Oxidation-stable amine-containing adsorbents for carbon dioxide capture

Kyungmin Min¹, Woosung Choi¹, Chaehoon Kim¹ & Minkee Choi¹

Amine-containing solids have been investigated as promising adsorbents for CO₂ capture, but the low oxidative stability of amines has been the biggest hurdle for their practical applications. Here, we developed an extra-stable adsorbent by combining two strategies. First, poly(ethyleneimine) (PEI) was functionalized with 1,2-epoxybutane, which generates tethered 2-hydroxybutyl groups. Second, chelators were pre-supported onto a silica support to poison p.p.m.-level metal impurities (Fe and Cu) that catalyse amine oxidation. The combination of these strategies led to remarkable synergy, and the resultant adsorbent showed a minor loss of CO₂ working capacity (8.5%) even after 30 days aging in O₂-containing flue gas at 110 °C. This corresponds to a ~50 times slower deactivation rate than a conventional PEI/silica, which shows a complete loss of CO₂ uptake capacity after the same treatment. The unprecedentedly high oxidative stability may represent an important breakthrough for the commercial implementation of these adsorbents.

¹Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea. Kyungmin Min and Woosung Choi contributed equally to this work. Correspondence and requests for materials should be addressed to M.C. (email: mkchoi@kaist.ac.kr)
Carbon capture and storage (CCS) has been investigated as an important option to reduce anthropogenic CO₂ emissions. CO₂ adsorption using aqueous amine solutions (e.g., monoethanolamine) is considered a benchmark technology for postcombustion CO₂ capture. However, despite the several decades of optimization, the technology still has inherent limitations, including volatile amine loss, reactor corrosion, and the high energy consumption for regeneration. To overcome these limitations, solid adsorbents that are noncorrosive and can lower the energy consumption have emerged as potential alternatives. Among various adsorbents, amine-containing solids are considered to be the most promising adsorbents because of their high CO₂ adsorption selectivity in a typical flue gas containing dilute CO₂ (<15% CO₂). Such materials can be prepared by the heterogenization of amines in porous supports via the impregnation of polymeric amines such as poly(ethyleneimine) (PEI), the grafting of aminosilanes, or the polymerization of amine monomers within the support pores.

For commercial implementation of adsorbents, they should be stable upon repeated CO₂ adsorption–desorption cycles over a long period. Generally, the low adsorbent stability necessitates the continuous addition of fresh adsorbents, which significantly increases the material cost for CO₂ capture. Amine-containing adsorbents are known to degrade via various chemical pathways including the oxidative degradation of amines, urea formation under the CO₂-rich atmosphere, and steam-induced degradation of the porous supports, and irreversible adsorption of SO₂. Aside from the oxidative degradation of amines, various solutions have been proposed for suppressing the degradation pathways. For instance, urea formation can be inhibited by selectively using secondary amines rather than primary amines or injecting steam during adsorbent regeneration. Steam-induced degradation can be solved by using porous supports with enhanced hydrothermal stability. In addition, the amine poisoning by SO₂ can be avoided by employing advanced desulfurization unit before CO₂ capture. Therefore, the oxidative degradation of amines remains the biggest hurdle for the practical applications of these adsorbents.

The most ubiquitous impurity in flue gas is O₂ (3–4%) in the presence of O₂, the amine-containing adsorbents undergo rapid deactivation because of amine oxidation. Amine oxidation is known to proceed via free radical formation by the reaction of O₂ with amines at elevated temperatures. The oxidation rate significantly depends on the amine structures. The isolated primary amines are known to be more stable than the isolated secondary amines. In the case of PEI, the linear PEI mainly containing secondary amines is more stable than the branched PEI with a mixture of primary, secondary, and tertiary amines. The results indicated that the co-existence of different types of amines can affect the oxidative degradation of amines. The polymers with only distant primary amines such as poly(allylamine) are more stable than conventional PEI. Recently, the use of propylene spacers between amine groups has been found to substantially increase amine stability compared with the PEI containing ethylene spacers. It has also been reported that the addition of poly(ethylene glycol) into polymeric amines can retard the amine oxidations due to hydrogen bonds between the hydroxy groups of poly(ethylene glycol) and the amines. Despite these efforts, it still remains a great challenge to improve the oxidative stability of amines to a commercially meaningful level.

