ARTICLE

<https://doi.org/10.1038/s43246-020-00109-8>

OPEN

Shaping and silane coating of a diamine-grafted metal-organic framework for improved CO₂ capture

Jong Hyeak Choe¹, Jeoung Ryul Park¹, Yun Seok Chae¹, Dae Won Kim¹, Doo San Choi¹, Hyojin Kim¹, Minjung Kang¹, Hwimin Seo², Yong-Ki Park² & Chang Seop Hong¹✉

Although metal-organic framework (MOF) powders can be successfully shaped by conventional methods, postsynthetic functionalization of the shaped MOFs remains almost unexplored, yet is required to overcome intrinsic limitations, such as CO₂ adsorption capacity and stability. Here, we present a scalable synthesis method for Mg₂(dobpdc) MOF and its shaped beads, which are obtained by using a spray dry method after mixing Mg₂(dobpdc) powders with alumina sol. The synthesized MOF/Al beads have micron-sized diameters with a moderate particle size distribution of 30–70 μm. They also maintain a high mechanical strength. N-ethylethylenediamine (een) functionalization and coating with long alkyl chain silanes results in een-MOF/Al-Si, which exhibits a significant working capacity of >11 wt% CO₂ capture and high hydrophobicity. The een-MOF/Al-Si microbeads retain their crystallinity and improved CO₂ uptake upon exposure to humid conditions for three days at a desorption temperature of 140 °C.

¹Department of Chemistry, Korea University, Seoul 02841, Korea. ²Center for Convergent Chemical Process, Korea Research Institute of Chemical Technology, Daejeon 305-600, Korea. ✉email: cshong@korea.ac.kr

After the industrial revolution, the concentration of CO₂ in the atmosphere has been steadily increasing because of the continuous consumption of fossil fuels. This can cause global warming and climate change, and consequently lead to environmental disaster¹. Carbon capture and sequestration technologies have been implemented to deal with the massive CO₂ emissions from coal-fired power plants^{2–4}. Among capture technologies, alkanolamine solution scrubbers are one of the most developed systems; however, they are affected by corrosiveness and amine evaporation and have a high energy penalty for regeneration^{5,6}. To address these limitations, noncorrosive solid materials with lower heat capacity have attracted considerable attention as alternative adsorbents^{7–9}.

Metal–organic frameworks (MOFs) with high surface area and tunable pores have been shown to possess superior CO₂ adsorption capacities compared with ordinary solid adsorbents such as zeolites, carbons, and amine-incorporated porous materials^{10–15}. In particular, expanded MOF-74 type frameworks, M₂(dobpdc) (M = Mg, Mn, Fe, Co, Ni, Zn; dobpdc^{4–} = 4,4′-dioxidobiphenyl-3,3′-dicarboxylate), exhibit exceptional CO₂ adsorption performances because of their high-density open metal sites that are functionalized by diamines, alcohols, amines, and alkoxyalkylamines^{16–21}. Among the series, diamine-functionalized Mg₂(dobpdc) with record-high adsorption capacities has been proven to be one of the most promising adsorbents for the post-combustion CO₂ capture process, while the shape of the isotherm and the ease with which the CO₂ can be removed play a much important role from a process point of view^{22,23}. Its adsorption and desorption behaviors can be modulated by selecting the appropriate amine structure^{24–28}. To improve the structural durability of the MOFs under humidification conditions, cyclic diamines or polyamines have been grafted onto the open metal sites of the Mg₂(dobpdc) platform^{29,30}. Coating the platforms with hydrophobic polymers also enhanced the structural stability in the presence of moisture³¹. Currently, diamine-grafted Mg₂(dobpdc) materials are prepared in the powdered form, which is not suitable for CO₂ capture processes because of disadvantages such as pressure drop, poor reusability and processability. In fact, MOF powders are shaped for practical applications via mechanical shaping including granulation, extrusion, pressing, and spray drying, template shaping including sol–gel method and electrospinning, and other shapings^{32,33}. Particularly, spray drying provides a cost-effective, rapid, and scalable method to continuously fabricate the shaped materials³⁴. Because diamine-grafted Mg₂(dobpdc) compounds have been extensively explored due to their exceptional CO₂ adsorption capacities for post-combustion capture processes^{16–20,24,25,27–31,35,36}, shaping of the MOF powders is important to increase their processability and mechanical strength for real-world CO₂ capture applications^{37,38}. Furthermore, to overcome the intrinsic limitations of pristine shaped MOFs such as CO₂ adsorption capacity and structural stability under humid conditions, their postsynthetic modifications are required but nearly unexplored.

In the present work, we report the scalable synthesis of Mg₂(dobpdc) as well as Mg₂(dobpdc)-alumina composite microbeads (MOF/Al) via the spray-dried shaping of MOF with alumina sol. The attrition index of the beads used was <0.6%, which meets the desirable mechanical property for the CO₂ capture process using solid sorbents. The shaped MOFs were further functionalized by *N*-ethylethylenediamine (een) and then coated by silanes to obtain een–MOF/Al–Si. The post-functionalized microbeads exhibited a substantial CO₂ capacity, >11 wt%, and improved long-term material stability under humid conditions.

