

Design of Amine-Containing Nanoporous Materials for Postcombustion CO₂ Capture from Engineering Perspectives

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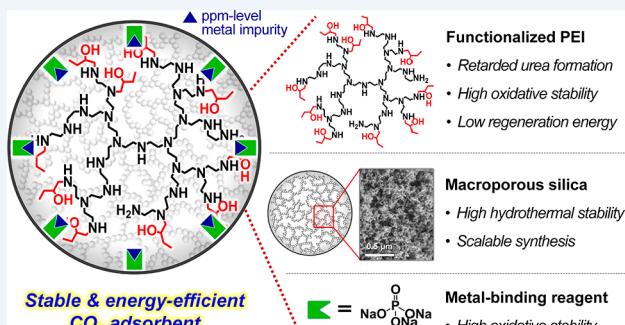
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CONSPECTUS: Carbon dioxide (CO₂) capture and storage (CCS) is a means to enable the continued use of fossil fuels in the short term. In particular, postcombustion CO₂ capture has attracted considerable attention because it can be retrofitted into existing power plants and industrial plants. Among various CO₂ capture technologies, the absorption of CO₂ using aqueous amines has been industrially employed for decades. However, such amine scrubbing technologies have inherent limitations of environmental and health concerns due to volatile amine loss, corrosion, and high energy demands for regeneration. To overcome these limitations, CO₂ adsorption using solid adsorbents has emerged as a promising alternative due to its noncorrosiveness and low energy demand.

Various amine-containing adsorbents have been synthesized and investigated for postcombustion CO₂ capture. These materials are prepared by physically impregnating low-vapor-pressure amine polymers or by chemically grafting amines onto nanoporous materials. A wide variety of amine guests and nanoporous hosts (e.g., SiO₂, Al₂O₃, zeolites, MOFs, and polymers) have been combined to develop advanced CO₂ adsorbents.

The design of CO₂ adsorbents is a multifaceted puzzle that must ultimately consider integration with large-scale CO₂ capture processes. Various engineering aspects need to be carefully considered. Unfortunately, a significant proportion of previous studies has primarily focused on the use of novel materials for improving the CO₂ adsorption capacity. In this Account, we describe key challenges and solutions to develop energy-efficient and stable amine-containing adsorbents for postcombustion CO₂ capture via temperature swing adsorption (TSA). We found that a high CO₂ working capacity, often overemphasized in the literature, does not necessarily guarantee a low energy demand for CO₂ capture. Suppressing coadsorption of H₂O during the CO₂ adsorption in humid flue gas is also a significant factor. Amine-containing adsorbents can be degraded through various pathways, including hydrothermal degradation of nanoporous hosts and chemical degradation of amine guests via urea formation and oxidation. To inhibit such degradation pathways, it is extremely important to properly design the nanoporous structures of the hosts and the molecular structures of the amine guests. By combining macroporous silica hosts, poly(ethylenimine) (PEI) functionalized with various alkyl epoxides, and phosphate-based oxidative stabilizers, we could synthesize adsorbents exhibiting low energy demands for CO₂ capture and unprecedentedly high thermochemical stability under TSA conditions. The macroporous silica host synthesized by assembling fumed silica particles via spray-drying exhibited high hydrothermal stability and enabled uniform distribution of bulky amine polymers within its pores. The functionalization of PEI with alkyl epoxides converted its primary amines into hindered secondary amines, leading to a significant reduction in energy demand for TSA cycles and a remarkable improvement in long-term stabilities. The oxidative stability of amines could be drastically improved by adding phosphate metal-binding reagents, which can poison ppm-level metal impurities that catalyze amine oxidation. The present discussions will provide important insights into designing practical adsorbents for CO₂ capture from engineering perspectives.



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- Commun.* **2016**, *7*, 12640.¹ Conversion of primary amines in poly(ethylenimine) to hindered secondary amines significantly increased CO₂ adsorption kinetics, regenerability, and thermochemical stabilities under practical TSA conditions.
- Min, K.; Choi, W.; Kim, C.; Choi, M. Oxidation-stable amine-containing adsorbents for carbon dioxide capture. *Nat. Commun.* **2018**, *9*, 726.² The oxidative stability of amine-containing adsorbents could be dramatically improved by adding small amounts of metal-binding reagents that can deactivate ppm-level metal impurities catalyzing amine oxidation.
 - Min, K.; Choi, W.; Kim, C.; Choi, M. Rational design of the polymeric amines in solid adsorbents for post-combustion carbon dioxide capture. *ACS Appl. Mater. Interfaces* **2018**, *10*, 23825–23833.³ The energy demand for adsorbent regeneration strongly depends on the H₂O coadsorption from humid flue gas. From an energy perspective, suppressing H₂O coadsorption may hold more significance than increasing the CO₂ capacity of the adsorbent.
 - Choi, W.; Park, J.; Kim, C.; Choi, M. Structural effects of amine polymers on stability and energy efficiency of adsorbents in post-combustion CO₂ capture. *Chem. Eng. J.* **2021**, *408*, 127289.⁴ The effects of amine polymer structures on CO₂ adsorption capacity, kinetics, stability, and regeneration heat were systematically investigated.

1. INTRODUCTION

Greenhouse gas (GHG) emissions have serious negative impacts on climate change, of which CO₂ accounts for nearly 75% of the global GHG impact.⁵ In this context, the Paris Agreement, which aims to limit global warming to less than 2 °C, requires the implementation of stringent policy measures to incentivize reductions in the level of CO₂ emissions. CO₂ capture and storage (CCS), especially from large point sources such as power plants using fossil fuels, is considered a vital technology for cost-effectively reducing anthropogenic CO₂ emissions.⁶ Among various CO₂ capture processes, CO₂ absorption using aqueous amine solutions is a mature technology that has been applied industrially for decades.⁷ Despite widespread implementation, these amine scrubbing technologies have inherent limitations, including potential environmental and health concerns due to a volatile loss of amines and their degradation products,^{8–10} corrosion,^{11,12} and large energy consumption for regeneration.¹³

To overcome these limitations, CO₂ capture using solid adsorbents has emerged as a promising alternative due to their noncorrosiveness and low energy demand.^{14–20} Adsorbents can be classified into two categories based on their heat of CO₂ adsorption: physisorbents and chemisorbents. Physisorbents (e.g., activated carbons and zeolites) adsorb CO₂ via weak van der Waals interactions, whereas chemisorbents (e.g., basic metal oxides and amine-containing solids) adsorb CO₂ through strong chemical reactions. Physisorbents are suitable for concentrated CO₂ streams, whereas chemisorbents are better suited for dilute CO₂ streams. Given the fact that most flue gases from large point sources have low CO₂ concentrations (<20%),²¹ chemisorbents have been more extensively investigated. In particular, amine-containing adsorbents have been widely investigated because of their ability to capture CO₂ under mild temperatures (<70 °C) and moderate heat of CO₂ adsorption leading to low energy demands for regeneration. These adsorbents have been

prepared by impregnating low-vapor-pressure amine polymers^{22–28} or by chemically grafting amines onto nanoporous materials.^{29–35} Various amine guests and nanoporous hosts (e.g., SiO₂,^{22–25,29–31} Al₂O₃,^{25,26,32} zeolites,^{25,33} MOFs,^{34,35} and polymers^{27,28}) have been combined to develop advanced CO₂ adsorbents. Important properties of adsorbents, such as the capacity of CO₂ adsorption, heat of adsorption, and thermochemical stability, can be tailored by designing the structures of amine guests and nanoporous hosts.