In the present work, we report the synthesis of a modified PEI–silica that shows unprecedentedly high oxidative stability. The adsorbent was prepared by combining two strategies. First, PEI was functionalized with 1,2-epoxybutane (EB), which generates tethered 2-hydroxybutyl groups. Second, small amounts of chelators (<2 wt%) were pre-supported into a silica support before the impregnation of functionalized PEI. We discovered that the polymeric amines contain p.p.m.-level metal impurities including Fe and Cu, which catalyse amine oxidation. The addition of chelators as a catalyst poison could significantly suppress the rate of amine oxidation. Notably, the combination of two strategies resulted in great synergy, compared to when each method was used separately.

**Results**

**PEI vs EB-functionalized PEI.** The EB-functionalization of PEI (Nippon Shokubai, Epomin SP-012, MW 1200) was carried out as reported previously. We reported that the functionalization can significantly increase the CO₂ adsorption kinetics and amine stabilities against urea formation, while it can also retard the amine oxidation to some extent. 50 wt% of PEI and EB-functionalized PEI (EB-PEI) were supported onto a macroporous silica synthesized by spray-drying a water slurry containing a fumed silica. The silica has a high CO₂ accessibility to the supported amines and excellent steam stability arising from its large pore diameter (56 nm in average) and thick framework (10–15 nm). The CO₂ adsorption–desorption behaviours of PEI/SiO₂ and EB-PEI/SiO₂ were compared under practical temperature swing adsorption (TSA) conditions; CO₂ adsorption was carried out with a simulated flue gas (15% CO₂, 10% H₂O, N₂...
balance) at 60 °C and desorption was carried out under 100% CO₂ at 110 °C. As shown in Fig. 2a, EB-PEI/SiO₂ (1.84 mmol g⁻¹) showed smaller CO₂ adsorption than PEI/SiO₂ (4.05 mmol g⁻¹) due to the reduced amine density after the EB-functionalization of PEI²¹. However, the amounts of desorbable CO₂ during the adsorbent regeneration (i.e., CO₂ working capacities) were similar for both samples (1.98 and 1.62 mmol g⁻¹ for PEI/SiO₂ and EB-PEI/SiO₂, respectively), because of inefficient CO₂ desorption in PEI/SiO₂ at 110 °C. The more efficient regeneration of EB-PEI/SiO₂ can be attributed to the fact that EB-functionalization lowers the heat of CO₂ adsorption by generating tethered 2-hydroxybutyl groups on amines. The functional groups are electron-withdrawing groups that lower the amine basicity and also provide steric hindrance, lowering the heat of CO₂ adsorption⁴⁴. According to differential scanning calorimetry, EB-PEI/SiO₂ exhibited a substantially lower heat of CO₂ adsorption (66.2 kJ mol⁻¹) than PEI/SiO₂ (80.5 kJ mol⁻¹).