Results and discussion

Synthesis and characterizations of MOF/Al microbeads. The dimethylformamide (DMF)-coordinated Mg₂(dobpdc) was synthesized by H₄dobpdc and MgCl₂·6H₂O in DMF/EtOH under a solvothermal reaction using a 300 mL reactor. We also successfully employed a 35 L steel bomb reactor to produce the analytically pure solid product in a kg scale. This was used for the MOF shaping. The Mg₂(dobpdc) sample was characterized by powder X-ray diffraction (PXRD), N₂ isotherms, and scanning electron microscopy (SEM) (for PXRD, N₂ isotherms, and SEM see Supplementary Fig. 1). Fully dried Mg₂(dobpdc) rod-shaped particles were ground to ensure the uniform distribution of the particles. The ground sample was mixed with 10 wt% alumina sol as a binder and was further treated with the ball-milling process for 30 min to obtain an aqueous slurry. The slurry of Mg₂(dobpdc) with alumina sol was injected into a spray drier to obtain DMF–MOF/Al spherical beads in the particle size range 30–70 μm (Fig. 1 and for SEM image see Supplementary Fig. 2). The SEM images and SEM-energy dispersive X-ray spectroscopy (SEM-EDS) data exhibited that the MOF rods and alumina particles were well distributed over the surface and the interior of the DMF–MOF/Al bead (Fig. 2c–f and for SEM-EDS mapping see Supplementary Fig. 3). The PXRD data revealed that the structure of the DMF–MOF/Al beads was consistent with that of Mg₂(dobpdc) (Fig. 2a and for PXRD see Supplementary Fig. 4). The infrared (IR) spectrum of the DMF–MOF/Al sample showed additional

Fig. 1 Schematic of the spray-drying process of MOF/Al microbeads.

a Scale-up synthesis of Mg₂(dobpdc) using 300 mL and 35 L steel bomb reactors. **b** Mixing Mg₂(dobpdc) and alumina sol binders through a ball-milling process. **c** Shaping of MOF/Al microbeads via spray dry method. **d** Functionalization of MOF/Al microbeads by *N*-ethylethylenediamine (een).

Fig. 2 Characterizations of MOF/Al microbeads and diamine-grafted MOF/Al microbeads. **a** PXRD data of DMF-MOF, DMF-MOF/Al, and een-MOF/Al. **b** N_2 isotherms for $Mg_2(dobpdc)$, MOF/Al, and een-MOF/Al at 77 K. **c** SEM image of the surface of DMF-MOF/Al. **d** Enlarged SEM image of the surface of DMF-MOF/Al. **e** SEM image of the inside of MOF-MOF/Al. **f** Enlarged SEM image of the inside of DMF-MOF/Al.

peaks at 1070 cm^{-1} , which are characteristic of Al–O stretching, and at 3330 and 3100 cm^{-1} , which are attributed to O–H stretching. This indicates the existence of alumina in the bead (for IR spectra see Supplementary Fig. 5). ICP-AES analysis revealed that the ratio of Mg to Al in the DMF-MOF/Al was 1:0.363 (for ICP-AES results see Supplementary Table 1). The binding energies of Al 2p and 2s orbitals in the XPS data of the DMF-MOF/Al beads also indicated the successful incorporation of the alumina binder into the spherical bead (for XPS data see Supplementary Fig. 6)³⁹. For practical applications, the shaped material should have the appropriate mechanical strength because the collisions of the beads with each other and the surface of the adsorption bed during the capture process will break the shaped particles into the powdered form. An attrition test was conducted to examine the mechanical properties of the microbeads. The attrition index was determined to be $\sim 0.6\%$, indicating that alumina-bound spheres are sufficiently robust for application in the CO_2 capture process^{40,41}.

To confirm the porous properties of DMF-MOF/Al beads, N_2 sorption was recorded at 77 K. The Brunauer–Emmett–Teller surface areas of $Mg_2(dobpdc)$ and MOF/Al were 3178 and $1656\text{ m}^2\text{ g}^{-1}$, respectively (Fig. 2b and for porous properties see Supplementary Table 2). The reduction in the surface area of MOF/Al indicates that the pore channel is partially blocked by the alumina binders. This is supported by the decreased pore volume and the unchanged pore channel size (for pore size distribution see Supplementary Fig. 7).

Preparation and characterizations of diamine-grafted MOF/Al microbeads. The functionalization of $Mg_2(dobpdc)$ with diverse diamines enhances CO_2 adsorption characteristics that are suitable for post-combustion CO_2 capture applications³⁵. To increase the CO_2 uptake, we grafted MOF/Al with *N*-ethylethylenediamine (een). Before the functionalization of een, DMF-MOF/Al was soaked in MeOH for 3 days at room temperature to replace the DMF molecules coordinated with the open metal sites with the readily removable MeOH. The absence of the C=O stretching vibration of DMF at 1663 cm^{-1} in the IR spectrum suggests the complete removal of DMF from the bead sample (for IR spectra see Supplementary Fig. 5). The SEM images and XPS data show that the shape and composition of MOF/Al were maintained after MeOH soaking (for SEM and XPS data see

Supplementary Figs. 2 and 6). We treated the MeOH-soaked sample (MeOH-MOF/Al) with 50 equivalents of een in *n*-hexane for 12 h at 50°C without stirring to obtain an een-functionalized phase, een-MOF/Al. After een grafting, the structure of $Mg_2(dobpdc)$ remained intact, and the morphology of the beads was identical to that of MOF/Al (for SEM image see Supplementary Fig. 2). N–H stretching vibration at 3300 cm^{-1} was observed in the IR spectrum, and the N1s peak was observed at 400 eV in the XPS profile. This indicates the existence of een in the sample (for IR and XPS data see Supplementary Figs. 5 and 6).