To date, many studies on amine-containing adsorbents have primarily focused on the utilization of novel materials to enhance CO₂ uptake. However, this research trend can be problematic, since materials with high CO₂ capacities may exhibit significant weaknesses in other critical engineering aspects. The design of CO₂ adsorbents is a multifaceted puzzle that must ultimately consider integration with large-scale CO₂ capture processes. Key engineering aspects, including the CO₂ adsorption capacity, kinetics, regeneration heat, stability, production cost, and scalability of the adsorbents, must be carefully addressed from the initial design stages. In this Account, we discuss the important obstacles encountered and solutions developed in our previous endeavors to develop energy-efficient and stable adsorbents for postcombustion CO₂ capture.

2. UNDERSTANDING ADSORPTION-BASED POSTCOMBUSTION CO₂ CAPTURE PROCESSES

An important consideration in designing CO₂ adsorption processes is how to regenerate saturated adsorbents. Regeneration can be accomplished by increasing the temperature (temperature swing adsorption; TSA), decreasing the pressure (vacuum/pressure swing adsorption; VSA/PSA), or a combination of the two (VTSA/PTSA).^{16,36} The choice of the regeneration method primarily depends on the heat of the CO₂ adsorption, which determines the shape of the CO₂ adsorption isotherm. Physisorbents with weak CO₂ adsorption are generally suitable for PSA, whereas chemisorbents with strong CO₂ adsorption are better suited for other processes. When CO₂ capture from low-concentration sources is targeted as in postcombustion CO₂ capture, combination of chemisorbents (e.g., amine-containing adsorbents) with TSA and VTSA can be considered. While VTSA presents significant merits, such as a low regeneration temperature and fewer detrimental effects on adsorbents' stability, the limited availability of large-capacity vacuum equipment and significant use of electricity present limitations.¹⁶ Therefore, if adsorbents can be designed to provide sufficient stability and regenerability (which is the primary focus of this Article), and renewable electricity is not available, TSA will provide more benefits over VTSA.^{37,38} In these regards, VTSA can be more suitable for Direct Air Capture (DAC), whereas TSA is better suited for postcombustion CO₂ capture from large point sources. Various types of reactors including fixed bed, moving bed, and fluidized bed reactors can be employed for TSA,³⁹ considering the properties of the adsorbent, target throughput, and level of process control required.

In the literature, amine-containing adsorbents have often been regenerated by increasing the temperature under an inert gas purge (e.g., N₂). It should be noted that these conditions cannot produce concentrated CO₂ suitable for storage and utilization. It appears that such conditions were preferred because they are beneficial for maximizing the working capacity of the CO₂ and minimizing the degradation of the adsorbents.

However, to produce concentrated CO₂, saturated adsorbents must be regenerated in a CO₂-rich atmosphere (separated CO₂ can be recycled as a sweep gas). Under such conditions, efficient CO₂ desorption is challenging due to high CO₂ partial pressures. Steam injection during regeneration can be beneficial³⁹ as it inhibits urea formation (dehydration reaction between amines and CO₂)³⁰ and reduces CO₂ partial pressure. However, under such conditions, the porous structures of adsorbents can collapse due to hydrothermal aging,^{26,40} and condensed water within the reactor can lead to the hydrolysis and leaching of amine species.^{20,41} Amine leaching can be particularly problematic for continuous moving bed and fluidized bed processes because the sticky amine compounds can cause coagulation of the adsorbent particles, diminishing the process operability.

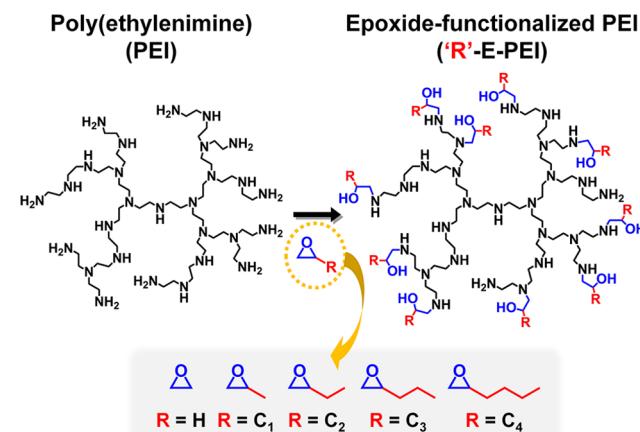
Therefore, to develop adsorbents for TSA processes, high regenerability and thermochemical stability are of prime importance. CO₂ adsorption should not be excessively strong to achieve efficient regeneration under a CO₂-rich atmosphere. However, most amine-based adsorbents developed so far exhibit strong CO₂ adsorption (>70 kJ mol⁻¹)¹ and require high regeneration temperatures, which lead to their degradation. At elevated temperatures during the regeneration step, CO₂ and amines can dehydrate to form urea. O₂-containing flue gas or air is often used as a purge gas during the cooling of adsorbents from desorption temperature to adsorption temperature. The contact with the O₂ can cause oxidative degradation of amines, leading to the permanent loss of the CO₂ capacity. Because adsorbents must be stable over at least thousands and ideally millions of cycles in the CO₂ capture processes, improving the thermochemical stability of the adsorbents can be even more important than increasing the CO₂ capacity. Various stability issues of amine-containing adsorbents have been comprehensively reviewed in a paper by Sayari et al.¹⁹

3. FUNCTIONALIZATION OF POLY(ETHYLENIMINE) WITH ALKYL EPOXIDES

Poly(ethylenimine) (PEI) impregnated on nanoporous hosts has been most extensively investigated as CO₂ adsorbents.^{14–24,26–30,39,40} PEIs are polymers composed of repeating units with amine groups separated by CH₂CH₂ spacers. Linear and branched PEIs with various molecular weights are commercially available. These polymers contain a large number of amines, which is beneficial for designing adsorbents with high CO₂ capacities. However, PEIs exhibit a large heat of CO₂ adsorption (~80 kJ mol⁻¹) and are difficult to regenerate under a CO₂-rich atmosphere.¹ Moreover, they are thermochemically unstable under the harsh regeneration conditions of TSA.