The CO₂ working capacities of PEI/SiO₂ and EB-PEI/SiO₂ before and after oxidative aging under 3% O₂ in N₂ at 110 °C for 24 h are shown in Fig. 2b. The adsorbents were aged at the adsorbent regeneration temperature (110 °C), because it is the highest temperature the adsorbents can experience in TSA. PEI/SiO₂ showed a 52% decrease in CO₂ working capacity after aging, whereas EB-PEI/SiO₂ showed only a 23% decrease. These results show that the EB-functionalization of PEI can increase the oxidative stability of amines, which is consistent with our earlier results²¹. The EB-functionalization converts the majority of the primary amines in PEI to secondary amines by alkylation with 2-hydroxybutyl groups. ¹³C NMR analysis showed that the primary:secondary:tertiary amine ratio in PEI is 36:37:27, whereas EB-PEI has a 10:56:34 ratio²¹. As Sayari pointed out, the oxidative degradation of amines in the PEI-type polymers is significantly affected by the co-existence of different types of amines¹⁶. Therefore, the increased stability of EB-PEI/SiO₂ might originate from the increased portion of secondary amines at the expense of primary amines. Alternatively, it can also be attributed to the generation of abundant hydroxy (–OH) groups after EB-functionalization, which can form hydrogen bonds with nearby amines. Chuang et al. reported that oxidative stability of amines could be improved in the presence of additives containing hydroxy groups (e.g., polyethylene glycol) because of their abilities to form hydrogen bonds with nearby amines. Chuang et al. also provided steric hindrance, lowering the heat of CO₂ adsorption than PEI/SiO₂ (4.05 mmol g⁻¹) because of ineficient CO₂ desorption in PEI/SiO₂ at 110 °C. The more efficient regeneration of EB-PEI/SiO₂ can be attributed to the fact that EB-functionalization lowers the heat of CO₂ adsorption by generating tethered 2-hydroxybutyl groups on amines. The functional groups are electron-withdrawing groups that lower the amine basicity and also provide steric hindrance, lowering the heat of CO₂ adsorption⁴⁴. According to differential scanning calorimetry, EB-PEI/SiO₂ exhibited a substantially lower heat of CO₂ adsorption (66.2 kJ mol⁻¹) than PEI/SiO₂ (80.5 kJ mol⁻¹).

Poisoning of metal impurities in amines. By coincidence, we discovered that the commercial PEI contains p.p.m.-level transition metal impurities, mainly Fe (17 p.p.m.) and Cu (6.9 p.p.m.) (Supplementary Table 1). Therefore, the EB-functionalized PEI had a more or less similar metal impurity content (Supplementary Table 1). Even though their concentrations are small, these metal species are known to catalyse amine oxidation by facilitating free radical formation via reaction with amines⁴²⁻⁴⁴. The Fe³⁺/Fe²⁺ and Cu²⁺/Cu⁰ redox cycles can oxidize amines to form amine radicals via single electron transfer⁴²⁻⁴⁴, which can significantly increase the amine oxidation rate. The catalytic effects of these metal species on amine oxidation have been comprehensively investigated in the case of aqueous amine solutions, because Fe ions are continuously leached out by reactor corrosion and Cu ions are often deliberately added into the amine solutions to inhibit reactor corrosion⁴²⁻⁴⁴. However, in the case of solid adsorbents, possible contamination of commercial amine sources with these metal impurities and their catalytic effects on amine oxidation have been completely ignored.

To study the catalytic effects of the metal impurities on amine oxidation, we pre-supported six different types of chelators (Fig. 3a) as catalyst poisons onto a silica support. Then, the silicas were further impregnated with PEI and EB-PEI (Fig. 1). The ionic chelators were not soluble in the polymeric amines (PEI and EB-PEI) and thus needed to be pre-dispersed on the silica surface to maximize their interaction with metal impurities. Because we introduced minor amounts of chelators (<2 wt% per composite), the CO₂ working capacities of the adsorbents were not affected by the presence of the chelators (Supplementary Tables 2, 3). All chelators were effective in inhibiting amine oxidation (Fig. 3b, c). As the loading of chelators increased, more CO₂ working capacities were retained after oxidative aging. Among the various chelators, phosphate or phosphonate sodium salts (1–3 in Fig. 3a) were the most effective at inhibiting amine oxidation in both PEI (Fig. 3b) and EB-PEI (Fig. 3c) systems. Notably, trisodiumphosphate (TSP, 1 in Fig. 3a), which is a completely inorganic and very economic chelator, showed the most promising inhibition effect. This is practically important because organic chelators themselves are known to be oxidatively degraded in the presence of oxygen and metal species⁴⁵. This is why organic chelators are not generally regarded as good oxidation inhibitors in aqueous amine solutions⁴⁶. Interestingly, TSP is known as a weak chelator that is ineffective in poisoning metal impurities in aqueous amine solutions.
Long-term oxidative stabilities of adsorbents. Because a real flue gas contains CO$_2$ and H$_2$O in addition to O$_2$, the adsorbents must be stable under this atmosphere rather than under an O$_2$/N$_2$ mixed gas. Sayari thoughtfully pointed out that amine oxidation is slower in a real flue gas than in O$_2$/N$_2$ mixtures, because of the preferential interaction of amines with CO$_2$ and H$_2$O$^{22}$. As shown in Fig. 4, we also confirmed that the addition of CO$_2$ and/or H$_2$O can substantially retard amine oxidation in both of PEI/SiO$_2$ and EB-PEI/SiO$_2$ systems containing varied amounts of TSP. This means that the earlier aging experiments (Figs. 2 and 3) under 3% O$_2$ in N$_2$ should be considered as accelerated aging because they were carried out in the absence of CO$_2$ and H$_2$O. Therefore, to evaluate the long-term stability in a more realistic condition, we analysed the CO$_2$ working capacities of adsorbents after aging in an O$_2$-containing flue gas (3% O$_2$, 15% CO$_2$, 10% H$_2$O in N$_2$) for 30 days.