From the N_2 isotherms of een-MOF/Al, the surface area was calculated as $611\text{ m}^2\text{ g}^{-1}$ (Fig. 2b and for surface area see Supplementary Table 2). Because the diamine was grafted onto the open metal sites of the framework, the surface area of een-MOF/Al was smaller than that of MOF/Al, and its pore size decreased from 18.4 to $14.8\text{ \AA}$ (for pore size distribution see Supplementary Fig. 7). The CO_2 isotherms of een-MOF/Al had a CO_2 uptake of 3.48 mmol g^{-1} at 150 mbar CO_2 , which is similar to that of een-MOF (for CO_2 isotherms see Supplementary Figs. 8 and 9)²⁸. This indicates that using alumina nanoparticles for shaping binds the MOF rods, while keeping the pores open for CO_2 diffusion. The CO_2 uptake of the sample was negligible at 1 bar CO_2 at 140°C , implying that CO_2 can be desorbed even under 100% CO_2 at that temperature. The complete desorption of the adsorbed CO_2 is important for the repeated reuse of the adsorbent for real-world post-combustion applications. The step pressure in the isotherms of the MOF beads suggests the mechanism of operation of CO_2 insertion, which was observed in diamine-functionalized $Mg_2(dobpdc)$ series³⁵. We calculated the isosteric heat of the adsorption (Q_{st}) using the dual-site Langmuir–Freundlich (L–F) and Clausius–Clapeyron equations (for isosteric heats of CO_2 adsorption see Supplementary Fig. 10). The $-Q_{st}$ of een-MOF/Al was in the range $69\text{--}82\text{ kJ mol}^{-1}$, attributed to the chemisorption.

Introducing hydrophobic silane into the MOF/Al. Flue gas emitted from coal-fired power plants contains 5–7% water vapor². Hydrophilic materials can readily adsorb water vapors; however, the desorption of the adsorbed water molecules requires high energy input⁴². Thus, a potential adsorbent for CO_2 capture should also be hydrophobic to preclude the access of water vapors

Fig. 3 Characterizations of een-MOF/Al-Si. **a** Contact angle of een-MOF/Al. **b** Photograph of een-MOF/Al after dropping water. **c** Contact angle of een-MOF/Al-Si. **d** Photograph of een-MOF/Al-Si after dropping water. **e** SEM image of een-MOF/Al-Si. **f–h** SEM-EDS mappings of een-MOF/Al-Si.

to the pores of the material. To examine the surface properties of DMF-MOF/Al and een-MOF/Al, we measured the contact angles using a water droplet. No contact angle was observed with MOF/Al and een-MOF/Al, indicating that the samples were hydrophilic (Fig. 3a, b and for contact angles see Supplementary Fig. 11). To enhance hydrophobicity, silanes $\text{H}-(\text{CH}_2)_n-\text{Si}(\text{OMe})_3$ with chains of different numbers of carbon atoms were introduced into the een-MOF/Al beads. When $n = 3$, there was no contact angle, and the hydrophilic characteristic remained (for contact angles see Supplementary Fig. 12). By increasing n , a high contact angle ($>105^\circ$) was obtained; however, it disappeared quickly. Remarkably, when octadecyltrimethoxysilane with $n = 18$ was used to obtain the silane-coated product, een-MOF/Al-Si, a contact angle $>100^\circ$ was maintained for 30 min (Fig. 3c, d). It is clear that a longer carbon chain with silane increases the contact angle of the sample because of the increased bulkiness and hydrophobicity. The PXRD pattern of een-MOF/Al-Si agreed with that of een-MOF/Al, indicating that the MOF structure was well-maintained during the silane coating (for PXRD data see Supplementary Fig. 13). In the IR spectra, the C–H stretching vibrations at 2850 and 2950 cm^{-1} were assigned to the long carbon chains of the silane moiety (for IR spectra see Supplementary Fig. 14). Both the SEM images and SEM-EDS data showed that the shape of the spherical beads was maintained and that the silanes were well distributed over the surface and interior of een-MOF/Al-Si (Fig. 3e–h and for SEM-EDS mapping see Supplementary Fig. 15). This is also corroborated by the XPS results in which Al and Si peaks were visible (for XPS data see Supplementary Fig. 16). The N_2 isotherm of een-MOF/Al-Si at 77 K exhibited a surface area of $17\text{ m}^2\text{ g}^{-1}$ (for N_2 isotherm see Supplementary Fig. 17). The silane coating of een-MOF/Al can obstruct the diffusion of N_2 gas by blocking the pore channels with the long carbon chain. This significantly reduces the surface area of een-MOF/Al-Si. Furthermore, the CO_2 isotherm was collected at 195 K (for CO_2 isotherm see Supplementary Fig. 18). The isotherm showed that een-MOF/Al-Si adsorbs CO_2 at that low temperature. This result suggests that CO_2 can be diffused into the MOF channel despite the interference of the long carbon chain on silane, which is due to the smaller size of CO_2 than N_2 .