To overcome these limitations, our group developed a methodology to functionalize PEIs with alkyl epoxides (Scheme 1).^{1–4} Epoxides are highly reactive toward nucleophilic amines and can preferentially convert primary (1°) amines into hindered secondary (2°) amines under ambient conditions using green solvents (water and alcohols) or even without solvents.¹ In the dendrimer-like molecular structure of PEIs, 1° amines are located at the outer rim. As a result, when reactive epoxides are added in stoichiometric amounts, the 1° amines have a higher likelihood of reacting with the epoxides. Furthermore, when the 1° amines react with the epoxides, the resulting 2° amines exhibit lower reactivity for further alkylation due to increased steric hindrance.^{42–44} The selective alkylation of 1° amines to 2° amines is crucial for maintaining high CO₂ adsorption capacity, because tertiary (3°) amines are inefficient for CO₂ capture.^{14–16} The epoxide functionalization generates

Scheme 1. Functionalization of Poly(ethylenimine) with Epoxides Having Different Side Alkyl Chains (Reproduced with permission from ref 3. Copyright 2018 American Chemical Society.)



hydroxyethyl (−CCH₂OH) groups at the amine sites. The electron-withdrawing group reduces amine basicity, weakening the amine–CO₂ interactions.^{1,45} Good insight can be obtained by noting that the basicity of the amine decreases in the order of ethylamine ($pK_a = 10.8$) > monoethanolamine ($pK_a = 9.5$) > diethanolamine ($pK_a = 9.0$) > triethanolamine ($pK_a = 7.7$). In addition, the side alkyl groups (represented as “R” in Scheme 1) can increase steric hindrance near the amine centers, further weakening the adsorption of CO₂. Therefore, by controlling the degree of functionalization and the side alkyl groups, we can precisely tailor the CO₂ adsorption properties of the resulting amine polymer. The epoxide-functionalization of PEIs provides a versatile material platform for designing adsorbents with optimal CO₂ adsorption properties for CO₂ sources with different concentrations (4–6% from natural gas power plants, 12–15% from coal power plants, and >20% from cement and biogas plants).

With increased PEI functionalization with epoxides (e.g., 1,2-epoxybutane; EB), the CO₂ adsorption capacity of the adsorbents decreased (Figure 1a).¹ This can be attributed to the reduced N content per gram of polymer and a slightly increased fraction of 3° amines after functionalization (Figure 1b). However, by sacrificing the CO₂ capacity, other important properties can be significantly improved. Weakened CO₂ adsorption allowed for more efficient CO₂ desorption in a CO₂-rich atmosphere (Figure 1a). Additionally, the CO₂ adsorption kinetics was markedly enhanced (Figure 1c) due to the formation of more branched amine polymer structures.⁴ Experimental and theoretical studies indicated that more branched amine polymers can enable faster CO₂ access to the amine sites.^{4,44} Fast CO₂ adsorption kinetics are particularly important in continuous TSA processes with short solid–gas contact times (e.g., fluidized bed).

The epoxide functionalization also provides a significant advantage in terms of enhanced thermochemical stabilities.^{1,3,4} Unmodified PEI/SiO₂ exhibited a high CO₂ working capacity (2.9 mmol g⁻¹) in the first TSA cycle (Figure 1d), but it rapidly decreased to 1.1 mmol g⁻¹ after 50 cycles due to urea formation (Figure 1e). With increasing EB functionalization, the cyclic stability of the adsorbents significantly improved (Figure 1d) due to suppressed urea formation (Figure 1e). At optimal functionalization (0.37EB-PEI/SiO₂ in Figure 1), a reasonably

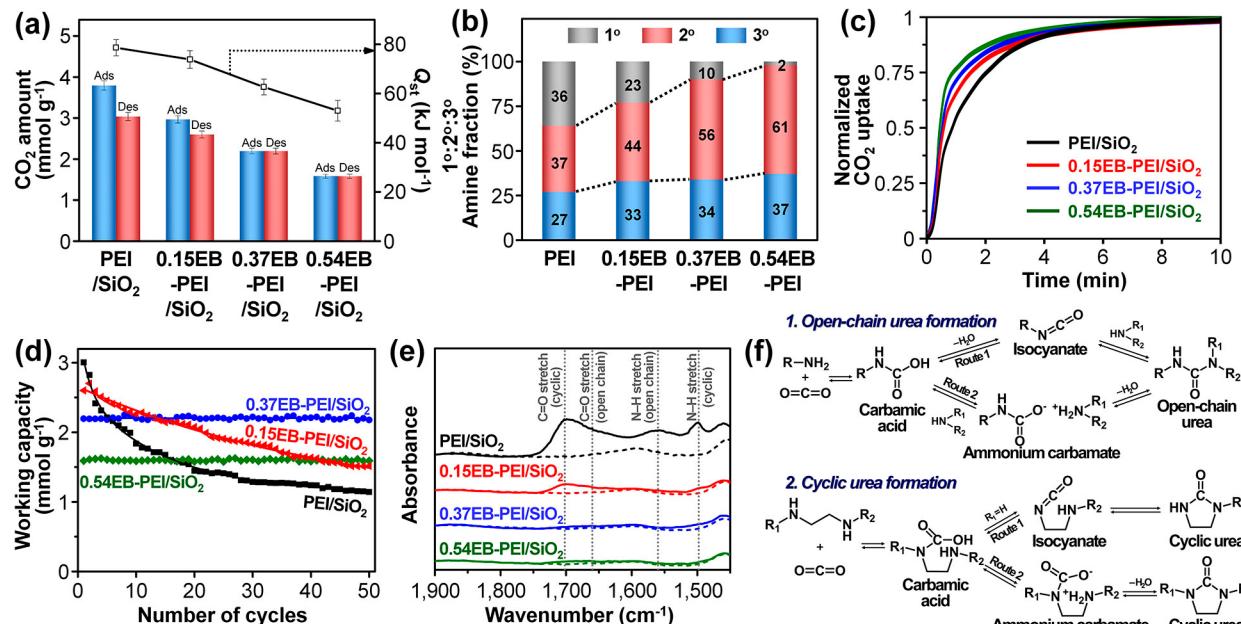


Figure 1. (a) CO₂ adsorption/desorption amounts (adsorption: 15% CO₂, 3% H₂O, and 2% Ar in N₂ balance at 40 °C; desorption: 100% CO₂ at 120 °C) and heats of CO₂ adsorption of PEI/SiO₂ and EB-functionalized PEI/SiO₂ adsorbents (denoted as “nEB-PEI/SiO₂”, where n indicates the molar ratio between EB and the nitrogen content of PEI used for functionalization). (b) Amine distributions of PEI and nEB-PEI analyzed by ¹³C NMR. (c) CO₂ uptake kinetics of the PEI/SiO₂ and nEB-PEI/SiO₂ adsorbents. (d) CO₂ working capacities of the adsorbents plotted over the number of TSA cycles. (e) FT-IR spectra of the spent adsorbents after 50 TSA cycles. Dashed lines indicate the spectra for freshly prepared samples, while solid lines indicate those for the samples after TSA cycles. (f) Reaction pathways for CO₂-induced urea formation. Reproduced with permission from ref 1. Copyright 2016 Springer Nature.

high working capacity of CO₂ (2.2 mmol g⁻¹) and outstanding stability could be simultaneously achieved. This improved stability can be explained based on the urea formation mechanism proposed by Sayari et al.^{30,46–48} and Jones et al.⁴⁹ (Figure 1f). Urea formation primarily occurs via the isocyanate pathway (route 1 in Figure 1f), which involves at least one 1° amine. The 1° amine can react with CO₂ to form a carbamic acid, which then dehydrates to form isocyanate. The resulting isocyanate can subsequently react with either 1° or 2° amines to form urea. Therefore, the conversion of 1° amines into hindered 2° amines via epoxide functionalization (Figure 1b) can inhibit the formation of isocyanate intermediates for urea formation. The hydroxyethyl groups generated through functionalization can further stabilize carbamic acid (or carbamate species) via OH···NH hydrogen bonding (solvation effects).^{1,50}