To separately understand the effects of EB-functionalization and TSP addition on long-term oxidative stabilities, four adsorbents, i.e., PEI/SiO$_2$ and EB-PEI/SiO$_2$ prepared with and without 2 wt% TSP, were investigated (Fig. 5a). Fitting with the first-order deactivation kinetics (trend lines in Fig. 5a) showed that each of the EB-functionalization of PEI (EB-PEI/SiO$_2$) and the TSP addition into PEI (PEI/SiO$_2$ + 2 wt% TSP) could reduce the deactivation rate constant ($k_{\text{deac}}$) approximately to half ($0.0546-0.0573$ day$^{-1}$), compared to that of PEI/SiO$_2$ ($0.123$ day$^{-1}$). Notably, the combination of both strategies (EB-PEI/SiO$_2$ + 2 wt% TSP) led to remarkable synergy, and the $k_{\text{deac}}$ ($0.00258$ day$^{-1}$) became ~50 times smaller than that of PEI/SiO$_2$. The adsorbent retained 91.5% of the initial CO$_2$ working capacity after 30-days aging, while PEI/SiO$_2$ showed a complete loss of CO$_2$ capacity. The great synergy between the EB-functionalization and TSP addition was attributed to the lower polarity of EB-PEI than that of PEI due to the presence of ethyl side groups (Fig. 1), which can increase the formation constants of metal phosphates (i.e., stronger poisoning of metal species). Our adsorption experiments showed that EB-PEI/SiO$_2$ adsorbed much less H$_2$O (0.7 wt%) than PEI/SiO$_2$ (4.7 wt%) under the simulated flue gas at 60 °C, which proved the lower polarity of EB-PEI.

In FT-IR spectra (Fig. 5b), PEI/SiO$_2$ without TSP showed a marked increase in C=O/C=N stretching bands (1670 cm$^{-1}$) with increasing loading of TSP.
Discussion

We synthesized oxidation-stable amine-containing adsorbents via the functionalization of PEI with 1,2-epoxybutane (EB) and the poisoning of the p.p.m.-level metal impurities with chelators. The combination of two different strategies could make remarkable synergy, because chelators form metal complexes more efficiently (i.e., stronger poisoning) in less polar EB-functionalized PEI. We believe that the amine-containing solid adsorbent is beneficial in terms of oxidative stability compared to conventional aqueous amine solutions, because the aqueous amine solutions cause the continuous leaching of metal species by reactor corrosion and these metals act as catalysts for amine oxidation. This requires the continuous and stoichiometric addition of inhibitors such as oxygen/radical scavengers or chelators, and also the removal of their decomposition products. In the case of solid adsorbents, the initial poisoning of the p.p.m.-level metal impurities in polymeric amines is sufficient to increase the oxidative stability over a long period because there is no continuous metal buildup from reactor corrosion. Furthermore, the polymeric amines less polar than water can also enable more efficient metal poisoning by chelators. The unprecedentedly high oxidative stability of amine-containing solid adsorbents may represent an important breakthrough toward their commercial implementation.

Methods

Functionalization of PEI with 1,2-epoxybutane (EB).