We supposed that silanes can react with the hydroxy groups on the alumina binders and with the non-coordinating functional groups of the ligands on the surface of MOF in een-MOF/Al via condensation among methoxy, hydroxyl, and carboxylic groups⁴³. To prove this hypothesis, we introduced octadecyltrimethoxysilane to een-MOF and alumina under the same conditions applied for bead coating. The silane-coated een-MOF

(een-MOF-Si) and alumina (alumina-Si) showed hydrophobicity with contact angles of 63° and 141° , respectively (for contact angles see Supplementary Fig. 19). The characteristic peaks were positioned at 2850 and 2950 cm^{-1} in the IR spectra of silane-coated alumina and een-MOF, which can be assigned to the C–H stretchings in silane (for IR spectra see Supplementary Fig. 20). Furthermore, the XPS analysis revealed that Si peaks were observed in een-MOF-Si and alumina-Si, indicating the presence of silane moiety in the samples (for XPS data see Supplementary Figs. 21 and 22). This demonstrates that the silanes are coated on the alumina surface as well as the MOF surface in een-MOF/Al-Si.

CO_2 adsorption-desorption behaviors of een-MOF/Al and een-MOF/Al-Si.

The CO_2 adsorption curves were measured at different temperatures to evaluate the CO_2 adsorption performance of een-MOF/Al-Si (Fig. 4a). The CO_2 uptake was 3.15 mmol g^{-1} at 150 mbar , which is still significant and only slightly lower than that of een-MOF/Al. The step pressure implies that the CO_2 insertion mechanism is operative even after the introduction of silane. For een-MOF/Al-Si, the step moved to a higher pressure because long carbon chains on silane slightly disturb CO_2 diffusion into the MOF channel at low partial CO_2 pressures (for CO_2 isotherms see Supplementary Fig. 9). To confirm a selectivity of CO_2/N_2 , N_2 isotherms were obtained at the same temperature ranges as the CO_2 isotherms (for N_2 isotherms see Supplementary Fig. 23). We calculated the selectivity using formula, $S = (q_{\text{CO}_2}/q_{\text{N}_2})/(P_{\text{CO}_2}/P_{\text{N}_2})$, where q_i and p_i are the adsorption capacity and the partial pressure, respectively, of component i . The selectivity at 15% CO_2 and 75% N_2 corresponded to $53,182$ at 40°C , 1260 at 60°C , 595 at 80°C , 523 at 100°C , 5 at 120°C , and 3 at 140°C (for selectivity see Supplementary Table 3). The tendency shows that the selectivity decreased as the temperature increased. The selectivity of 595 at the adsorption temperature of 80°C indicates that the presence of N_2 could be ignorable during adsorption of CO_2 . The calculated Q_{st} of een-MOF/Al-Si was in the range $71\text{--}73\text{ kJ mol}^{-1}$, which is similar to that of een-MOF/Al (for isosteric heats of CO_2 adsorption see Supplementary Fig. 10). For een-MOF/Al-Si, we observed the change in $\Delta T = T_{\text{des}} - T_{\text{ads}}$ with the adsorption temperature (T_{ads}) at the desorption temperature (T_{des}) of 130 and 140°C , respectively, under 2.5 and 15% CO_2 (for correlation diagram see Supplementary Fig. 24). At $T_{\text{des}} = 140^\circ\text{C}$, the working capacity increased from 11.1 to $12.6\text{ wt\%}$, even under a low pressure of 2.5% CO_2 as ΔT increased from 50 to 100°C . The

Fig. 4 Gas sorption behaviors and long-term stability test under humid condition. **a** Adsorption isotherms of CO₂ for een-MOF/Al-Si at various temperatures. **b** Water vapor isotherms of een-MOF, een-MOF/Al, and een-MOF/Al-Si. **c** CO₂ adsorption capacity of een-MOF, een-MOF/Al, and een-MOF/Al-Si after exposure to ambient air by using TGA. **d** CO₂ adsorption capacity of een-MOF, een-MOF/Al, and een-MOF/Al-Si after exposure to 10% H₂O and 90% CO₂ at 140 °C by using TGA. The flow rate was 50 cc min⁻¹.

observed working capacity was in the upper bound of the CO₂ capacity observed for solid adsorbents^{7,35}. We investigated the adsorption capacities of een-MOF/Al-Si using Thermogravimetric analyses (TGA) at different CO₂ concentrations and temperatures as a function of time (for adsorption capacities see Supplementary Fig. 25). To display adsorption rate clearly, we differentiated CO₂ uptake curve with respect to time (for adsorption rate see Supplementary Fig. 26). From the differentiated data, CO₂ adsorption rate increased as the CO₂ partial pressure increased and the temperature decreased. For example, adsorption rates at 40 °C changed from 4.57 wt% min⁻¹ at 2.5% CO₂ to 22.6 wt% min⁻¹ at 15% CO₂ to 53.72 wt% min⁻¹ at 100% CO₂. At 15% CO₂, the adsorption rate of 22.61 wt% min⁻¹ at 40 °C was significantly reduced to 0.15 wt% min⁻¹ at 140 °C. These results unveiled that een-MOF/Al-Si has a high adsorption rate even in the form of beads^{28,36,44}. We also performed temperature swing adsorption (TSA) cycle tests of een-MOF/Al-Si to evaluate the reusability (for TSA cycles see Supplementary Fig. 27). Adsorption was conducted at 15% CO₂ and 80 °C for 5 min and desorption took place at 100% CO₂ and 140 °C for 1 min. After 100 cycles, the adsorption amount of een-MOF/Al-Si was maintained without a capacity loss. Thus, een-MOF/Al-Si is a promising adsorbent with high working capacity, high adsorption rate, and reusability.

