports is the possibility of replacing, recycling, or re-functionalizing the degraded amine without replacing the support.⁶⁶ The optimum replacement time can be determined from the measured degradation rate and other sorbent parameters.¹⁰

We previously determined that for BECCS to be economically feasible (defined by a levelized cost of CO_2 capture below $\$100/\text{t-CO}_2$), a sorbent must have a lifetime of at least two years and an exponential half-life of 1.3 years when a degradation-induced capacity loss is considered.¹⁰ When comparing these stability results to that metric, it is important to note that the 6-12 hours of exposure here does not directly correspond to 6-12 hours of process time. The experimental setup did not have the suite of flue gas clean-up techniques that could be implemented in an industrial process. While the bubbler did achieve some flue gas clean-up, some components are at higher concentrations than they would be in the industrial process, likely resulting in accelerated degradation (i.e., this 6-hr. exposure would correspond to many more exposure hours in an actual process). To compare the exposure time to process time, the ppm-days parameter discussed previously can be used. However, the observed degradation in the exposure experiments here was the result of only one adsorption step (the 6-12 hr. exposure) and one desorption step. Sorbents will be cycled much more frequently in the BECCS process and could exhibit more degradation as a result.

Conclusions

Pre- and post-exposure characterization of the sorbents revealed three responses to the flue gas exposure: no degradation, mechanical degradation, and chemical degradation. Zeolite 13X and UiO-66 demonstrated little change after exposure, and ZIF-8 showed noticeable degradation only after 12 hours of exposure. Ni-MOF-74 had a reduction in surface area after exposure, attributed to fouling or species filling the pores. The BECCS flue gas led to a significant reduction in the CO_2 capacity of PEI-infused silica/cellulose acetate fibers, likely due to SO_x poisoning of the amine sites. Overall, these results emphasize the need for stability evaluations of adsorbents in comprehensive flue gas mixtures rather than just

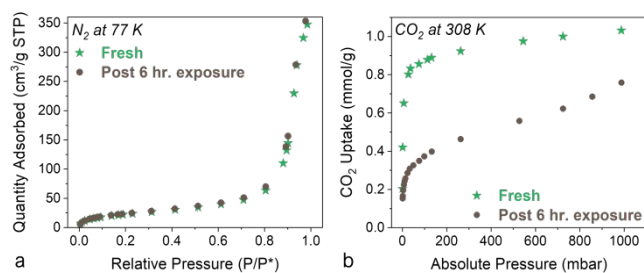


Fig. 3 Polyethylenimine-infused silica/cellulose acetate fibers (a) N_2 isotherm at 77 K and (b) CO_2 isotherm at 308 K before ("fresh", green stars) and after 6-hour exposure to biomass combustion flue gas ("post 6 hr. exposure", brown circles).

selected components.²¹ To enable economic feasibility of negative emission technologies such as BECCS, more long-term adsorbent stability research is vital, along with viable mitigation or regeneration strategies for adsorbents that suffer from degradation.

There are a few key limitations of this work. This is a preliminary evaluation of chemical and structural adsorbent degradation in a comprehensive and realistic BECCS flue gas, but more analysis will be necessary to determine detailed degradation mechanisms. Moreover, some components are at higher concentrations than they would be in the industrial process due to inadequate flue gas clean-up techniques, likely resulting in accelerated degradation (i.e., this 6-hr. exposure would correspond to many more exposure hours in an actual process). The experiments also correspond to only one adsorption-desorption cycle; more frequent cycles in BECCS could lead to enhanced degradation of some sorbents. Finally, the bench-scale combustion stove used here may not reach the temperatures necessary to replicate industrial biomass combustion, so the flue gas composition could differ in an industrial process. However, adsorbents that demonstrate stability in this setup will likely be stable in a more sophisticated BECCS process with appropriate pre-treatments. Future work should focus on expanding the adsorbent list and evaluating the adsorbents after longer exposure times. Accelerated aging testing can be employed to evaluate sorbent stability in reasonable time frames.⁶⁷⁻⁶⁹ Ultimately, these results highlight the range of possible degradation mechanisms in BECCS due to structural differences in adsorbents and emphasize the need for stability research and mitigation strategies.

Conflicts of interest

There are no conflicts to declare.

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