EB-functionalization of a commercial PEI (Nippon Shokubai, Epomin SP-012, MW 1200) was carried out as we reported previously. In a typical synthesis, 12 g of 1,2-epoxybutane (Sigma-Aldrich, 99%) was added dropwise to 60 g of a 33 wt% methanolic solution of PEI. The molar ratio between 1,2-epoxybutane and the nitrogen content in PEI (22 mmol N g⁻¹) was fixed at 0.37. The reaction was carried out at room temperature for 12 h with stirring. The resultant methanolic solution containing 44 wt% EB-PEI was directly used for impregnation into a silica support.

Preparation of a macroporous silica support.

A highly macroporous silica support was prepared following the procedure we reported previously. The silica was synthesized by spray-drying a water slurry containing 9.5 wt% fumed silica (OCI, KONASIL K-300) and 0.5 wt% silica sol (Aldrich, Ludox AS-30) as a binder. In a typical synthesis, 0.95 kg fumed silica, 0.05 kg silica sol, and 9 kg water were mixed and the resultant slurry was injected for spray-drying. The spray-drying was carried out using a spray dryer with a co-current drying configuration and a rotary atomizer (Zeustec ZSD-25). The injection rate was 30 cm² min⁻¹, and the rotating speed of the rotary atomizer was set to 4000 r.p.m. The air blowing inlet temperature was 210 °C and the outlet temperature was 150 °C. The resultant silica particles were calcined in dry air at 600 °C to sinter the fumed silica into a three-dimensional porous network.

Impregnation of chelators into the silica support.

In the present work, chelators in a completely basic form (all acidic functional groups were titrated with Na⁺) were impregnated into the macroporous silica support using their aqueous solutions (typically, 0.25–2.0 wt% chelator concentrations). For the preparation of the aqueous solutions, trisodiumphosphate (1 mmol N g⁻¹) was fixed to 50 wt% TSP and the chelator content was controlled in the range of 0–4 wt% with respect to the mass of the fixed metal poison.

Preparation of the PEI/SiO₂ and EB-PEI/SiO₂ adsorbents.

Methanolic solutions of PEI and EB-PEI were impregnated into the macroporous silica supports pre-impregnated with 0–4 wt% chelators. After impregnation, the samples were dried at 60 °C for 12 h in a vacuum oven to remove methanol completely. With respect to the mass of the final composite adsorbents, the polymer content was fixed to 50 wt % and the chelator content was controlled in the range of 0–2 wt%.

Material characterization.

The heat of CO₂ adsorption was measured by differential scanning calorimetry (Setaram Instrumentation, Setsys Evolution). Before

and a decrease in C–H stretching band (2800–3000 cm⁻¹) after the 30-days aging. The result indicates the formation of amide/imine species, which can be thermally evaporated. The chain degradation may be the consequence of complex amine oxidation reactions. It has been proposed that the ethylenediaminetetraacetic acid tetrasodium salt dihydrate (2.0 wt% chelator concentrations). For the preparation of the aqueous solutions, trisodiumphosphate (1.1 mol N g⁻¹) was fixed to 50 wt% TSP and the chelator content was controlled in the range of 0–4 wt% with respect to the mass of the fixed metal poison.

Preparation of the PEI/SiO₂ and EB-PEI/SiO₂ adsorbents.

Methanolic solutions of PEI and EB-PEI were impregnated into the macroporous silica supports pre-impregnated with 0–4 wt% chelators. After impregnation, the samples were dried at 60 °C for 12 h in a vacuum oven to remove methanol completely. With respect to the mass of the final composite adsorbents, the polymer content was fixed to 50 wt % and the chelator content was controlled in the range of 0–2 wt%.

Material characterization.