4. EFFECTS OF AMINE POLYMER STRUCTURES ON CO₂ CAPTURE ENERGETICS

The functionalized PEIs have lower CO₂ capacities than PEIs due to reduced N contents. At first glance, one may assume that such a decrease in the CO₂ capacity would increase the energy demand for CO₂ capture. For similar reasons, previous studies in the literature have focused on improving the CO₂ working capacities of adsorbents. However, this common belief may not be true. In the TSA cycle, the heat required for adsorbent regeneration consists of three major contributions: (i) sensible heat required for heating the adsorbent from adsorption temperature to desorption temperature, (ii) latent heat of CO₂ desorption needed to overcome the chemical interaction between CO₂ and amines, and (iii) latent heat of H₂O desorption for removing H₂O coadsorbed from humid flue gas (amines are generally hydrophilic).^{51,52} It is noteworthy that the larger the CO₂ working capacity, the fewer TSA cycles are

required to capture a fixed amount of CO₂, thus reducing the sensible heat (i). However, this is only one of the three major heat contributions, and a more comprehensive examination of all individual heat contributions is needed to properly estimate the total regeneration heat.

To investigate the effects of amine polymer structures on CO₂ capture energetics, we synthesized a series of PEI/SiO₂ adsorbents functionalized with various epoxides (Scheme 1).³ Their physical properties, including specific heat capacity, heats of adsorption of CO₂ and H₂O, and adsorption/desorption amounts of CO₂ and H₂O during a simulated TSA cycle, were carefully measured to calculate the regeneration heat. Unmodified PEI/SiO₂ showed the largest heat of adsorption for both CO₂ (80.5 kJ mol⁻¹) and H₂O (47.1 kJ mol⁻¹; Figure 2a). The epoxide-functionalized PEI/SiO₂ samples exhibited a substantially lower heat of adsorption for CO₂ (64.9–73.5 kJ mol⁻¹) and H₂O (37.3–44.7 kJ mol⁻¹), which decreased gradually with longer side alkyl chains (R). The side alkyl chains provide additional steric hindrance and hydrophobicity at the amine sites, weakening the interaction with CO₂ and H₂O. Both working capacities of CO₂ and H₂O decreased after functionalization with epoxides having longer alkyl chains (Figure 2b). However, the decrease in the H₂O working capacity was much more prominent than the decrease in the CO₂ working capacity.

Based on the experimental data, three major contributions to regeneration heat were calculated (Figure 2c).³ Unmodified PEI/SiO₂ exhibited the smallest sensible heat due to its largest CO₂ working capacity. However, the adsorbent required the largest latent heat of CO₂ desorption due to strong CO₂ adsorption (80.5 kJ mol⁻¹). In comparison, the epoxide-functionalized adsorbents required larger sensible heats due to their smaller CO₂ working capacities, but they required smaller latent heats of CO₂ desorption due to weakened CO₂ adsorption

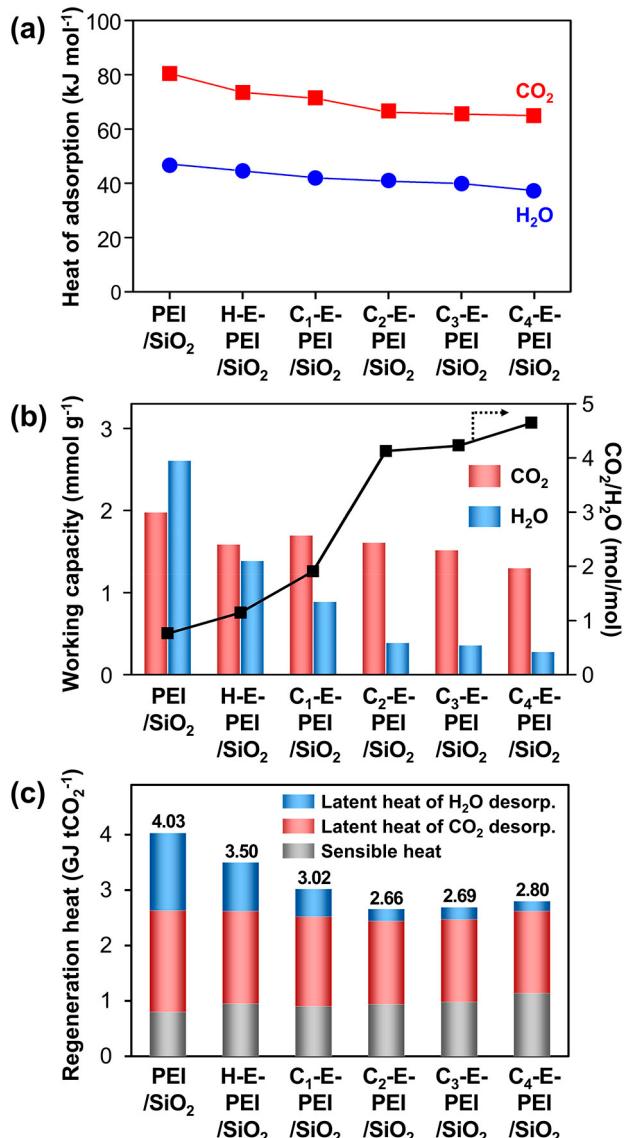


Figure 2. (a) Heats of CO_2 and H_2O adsorption of the PEI/SiO₂ adsorbents functionalized with epoxides having different side alkyl chains (Scheme 1). (b) CO_2 and H_2O working capacities of the adsorbents and their ratios in TSA conditions (adsorption: 15% CO_2 , 3% O_2 , 10% H_2O , and 2% Ar in N_2 balance at 60 °C; desorption: 100% CO_2 at 110 °C). (c) Heat required for the regeneration of adsorbents. Reproduced with permission from ref 3. Copyright 2018 American Chemical Society.

(64.9–73.5 kJ mol^{-1}). Notably, the sum of sensible heat (*i*) and latent heat of CO_2 desorption (*ii*) was quite similar for all adsorbents (2.44–2.63 GJ tCO₂⁻¹). This implies that adsorbents with higher CO_2 working capacities are generally more difficult to regenerate due to stronger CO_2 adsorption. As a result, the critical factor determining the overall energetics was the remaining heat contribution, namely, the latent heat of H_2O desorption (*iii*). The latent heat of H_2O desorption decreased with increasing side alkyl chain length due to the suppressed H_2O coadsorption from humid flue gas (Figure 2b). Under the simulated TSA conditions, EB-functionalized PEI/SiO₂ (“C₂-E-PEI/SiO₂” in Scheme 1 and Figure 2) required the lowest regeneration heat (2.66 GJ tCO₂⁻¹), which was 34% less than that of unmodified PEI/SiO₂ (4.03 GJ tCO₂⁻¹). This is

remarkable considering that C₂-E-PEI/SiO₂ exhibited a 19% lower CO_2 working capacity than PEI/SiO₂.