CO₂ adsorption mechanisms of een-MOF/Al and een-MOF/Al-Si. To examine the CO₂ adsorption mechanism of een-MOF/Al and een-MOF/Al-Si, we performed *in situ* IR spectroscopy under CO₂ and plotted the results as a function of time (for IR spectra see Supplementary Figs. 28 and 29). The samples were activated at 140 °C for 2 h under N₂ and then exposed to a stream of 100% CO₂ at 40 °C. For both samples, new peaks emerged at 3429, 3408, 1651, and 1319 cm⁻¹ after exposure for 1 min. The first two peaks (3429 and 3408 cm⁻¹) were attributed to the N-H stretchings, and the other two (1651 and 1319 cm⁻¹) were assigned to C-O and C-N vibrations, respectively. This reveals

that carbamate species (R-NH-CO₂⁻) is generated in een-MOF/Al and een-MOF/Al-Si, which is in good agreement with the CO₂ insertion mechanism observed in diamine-functionalized Mg₂(dobpdc) frameworks^{17,28}. Furthermore, we acquired the solid-state ¹³C NMR spectra of een-MOF/Al and een-MOF/Al-Si before and after CO₂ uptake. In the spectra of een-MOF/Al-Si, the carbons on een were observed in the range 35–56 ppm, carbons on octadecylsilane at 31 ppm, benzene carbons of dobpdc⁴⁻ in the range 120–133 ppm, benzene carbon adjacent to oxygen at 167 ppm, and carboxylate carbon at 174 ppm. After CO₂ adsorption, the positions of the carbons in the carboxylate group and een groups changed slightly, indicating that these groups were affected by CO₂ insertion due to the proximity to the insertion site. Moreover, a new peak appeared at 163 ppm, which is attributed to the carbamate carbon generated after CO₂ adsorption (for solid-state ¹³C NMR spectra see Supplementary Fig. 30)⁴⁵. Meanwhile, the peaks related to the carbons of the silane were mostly unchanged, suggesting that the silane does not affect the CO₂ adsorption mechanism. In the solid-state ¹⁵N NMR spectra of een-MOF/Al and een-MOF/Al-Si, two peaks were observed at 15.1 and 33.7 ppm; these were assigned to the two nitrogen atoms of een. After CO₂ uptake, the peaks shifted to 40.3 and 74.6 ppm, corresponding to ammonium and carbamate nitrogen atoms, respectively. The nuclear magnetic resonance (NMR) results revealed that the adsorption mechanism involves even after the MOF shaping and silane coating (for solid-state ¹⁵N NMR spectra see Supplementary Fig. 31).

Long-term stability test under humid conditions. The water vapor isotherms of een-MOF, een-MOF/Al, and een-MOF/Al-Si were collected at 25 °C (Fig. 4b). The water uptake of een-MOF/Al-Si was lower than that of een-MOF and een-MOF/Al, indicating that the silane coating makes the material more hydrophobic by impeding the access of water molecules. To examine the effect of coating on the structural stability and CO₂

performance³¹, we exposed the samples to ambient air for 15 days. The CO₂ adsorption amount decreased almost linearly for een-MOF and een-MOF/Al as the exposure time increased, reaching 83% (11.33 wt%) and 78% (11.95 wt%) of the initial capacity, respectively. In contrast, for the silane-coated een-MOF/Al-Si, the CO₂ uptake remained almost constant with maintaining a capacity of >12 wt% after exposure for 15 days (Fig. 4c). The PXRD data revealed that the silane-coated sample retained its structural integrity, while the structures of the other samples partially collapsed (for PXRD data see Supplementary Fig. 32). To further investigate the material's stability in the presence of water vapor, we exposed it to harsh conditions of 10% H₂O and 90% CO₂ at a desorption temperature of 140 °C, which are more practical environments for real-world post-combustion CO₂ capture applications (Fig. 4d). The adsorption capacity of een-MOF/Al linearly decreased to 76% (11.07 wt%) of the original capacity after 3 days. The capacity loss was due to the structural collapse (for PXRD data see Supplementary Fig. 33). It is noted that the capacity of een-MOF/Al-Si was almost retained with a capacity of ~12 wt% after 3 days of exposure (Fig. 4d). This result demonstrates that the silane coating significantly enhances structural stability and performance durability (for CO₂ adsorption capacities see Supplementary Fig. 33).