The heat of CO₂ adsorption was measured by differential scanning calorimetry (Setaram Instrumentation, Setsys Evolution). Before
the measurements, the samples were degassed at 100 °C for 1 h under N2 flow (50 cm3 min−1). Then, the samples were cooled to 60 °C. Subsequently, the gas was switched to 15% CO2 (50 cm3 min−1). The heat of adsorption was calculated through the integration of the heat flow curve. Fourier transform infrared (FT-IR) spectra were recorded using an FT-IR spectrometer (Thermo Nicolet NEXUS 470). Prior to the analysis, 3 mg of the adsorbents were grinded with 18 mg of the silica (macroporous silica support) as a diluent. The mixtures were pressed into a self-supporting wafer. Before the FT-IR measurements, each sample was degassed at 100 °C for 3 h under vacuum in an in situ infrared cell equipped with CaF2 windows. FT-IR spectra were collected at room temperature. Elemental compositions (C, H, and N) of the adsorbents were analysed using a FLASH 2000 (Thermo Scientific) instrument. The contents of transition metal impurities (Fe, Cu, etc.) in PEI and EB-PEI were determined by inductively coupled plasma mass spectrometry (ICP-MS) using an ICP-MS 7700s instrument (Agilent). In the case of EB-PEI, the metal concentrations were determined after the complete evaporation of the methanol solvent at 60 °C for 12 h under vacuum after its synthesis.

**CO2 adsorption-desorption experiments.** CO2 adsorption–desorption profiles were collected by a thermogravimetric analysis-mass spectrometry (TGA-MS) setup. Prior to the measurements, all samples were degassed at 100 °C for 1 h under N2 flow (50 cm3 min−1). CO2 adsorption was carried out using a simulated wet flue gas containing 15% CO2, 10% H2O, and N2 balance at 60 °C. After 30 min adsorption, the gas was switched to 100% CO2 flow (50 cm3 min−1) and the temperature was increased to 110 °C (ramp: 20 °C min−1). Then the temperature was maintained for 30 min for the desorption process. The adsorbed amount of CO2 was calculated by subtracting the amount of adsorbed H2O (determined by mass spectrometry) from the total mass increase determined by TGA. To confirm the reliability of the TGA-MS results, the CO2 uptake was also cross-checked with an automated chemisorption analysis (Micromeritics, AutoChem II 2920) specifically equipped with a cold trap (−10 °C) for H2O removal in front of the TCD detector.

**Data availability.** The data that support the findings of this study are available from the corresponding author upon request.

Received: 2 November 2017 Accepted: 22 January 2018
Published online: 20 February 2018