The present results suggest that while the CO_2 working capacity is important, it is not the sole decisive factor in determining the CO_2 capture energetics. Instead, significant attention should also be paid to suppressing H_2O coadsorption to reduce regeneration heat. Amines are generally hydrophilic and coadsorb significant amounts of H_2O from humid flue gas, requiring substantial latent heat for H_2O desorption. Since the heat demand for adsorbent regeneration also depends on the specifics of the process design, the aforementioned estimation should be considered a rough guideline. Nevertheless, these results highlight the necessity of carefully considering both the CO_2 working capacity and H_2O coadsorption. The negative impact of H_2O coadsorption can be more pronounced as the CO_2 concentration decreases and the relative humidity increases in flue gas compositions.

5. ENHANCING AMINE OXIDATIVE STABILITY

O_2 is a ubiquitous component in flue gases (3–4%)¹⁴ and adsorbents naturally come into contact with O_2 during the adsorption step. In addition, air or flue gas is often used as a purge gas during the cooling process from the desorption temperature to the adsorption temperature. Under these conditions, adsorbents can undergo rapid deactivation due to amine oxidation. Amine oxidation is believed to be initiated through radical generation by the reaction between O_2 and amines.^{53–55} The oxidative stability of amines depends on their molecular structures, with isolated 1° amines being more stable than 2° amines.^{56,57} In the case of amine polymers, poly(allylamine),⁵⁸ poly(propylenimine),⁵⁹ and epoxide-functionalized PEIs^{1–4} exhibit significantly enhanced stability compared to typical PEIs. However, the use of different amine compounds can also significantly affect the adsorption properties, of the $\text{CO}_2/\text{H}_2\text{O}$ adsorption, and this strategy alone is generally insufficient to improve oxidative stability beyond commercially meaningful levels.

We coincidentally discovered that all amine polymers contain trace amounts of metal impurities, such as Fe and Cu.^{2,4} These impurities may originate from the amine polymers' strong metal chelating ability, which causes corrosion of metal reactors and containers during production and storage. Despite their low concentrations (<200 ppm), these metal impurities can catalyze amine oxidation by facilitating radical generation through $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Cu}^{2+}/\text{Cu}^+$ redox cycles. The detrimental effects of these metal species on amine oxidation have been extensively studied in aqueous amine scrubbing, where Fe ions are continuously leached from reactor surfaces due to corrosion and Cu ions are often added to inhibit reactor corrosion.^{53–55} However, the potential contamination of amine sources with metal impurities has been overlooked in the case of solid adsorbents. For PEI-type polymers, the metal impurity content increased with decreasing molecular weight, and thus PEIs with larger molecular weights exhibited higher oxidative stabilities.⁴ Notably, we found that adding a small amount of metal-binding reagents (<2 wt %) to deactivate metal impurities can effectively suppress the rate of amine oxidation (Figure 3a–c).^{2,60} Among various additives, trisodiumphosphate (TSP, 1 in Figure 3a) was found to be a highly promising stabilizer for both PEI/SiO₂ (Figure 3b) and EB-PEI/SiO₂ (Figure 3c). The oxidative stabilities of PEI/SiO₂ and EB-PEI/SiO₂, with and without 2 wt % TSP, were compared under simulated O_2 -containing flue gas at 110 °C over 30 days (Figure 3d). The combination of EB-

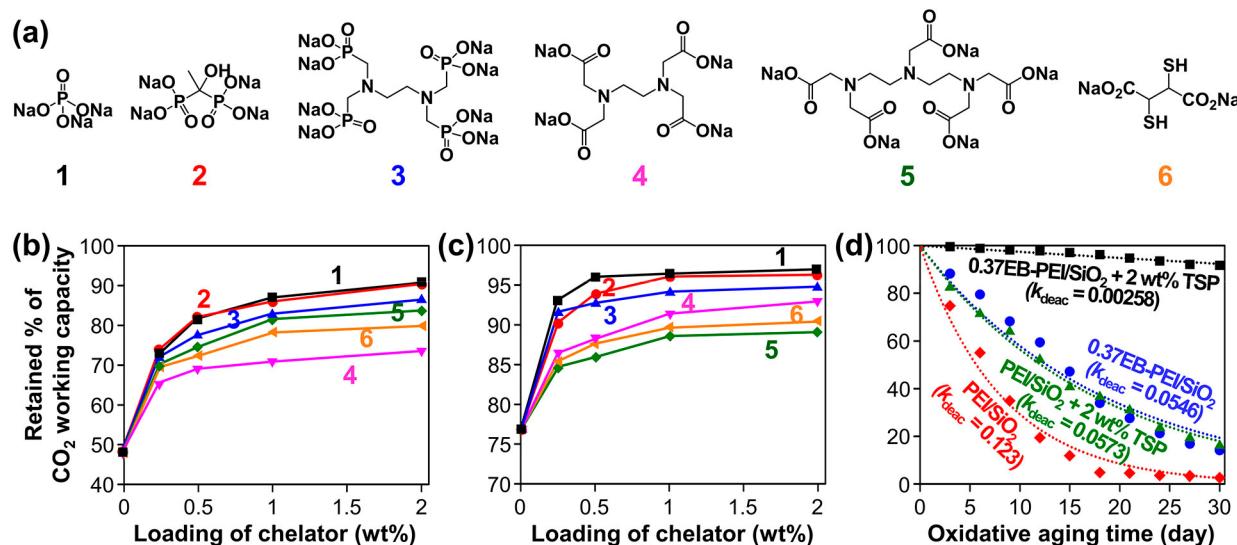


Figure 3. (a) Types of metal-binding reagents and retained CO_2 working capacities of (b) PEI/SiO_2 and (c) $\text{EB-PEI}/\text{SiO}_2$ (the molar ratio between EB and N content within PEIs was fixed at 0.37) with various loadings of metal-binding reagents after oxidative aging under 3% O_2 in N_2 balance at 110 °C for 1 day. The numbers on the plots of b and c indicate the types of metal-binding reagents shown in a. (d) Long-term oxidative stabilities of PEI/SiO_2 and $\text{EB-PEI}/\text{SiO}_2$ prepared with and without 2 wt % TSP (aging conditions: 15% CO_2 , 3% O_2 , and 10% H_2O in N_2 balance at 110 °C). Reproduced with permission from ref 2. Copyright 2018 Springer Nature.

functionalization and TSP addition exhibited a remarkable synergistic effect, resulting in a dramatically decreased deactivation rate compared with unmodified PEI/SiO_2 .