Furthermore, to investigate CO₂ adsorption in the presence of water vapor, we collected CO₂ uptake at dry conditions of 80 °C under 15% CO₂, 85% He, and a flow rate of 10 cc min⁻¹. The CO₂ adsorption was recorded at wet conditions of 80 °C under 15% CO₂, 3.75% H₂O, 81.25% He, and a flow rate of 10 cc min⁻¹. The water vapor was generated from a bubbler and was removed at a trap after passing through the sample before reaching the thermal conductivity detector (TCD). The CO₂ adsorption capacity and rate for een-MOF/Al-Si were similar to those of TGA results. The amount of CO₂ uptake was 10.24 wt% in the dry conditions and 10.88 wt% in the wet conditions. The CO₂ adsorption capacity was a little higher at wet conditions than dry conditions, which was commonly observed in diamine-grafted Mg₂(dobpdc) frameworks^{24,28,31}. Thus, een-MOF/Al-Si can selectively adsorb CO₂ even in the presence of water vapor.

Since amines can be degraded in the presence of O₂ from the flue gas, potential adsorbents are required to be stable under O₂^{12,13}. To confirm the O₂ stability of een-MOF/Al-Si, adsorption were carried out under a mixed gas of 15% CO₂ and 5% O₂ and at 80 °C for 5 min, while desorption occurred at 100% CO₂ and 140 °C for 1 min (for TSA cycles see Supplementary Fig. 35). After 50 cycles, it was confirmed the CO₂ adsorption capacity was almost maintained at 9.52 wt% when compared to 9.96 wt% in the first cycle.

Conclusion

We demonstrated the scalable synthesis of Mg₂(dobpdc) as well as shaped MOF microbeads via a spray dry method. The microbeads exhibited excellent mechanical properties, which are important for practical applications. We also performed the sequential postsynthetic functionalizations such as diamine grafting and silane coating of the beads to obtain a hydrophobic material with a significant working capacity and enhanced structural stability under humid conditions. The post-functionalized MOF microbead materials with the remarkable long-term performance can be applied as adsorbents in real-world CO₂ capture processes.

Methods

Preparation. H₄dobpdc was synthesized according to the previous literature¹⁶. MgCl₂·6H₂O (≥98.0%), N-ethylethylenediamine (een, ≥98.0%) and octadecyltrimethoxysilane were obtained from Sigma-Aldrich. All solvents were reagent

grade (≥99.0%) and used as received. Alumina sol (10 wt%, pH = 4, particle size = 10–20 nm) was purchased from Alutec company.

Synthesis of Mg₂(dobpdc) in a g scale. Mg₂(dobpdc) was synthesized through a previous synthesis method, and synthesized through a 300 mL high-pressure reactor. MgCl₂·6H₂O (19.7 g, 970 mmol) was dissolved in EtOH (100 mL) and H₄dobpdc (7.60 g, 277 mmol) was dissolved in DMF (100 mL). The resulting solutions were poured into a 300 mL autoclave. The mixture was reacted for 72 h at 130 °C. After the reaction, the resulting powder was separated via filtration and soaked in DMF.

Synthesis of Mg₂(dobpdc) in a kg scale. Scale-up Mg₂(dobpdc) was synthesized in the following method. MgCl₂·6H₂O (1.50 kg, 7.29 mol) was dissolved in EtOH (10.0 L) and H₄dobpdc (1.00 kg, 3.64 mol) was dissolved in DMF (10.0 L). The resulting solutions were poured into a 35 L autoclave. The mixture was reacted for 72 h at 140 °C. After the reaction, the resulting powder was separated via filtration and soaked in mother liquid.

Synthesis of Mg₂(dobpdc)/alumina beads (DMF-MOF/Al). DMF-MOF/Al was manufactured in the following method. DMF-MOF was dried in an oven for 24 h at 100 °C. The resultant sample (100 g) was grounded with water (340 mL) and alumina sol (111 g, alumina content 10 wt%) using 3 mm ZrO₂ ball (130 g) in a ball-mill instrument for 30 min under 300 rpm. After grinding, the obtained MOF/Al slurry was injected into a spray drier using a feeding machine. The MOF/Al slurry, which passed through the atomizer, was formed into spherical particles. When the high-temperature gas was blown to the spherical particles, it hardened immediately (input gas temperature = 290 °C, output gas temperature = 130 °C). The dried particles were collected in a dry particle collector to yield DMF-MOF/Al beads (58 g).

Synthesis of een-Mg₂(dobpdc)/alumina beads (een-MOF/Al). DMF-MOF/Al was soaked in MeOH for 72 h and refreshed everyday with MeOH. The MeOH-soaked sample was placed in a 100-mL Schlenk flask and dried for 24 h at 150 °C under vacuum. The dried sample (300 mg, 0.78 mmol) was replaced in a 100-mL one-neck round flask. N-ethylethylenediamine (4.12 mL, 39.1 mmol) and hexane (20 mL) were put into the flask using cannula. The mixture was soaked for 12 h at 50 °C. After the reaction, the mixture was filtered and washed with hexane. Light purple products were dried under vacuum for 2 h.

Synthesis of een-Mg₂(dobpdc)/alumina-silane beads (een-MOF/Al-Si). Dried een-MOF/Al (300 mg) was placed in a 100-mL one-neck round flask. Octadecyltrimethoxysilane (1.5 g) and hexane (40 mL) were poured into the flask. The mixture was soaked for 72 h at 50 °C. After the reaction, the mixture was filtered and washed three times with hexane. Gray products were dried under vacuum for 2 h.