References

1. D’Alessandro, D. M., Smit, B. & Long, J. R. Carbon dioxide capture: prospects for new materials. Angew. Chem. Int. Ed. 49, 6058–6082 (2010).
2. Hasezdenie, R. S. Carbon capture and storage: how green can black be? Science 325, 1657–1652 (2009).
3. Rochele, G. T. Amine scrubbing for CO2 capture. Science 325, 1652–1654 (2009).
4. Figueroa, J. D., Fout, T., Playsnky, S., Mclvried, H. & Srivastava, R. D. Advances in CO2 capture technology—the U.S. department of energy’s carbon sequestration program. Int. J. Greenh. Gas Control 2, 9–20 (2008).
5. Nguyen, T., Hilliard, M. & Rochele, G. T. Amine volatility in CO2 capture. Int. J. Greenh. Gas Control 4, 707–715 (2010).
6. Wang, J. et al. Recent advances in solid sorbents for CO2 capture and new development trends. Energy Environ. Sci. 7, 3478–3518 (2014).
7. Choi, S., Drese, J. H. & Jones, C. W. Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. J. Phys. Chem. C. 118, 12302–12311 (2014).
8. Rezaei, F. & Jones, C. W. Stability of supported amine adsorbents to SO2 and NOx in postcombustion CO2 capture. 1. Single-component adsorption. Ind. Eng. Chem. Res. 52, 12192–12201 (2013).
9. Bollini, P., Choi, S., Drese, J. H. & Jones, C. W. Oxidative degradation of amine supported carbon dioxide adsorbents relevant to postcombustion CO2 capture. Energy Fuels. 25, 2416–2425 (2011).
10. Heydari-Gorji, A. & Sayari, A. Thermal, oxidative, and CO2-induced degradation of supported polyethylenimine-MCM-41. J. Am. Chem. Soc. 132, 6312–6314 (2010).
11. Sayari, A., Heydari-Gorji, A. & Yang, Y. CO2-induced degradation of amine-containing adsorbents: reaction products and pathways. J. Am. Chem. Soc. 134, 13834–13842 (2012).
12. Drage, T. C., Arenillas, A., Smith, K. M. & Snape, C. E. Thermal stability of polyethylenimine based carbon dioxide adsorbents and its influence on selection of regeneration strategies. Microporous Mesoporous Mater. 116, 504–512 (2008).
13. Min, K., Choi, W. & Choi, M. Macroporous silica with thick framework for steam-stable and high-performance poly(ethylenimine)/silica CO2 adsorbent. ChemSusChem 10, 2518–2526 (2017).
14. Chaikittisilp, W., Kim, H. J. & Jones, C. W. Mesoporous aluminophosphate supported amine sorbents as potential steam-stable adsorbents for capturing CO2 from simulated flue gas and ambient air. Energy Fuels. 25, 5528–5537 (2011).
15. Hammache, S. et al. Comprehensive study of the impact of steam on polyethylenimine on silica for CO2 capture. Energy Fuels. 27, 6899–6905 (2013).
16. Rezaei, F. & Jones, C. W. Stability of supported amine adsorbents to SO2 and NOx in postcombustion CO2 capture. 1. Single-component adsorption. Ind. Eng. Chem. Res. 52, 12192–12201 (2013).
17. Bollini, P., Choi, S., Drese, J. H. & Jones, C. W. Oxidative degradation of amine-supported carbon dioxide adsorbents in the presence of oxygen-containing gases. Microporous Mesoporous Mater. 145, 146–149 (2011).
18. Ahmadalinezhad, A., Tailor, R. & Sayari, A. Molecular-level insights into the oxidative degradation of grafted amines. Chem. Eur. J. 19, 10543–10550 (2013).
19. Didas, S. A., Zhu, R., Brunelli, N. A., Sholl, D. S. & Jones, C. W. Thermal, oxidative and CO2 induced degradation of primary amines used for CO2 capture: effect of alkyl linker on stability. J. Phys. Chem. C. 118, 12302–12311 (2014).
20. Sayari, A., Belmakhbouk, Y. & D’ana, E. CO2 deactivation of supported amines: does the nature of amine matter? Langmuir 28, 4241–4247 (2012).
21. Kim, C., Cho, H. S., Chang, S., Cho, S. J. & Choi, M. An ethylenediamine-grafted Y zeolite: a highly regenerable carbon dioxide adsorbent via temperature swing adsorption without urea formation. Energy Environ. Sci. 9, 1803–1811 (2016).
22. McDonald, T. M. et al. Cooperative insertion of CO2 in diame-appended metal-organic frameworks. Nature 519, 303–308 (2015).
23. Khatri, R. A., Chuang, S. S. C., Soong, Y. & Gray, M. Thermal and chemical stability of regenerable solid amine sorbent for CO2 capture. Energy Fuels. 20, 1514–1520 (2006).
24. Belmakhbouk, Y. & Sayari, A. Isothermal versus non-isothermal adsorption–desorption cycling of triamine-grafted pore-expanded MCM-41 mesoporous silica for CO2 capture from flue gas. Energy Fuels. 24, 5273–5280 (2010).
25. Qi, G., Fu, L. & Giannelis, E. P. Sponges with covalently tethered amines for high-efficiency carbon capture. Nat. Commun. 5, 5796 (2014).
26. Hicks, J. C. et al. Designing adsorbents for CO2 capture from flue gas: hyperbranched aminosilicas capable of capturing CO2 reversibly. J. Am. Chem. Soc. 130, 2902–2903 (2008).
Acknowledgements
This work was supported by Korea CCS R&D Center (KCRC) grant funded by the Korea government (Ministry of Science, ICT & Future Planning) (NRF-2014M1A8A1049256) and the Basic Science Research Program through the National Research Foundation of Korea (NRF-2017R1A2B2002346).

Author contributions
M.C. conceived and designed this study. K.M., W.C., and C.K. performed material synthesis, characterizations, and CO2 adsorption–desorption experiments. M.C. wrote the manuscript with assistance from K.M., W.C., and C.K. All authors discussed the results and commented on the manuscript.

Additional information
Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-018-03123-0.

Competing interests: The authors declare no competing financial interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2018