The oxidative stability of amine polymers depends not only on intrinsic material properties but also on the process conditions. In particular, lowering the regeneration temperature is important because the rate of amine oxidation increases with temperature. This means that the use of adsorbents with excessively strong CO_2 adsorption should be avoided. Previous studies have shown that amine oxidation is slower in O_2 -containing flue gas compared to dry air due to the preferential interaction of amines with CO_2 than O_2 .^{2,46} This indicates that using flue gas as a purge gas during adsorbent cooling from the desorption temperature to the adsorption temperature is more desirable than using air to suppress amine oxidation. With careful selection of process conditions, solid amine adsorbents can offer significant advantages in terms of oxidative stability compared with aqueous amine solutions. In the case of aqueous amine solutions, continuous reactor corrosion necessitates the continuous addition of stabilizers (e.g., oxygen/radical scavengers or metal-binding reagents) and the removal of their decomposition products.⁵⁵ Conversely, the ppm-level metal impurities in solid adsorbents can be effectively deactivated by incorporating small amounts of metal-binding reagents during their synthesis. Reactor corrosion is not a significant concern in solid adsorbent-based adsorption processes.

6. SYNTHESIS OF MACROPOROUS SILICA HOST

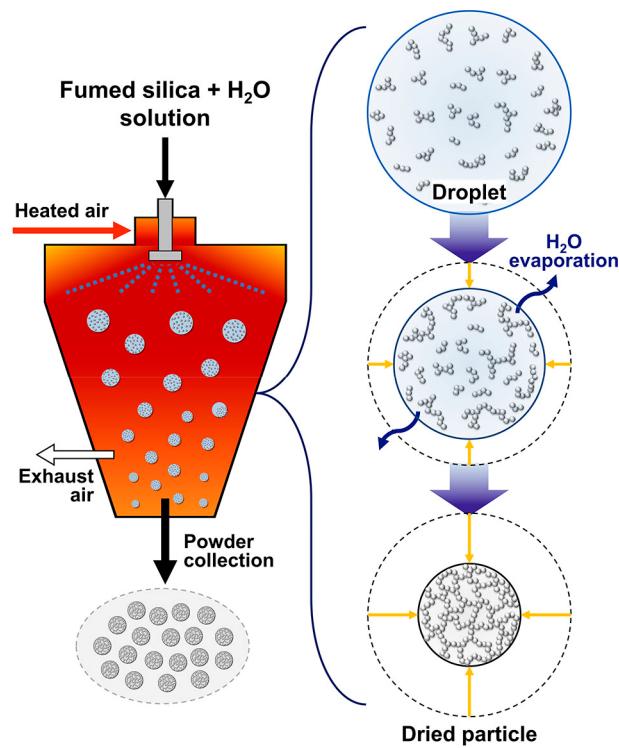
In amine-containing adsorbents, porous hosts stabilize amine species, provide efficient CO_2 diffusion pathways, and offer mechanical stability after shaping. Various host materials like SiO_2 ,^{22–25,29–31,41} Al_2O_3 ,^{25,26,32} zeolites,^{25,33} MOFs,^{34,35} and polymers^{27,28} have been tested. In particular, SiO_2 has been extensively investigated due to its cost-effectiveness and versatility in synthesis. Mesoporous silicas, such as MCM-41, SBA-15, and mesocellular foam (MCF), have been widely investigated due to their large surface area and pore volume suitable for high amine loading.^{14–24,29–31,39,40,46–49,56,57,59}

These mesoporous hosts (pore diameters >2 nm) are advantageous for uniformly distributing bulky amine polymers compared to microporous hosts with smaller pore diameters (zeolites and MOFs). However, the synthesis of these mesoporous silicas involves expensive organic structure-directing agents and caustic acidic/basic media, posing challenges for scale-up. Moreover, these silicas have limited hydrothermal stability due to very thin framework (<3 nm).^{40,61} The use of hydrothermally stable host materials is essential,^{39–41} because the adsorbents always coadsorb a substantial amount of H_2O from humid flue gas.

To solve these problems, we synthesized macroporous silica microspheres (MacS) by spray-drying a water slurry of fumed silica, followed by calcination (Scheme 2).^{1,61} During spray-drying, the fumed silica particles inside each slurry droplet assembled into a three-dimensional network, forming spherical MacS particles in the size range 75–200 μm (Figure 4a). This particle size distribution makes MacS suitable for continuous fluidized bed operation for CO_2 capture. N_2 adsorption–desorption isotherms (Figure 4b) revealed that MacS had a much lower surface area ($261 \text{ m}^2 \text{ g}^{-1}$) than typical mesoporous silicas ($>800 \text{ m}^2 \text{ g}^{-1}$) due to its large framework thickness (10–15 nm).⁶¹ MacS had a large pore volume ($1.80 \text{ cm}^3 \text{ g}^{-1}$) due to the presence of macropores with an average pore diameter of 56 nm (Figure 4c). The large pore diameter of MacS enabled uniform distribution of bulky PEI molecules within the silica pores with minimal pore occlusion.⁶¹ Consequently, MacS enabled faster CO_2 adsorption kinetics and a larger CO_2 adsorption capacity (amine efficiency) compared to mesoporous silicas when supporting the same PEI loading of 50 wt % (Figure 4d).

Due to the large framework thickness of MacS (10–15 nm), PEI/MacS showed remarkably high hydrothermal stability. Accelerated hydrothermal aging was conducted by treating the adsorbent with 100% steam at 120 °C for up to 14 days (Figure 5). Even after the harsh 14-day steam treatment, PEI/MacS showed only a slight decrease in CO_2 adsorption capacity (<10% decrease). In contrast, PEI/MCM-41, PEI/SBA-15, and PEI/

Scheme 2. Synthesis of Macroporous Silica Microspheres (MacS) Using a Spray-Drying Method



MCF exhibited significant decreases (42–62% decreases). To understand the degradation, the steam-treated adsorbents were calcined, and the structures of the silica hosts were reanalyzed. Transmission electron microscopy (TEM) investigation revealed that the pore structure of MacS remained nearly

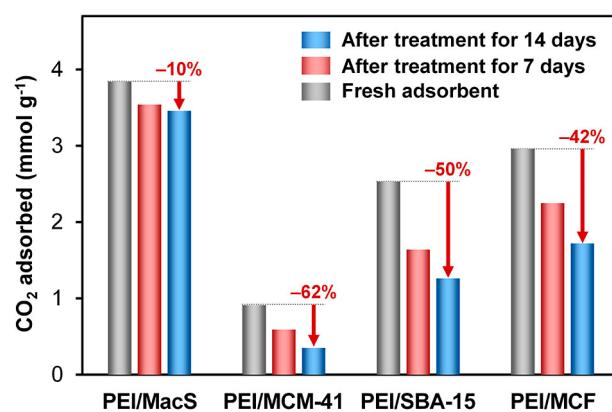


Figure 5. CO₂ adsorption amounts of fresh and steam-treated 50 wt % PEI/silica materials (adsorption conditions: 15% CO₂ and 3% H₂O in N₂ balance at 40 °C). Reproduced with permission from ref 61. Copyright 2017 Wiley-VCH.

unchanged (Figure 6a), while MCM-41, SBA-15, and MCF exhibited significant pore collapse and framework ripening. According to N₂ adsorption–desorption isotherms (Figure 6b), MacS exhibited only a slight decrease in pore volume after steam treatment (4% decrease). In contrast, MCM-41, SBA-15, and MCF showed substantial reductions in pore volume (>41%). Elemental analysis of the composite adsorbents after the 14-day steam treatment indicated minimal PEI leaching from PEI/MacS (<4%), whereas significant PEI losses were observed for PEI/MCM-41, PEI/SBA-15, and PEI/MCF (34%, 25%, and 16%, respectively). These results suggest that PEIs inside the silica pores are stabilized against leaching, whereas those squeezed out of the collapsed pores are prone to leaching (Scheme 3).