Synthesis of een-MOF-Si and alumina-Si. een-MOF-Si was synthesized in the following method. Dried een-MOF (300 mg) was placed in a 100-mL one-neck round flask. Octadecyltrimethoxysilane (1.5 g) and hexane (40 mL) were put into the flask. The mixture was soaked for 72 h at 50 °C. After the reaction, the mixture was filtered and then soaked in fresh hexane for 3 days in order to eliminate unreacted octadecylsilane. After 3 days, een-MOF-Si was collected by filtration. Alumina-Si was synthesized in the similar reaction using alumina. After heating of alumina sol at 100 °C for 6 h under vacuum, alumina in a solid state was obtained. Obtained alumina was grounded by a mortar to make fine powders. Ground alumina (300 mg) was placed in a 100-mL one-neck round flask. Octadecyltrimethoxysilane (1.5 g) and hexane (40 mL) were put into the flask. The mixture was soaked for 72 h at 50 °C. After the reaction, the mixture was filtered and then soaked in fresh hexane for 3 days in order to eliminate unreacted octadecylsilane. After 3 days, alumina-Si was collected by filtration.

Physical measurements. PXRD patterns were recorded using Cu Kα radiation (λ = 1.5406 Å) with a Rigaku Ultima III diffractometer with a scan rate of 2° min⁻¹ and a step interval of 0.02°. Contact angle was measured by Phoenix-MT(T). X-ray photoelectron spectroscopy (XPS, K-Alpha+) data were taken at Hanyang University. SEM images were collected using S-4600 at Korea Basic Science Institute (KBSI).

Attrition test. Attrition test was carried out by a crafted device at Korea Research Institute of Chemical Technology based on ASTM D5757 standard method⁴⁶. This device is composed of distributor, attrition tube, setting chamber, and fine collection assembly. The distributor and attrition tube have a tube with 35 mm inside diameter, 710 mm in length, and three 0.397 mm holes on the distributor. The attrition tube is linked to a setting chamber and a fines collector. The sample was injected to the distributor by blowing air in a rate of 10 L min⁻¹. The sample that was passed through the three holes on the distributor collided with each other in the attrition tube. The crashed sample in the attrition tube was transferred to the setting chamber, and the finely ground sample was transported through the internal filter of the chamber to the fines collector. This process was performed for

5 h under dry air. The attrition index was calculated by following formula:

$$\text{Attrition index (AI)} = \frac{\text{Weight of collected sample on fine collection assembly}}{\text{Weight of initial sample}} \times 100 \quad (1)$$

Gas adsorption measurements. Gas sorptions with CO₂ (99.999%) and N₂ (99.999%) were performed using a Micromeritics 3flex instrument after the pre-treatment of each sample. Density functional theory pore size distributions for Mg₂(dobpdc) (MOF), MOF/Al, een-MOF/Al, and een-MOF/Al-Si were estimated from N₂ isotherms at 77 K using the model of cylindrical pores with oxide surface. The water vapor isotherms were recorded by ASAP 2020 instrument after the treatment of samples at 298 K. To investigate the CO₂ adsorption capacity in the presence of water vapor, we used modified temperature-programmed desorption (TPD) processes in the BELCAT-II instrument. We obtained TCD signals for CO₂ under dry and wet conditions during TPD processes and quantized the amount of CO₂ uptake versus time through the area of TPD signals for CO₂.

Thermogravimetric analyses and water vapor exposure test. TGA were obtained at a ramp speed of 20 °C min⁻¹ in a stream of 15% CO₂ and 100% CO₂ using a TA instrument Discovery TGA with a flow rate of 70 mL min⁻¹ for all gases. The water vapor exposure test was conducted by a homemade setup. The water vapor (about 10% H₂O) was formed from a round-bottomed flask in which water was warmed at 50 °C. CO₂ (99.999%) gas was flowed through the flask and then passed into the sample chamber heated at 140 °C. After exposure test, the samples were recollected to measure adsorption capacity using a TGA instrument under 15% CO₂ for 30 min after activation under N₂ atmosphere.

Exposure tests. For air exposure, each sample (100 mg) was put into a 20 mL vial and exposed to an ambient air. Then, we measured adsorption uptake of the sample using a TGA instrument at 15% CO₂ for 30 min after activation under N₂. For humidity exposure, water vapor (about 10% H₂O) was generated from a round-bottomed flask by warming water at 50 °C. CO₂ (99.999%) was passed through the flask and then injected into a homemade sample chamber heated at 140 °C. After the exposure tests, samples were recollected to measure adsorption capacity using a TGA instrument under 15% CO₂ for 30 min after activation under N₂.

Spectroscopic measurements. IR spectra were recorded using a Nicolet iS10 FTIR spectrometer. In situ IR spectra were taken with an air-tight homemade IR cell containing KBr windows. Prior to the IR measurements, high-purity N₂ (99.999%) was flowed into the sample chamber for removal of atmospheric CO₂ from the IR instrument. Solid-state NMR spectroscopy was collected with a Bruker AVANCE II + 400 MHz NMR system at KBSI Seoul Western Center.