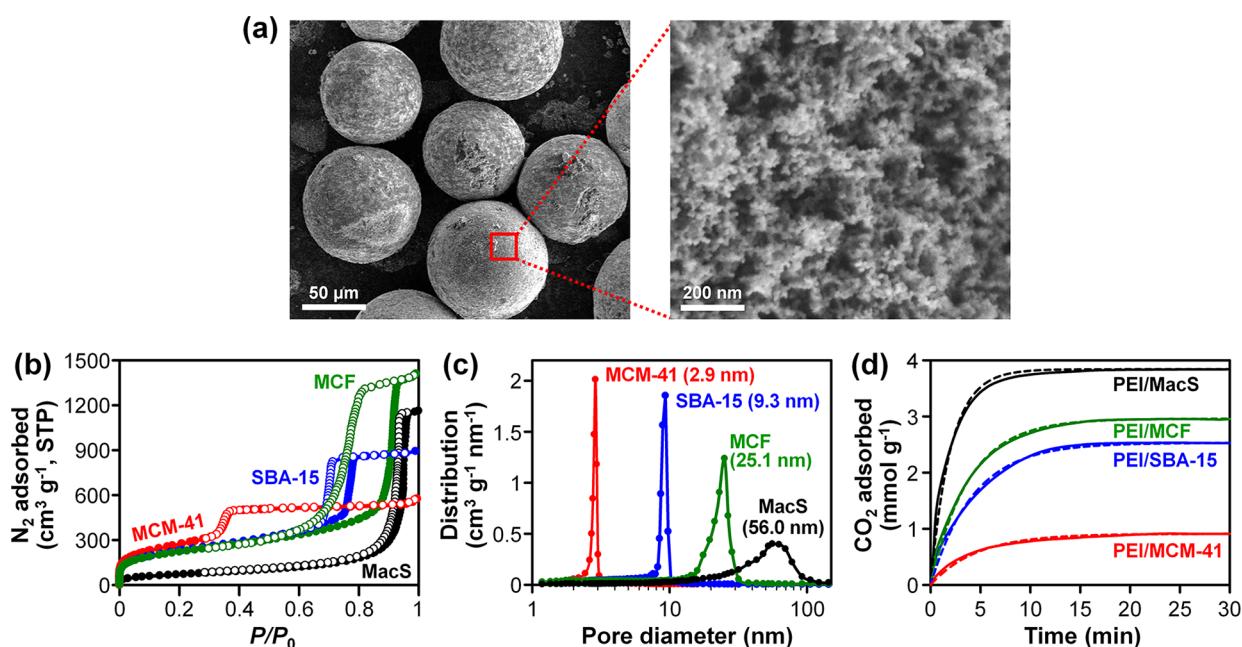


Figure 4. (a) SEM images of MacS. (b) N₂ adsorption–desorption isotherms and (c) corresponding pore size distributions of MacS and various mesoporous silicas. (d) CO₂ adsorption profiles of the PEI-loaded silica materials (adsorption conditions: 15% CO₂ and 3% H₂O in N₂ balance at 40 °C). The solid lines indicate the measured data, and the dashed lines indicate the fitting curves obtained using the pseudo-first-order kinetic equation. Panel a reproduced with permission from ref 1. Copyright 2018 Springer Nature. Panels b–d reproduced with permission from ref 61. Copyright 2017 Wiley-VCH.

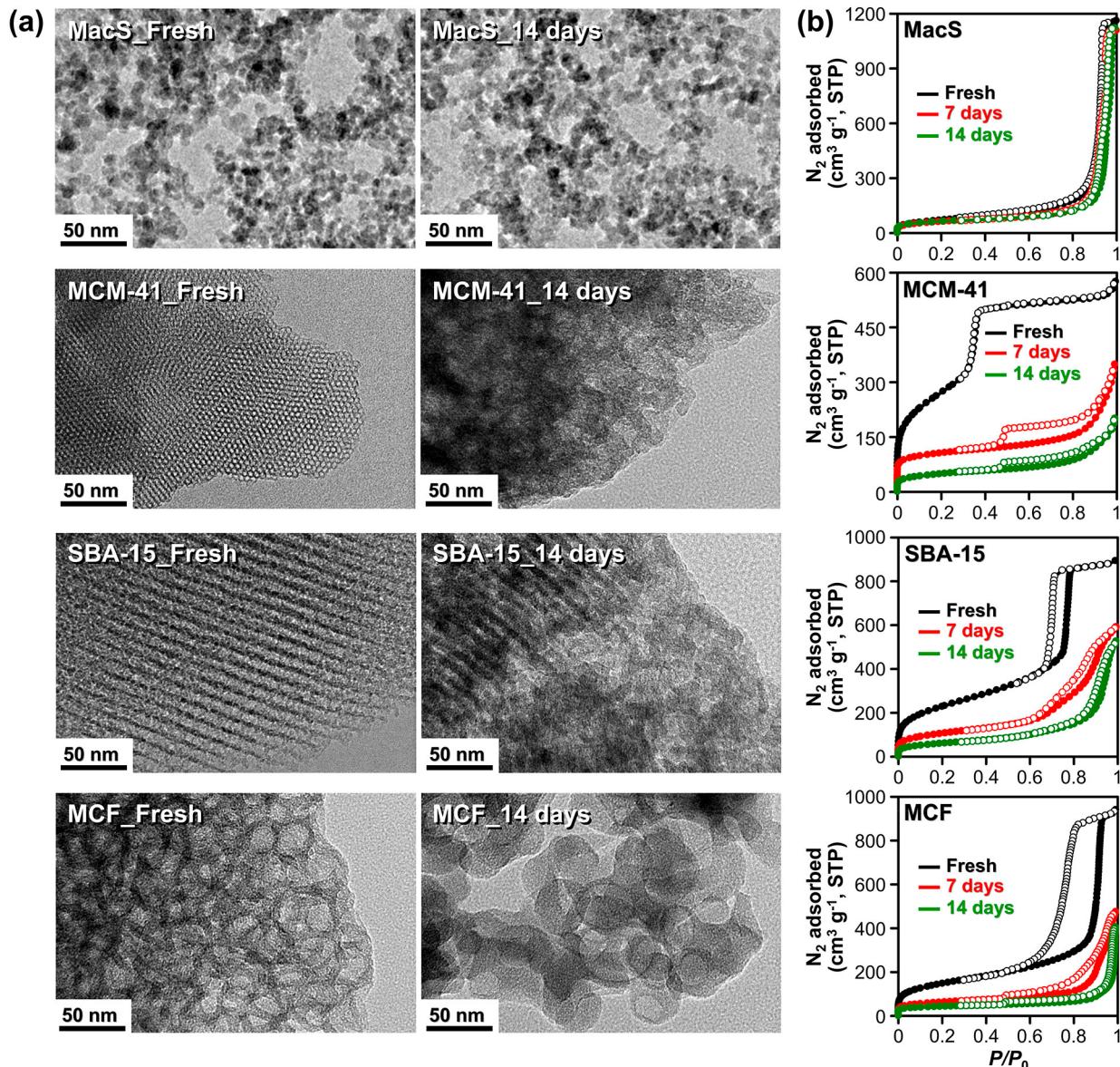


Figure 6. (a) TEM images and (b) N_2 adsorption–desorption isotherms of the silica supports in fresh adsorbents and those steam-treated at 120°C . The data were collected after calcination of the fresh and steam-treated PEI/silica adsorbents at 600°C . Reproduced with permission from ref 61. Copyright 2017 Wiley-VCH.

The mechanical stability of adsorbents is crucial for their practical applications, particularly for continuous fluidized or moving bed processes. Because MacS has a suitable particle size ($75\text{--}200\ \mu\text{m}$) for fluidized bed operations, its attrition index (AI) was investigated following the ASTM D5757-95 method.¹ The attrition test showed that 74% of MacS fines were collected in a thimble, indicating the low mechanical stability of the highly porous silica. This is expected since the mechanical stability of inorganic oxides is inversely proportional to their porosity. However, after loading viscous PEI-type polymers, the generated fines were less than 2.5%. This AI value is comparable to or even smaller than those of commercial fluid catalytic cracking (FCC) catalysts (1.6–8.2) used in the refinery industry.⁶² The results demonstrate that impregnating brittle silica structures with viscous amine polymers can significantly enhance the mechanical stability, thanks to the synergistic effect between organic and inorganic components.

7. PROCESS ASSESSMENT USING THE AMINE-CONTAINING ADSORBENTS

As mentioned above, stable and energy-efficient CO_2 adsorbents could be developed by combining the epoxide-functionalized PEI, an oxidative stabilizer, and a macroporous silica host. Energy demand analysis and bench-scale CO_2 capture tests have been conducted by several research groups using these adsorbents.^{63,64} Jung et al. performed an energy demand analysis through mathematical modeling of a fluidized bed adsorption process.⁶³ The proposed processes considered internal heat integration using a moving bed heat exchanger. The pseudo counter-current operation in the adsorption bed enabled a higher CO_2 working capacity ($2.15\ \text{mmol g}^{-1}$) at 80% CO_2 recovery compared to the cocurrent operation process ($1.65\ \text{mmol g}^{-1}$). The thermal energy demand was calculated to be $2.23\ \text{GJ tCO}_2^{-1}$ (Table 1), which was comparable to those of the mature amine-based absorption processes ($2.7\text{--}3.3\ \text{GJ tCO}_2^{-1}$).⁶⁵ Park et al. built a bench unit for a fluidized bed

Scheme 3. Effects of Hydrothermal Stability of Silica Supports on PEI Leaching (Reproduced with permission from ref 61. Copyright 2017 Wiley-VCH.)

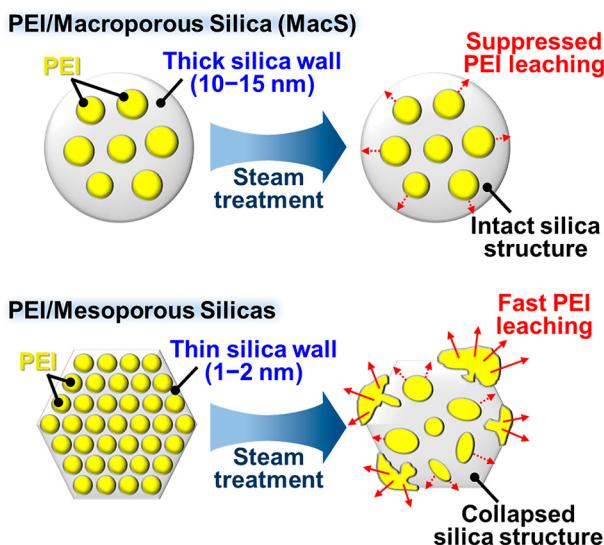


Table 1. Operation Conditions and Results of CO₂ Capture Processes Using Epoxide-Functionalized Amine-Based Adsorbents

	pseudocounter current fluidized bed process ⁶³	multistage fluidized bed process ⁶⁴
flue gas composition	15% CO ₂ ^a	12% CO ₂ , 84.5% air, 3.5% H ₂ O
sweep gas	100% CO ₂	100% CO ₂
adsorption temperature (°C)	40	50
desorption temperature (°C)	127	130
superficial velocity of flue gas (m/s)	1.0	0.77
CO ₂ recovery (%)	80	80
thermal energy demand for regeneration (GJ tCO ₂ ⁻¹)	2.23	2.37

^aBalance gas compositions are not provided in the literature.

process operated at $60 \text{ N m}^3 \text{ h}^{-1}$.⁶⁴ This process consists of adsorption–desorption stages with intra- and interstage heat exchangers. At optimized operating conditions (three-stage operation), the regeneration energy was estimated as $2.37 \text{ GJ tCO}_2^{-1}$ at 80% CO₂ recovery (Table 1). Process development using amine-containing adsorbents is still in its infancy and requires further studies. Nevertheless, it is clear that efficient heat integration is essential for developing energy-efficient CO₂ capture processes using solid adsorbents.

8. CONCLUSION AND PERSPECTIVES

In this Article, we present our efforts in developing stable and energy-efficient amine-containing adsorbents for postcombustion CO₂ capture. We developed a versatile method to functionalize PEIs using alkyl epoxides that can convert 1° amines into hindered 2° amines. This improved regenerability and CO₂ adsorption kinetics of adsorbents under TSA conditions. In addition, we addressed the degradation pathways of amine-containing adsorbents including urea formation, hydrothermal degradation, and oxidative degradation. Urea formation could be effectively inhibited by the epoxide-functionalization of PEI, because hindered 2° amines are

resistant to urea formation. Hydrothermal degradation could be prevented by employing a macroporous silica host with enhanced hydrothermal stability. To improve the oxidative stability of amine-containing adsorbents, we added a small amount of metal-binding reagents to deactivate ppm-level Fe and Cu impurities that can catalyze amine oxidation. We hope to emphasize that maximizing the CO₂ capacity, often overly emphasized in the literature, does not always guarantee low heat consumption for CO₂ capture. While adsorbents with high CO₂ capacities require less sensible heat during regeneration, they often exhibit excessively strong CO₂ adsorption, leading to a greater demand for the latent heat of CO₂ desorption. Moreover, these high-capacity adsorbents often contain a large amount of hydrophilic 1° amines, leading to significant H₂O coadsorption from humid flue gas. Consequently, there is a large additional heat demand for H₂O desorption. To minimize the overall heat requirement for CO₂ capture, it may be more effective to design a hydrophobic CO₂ adsorbent that suppresses H₂O coadsorption, rather than focusing solely on enhancing CO₂ capacity. These findings highlight the importance of considering multiple factors beyond CO₂ capacity alone and provide valuable guidelines for the development of process-ready adsorbents for postcombustion CO₂ capture.

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Notes

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