Isosteric heats of adsorption calculations. We employed the dual-site L-F equation (Eq. (2)) to analyze the CO₂ adsorption characteristics in the whole range of the isotherm for een-MOF/Al and een-MOF/Al-Si:

$$q = \frac{q_{\text{sat,A}} b_A p^{\alpha_A}}{1 + b_A p^{\alpha_A}} + \frac{q_{\text{sat,B}} b_B p^{\alpha_B}}{1 + b_B p^{\alpha_B}} \quad (2)$$

here, q represents the amount of CO₂ (mmol g⁻¹), p the pressure (bar), q_{sat} the saturation amount (mmol g⁻¹), b the L-F parameter (bar^{-α}), and α the L-F exponent (dimensionless) toward two adsorption sites A and B:

$$(\ln p)_q = \left(\frac{Q_{\text{st}}}{R} \right) \left(\frac{1}{T} \right) + C \quad (3)$$

The isotherm fits were utilized to determine the exact pressures, p , corresponding to constant amounts of CO₂ adsorbed, q , at three temperatures. The Clausius-Clapeyron equation (Eq. (3)) was applied to attain the isosteric heats of adsorption (Q_{st}).

Data availability

The data supporting the observations of this work are included in this paper and its Supplementary information.

Received: 24 August 2020; Accepted: 25 November 2020;

Published online: 04 January 2021

References

- Karl, T. R. & Trenberth, K. E. Modern global climate change. *Science* **302**, 1719–1723 (2003).
- Sumida, K. et al. Carbon dioxide capture in metal-organic frameworks. *Chem. Rev.* **112**, 724–781 (2012).
- Pera-Titus, M. Porous inorganic membranes for CO₂ capture: present and prospects. *Chem. Rev.* **114**, 1413–1492 (2014).
- Bui, M. et al. Carbon capture and storage (CCS): the way forward. *Energy Environ. Sci.* **11**, 1062–1176 (2018).
- Rochelle, G. T. Amine scrubbing for CO₂ capture. *Science* **325**, 1652–1654 (2009).
- Figueroa, J. D., Fout, T., Plasynski, S., McIlvried, 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).
- Choi, S., Drese, J. H. & Jones, C. W. Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. *ChemSusChem* **2**, 796–854 (2009).
- D'Alessandro, D. M., Smit, B. & Long, J. R. Carbon dioxide capture: prospects for new materials. *Angew. Chem.* **49**, 6058–6082 (2010).
- Bollini, P., Didas, S. A. & Jones, C. W. Amine-oxide hybrid materials for acid gas separations. *J. Mater. Chem.* **21**, 15100–15120 (2011).
- Pardakhti, M. et al. Trends in solid adsorbent materials development for CO₂ Capture. *ACS Appl. Mater. Interfaces* **11**, 34533–34559 (2019).
- Ding, M., Flaig, R. W., Jiang, H. L. & Yaghi, O. M. Carbon capture and conversion using metal-organic frameworks and MOF-based materials. *Chem. Soc. Rev.* **48**, 2783–2828 (2019).
- Choi, W. et al. Epoxide-functionalization of polyethyleneimine for synthesis of stable carbon dioxide adsorbent in temperature swing adsorption. *Nat. Commun.* **7**, 12640 (2016).
- Min, K., Choi, W., Kim, C. & Choi, M. Oxidation-stable amine-containing adsorbents for carbon dioxide capture. *Nat. Commun.* **9**, 726 (2018).
- Liang, W. et al. A tailor-made interpenetrated MOF with exceptional carbon-capture performance from flue gas. *Chem* **5**, 950–963 (2019).
- Li, J., Bhatt, P. M., Li, J., Eddaoudi, M. & Liu, Y. Recent progress on microfine design of metal-organic frameworks: structure regulation and gas sorption and separation. *Adv. Mater.* **32**, 2002563 (2020).
- McDonald, T. M. et al. Capture of carbon dioxide from air and flue gas in the alkylamine-appended metal-organic framework mmen-Mg₂(dobpdc). *J. Am. Chem. Soc.* **134**, 7056–7065 (2012).
- McDonald, T. M. et al. Cooperative insertion of CO₂ in diamine-appended metal-organic frameworks. *Nature* **519**, 303–308 (2015).
- Lee, W. R. et al. Exceptional CO₂ working capacity in a heterodiamine-grafted metal-organic framework. *Chem. Sci.* **6**, 3697–3705 (2015).
- Lee, W. R. et al. Diamine-functionalized metal-organic framework: exceptionally high CO₂ capacities from ambient air and flue gas, ultrafast CO₂ uptake rate, and adsorption mechanism. *Energy Environ. Sci.* **7**, 744–751 (2014).
- Mao, V. Y. et al. Cooperative carbon dioxide adsorption in alcoholamine- and alkoxalkylamine-functionalized metal-organic frameworks. *Angew. Chem.* <https://doi.org/10.1002/anie.201915561> (2020).
- Zhang, H., Yang, L. M. & Ganz, E. Adsorption properties and microscopic mechanism of CO₂ capture in 1,1-dimethyl-2-ethylenediamine-grafted metal-organic frameworks. *ACS Appl. Mater. Interfaces* **12**, 18533–18540 (2020).
- Joss, L., Hefti, M., Bjelobrk, Z. & Mazzotti, M. On the potential of phase-change adsorbents for CO₂ capture by temperature swing adsorption. *Energy Procedia* **114**, 2271–2278 (2017).
- Pai, K. N., Baboolal, J. D., Sharp, D. A. & Rajendran, A. Evaluation of diamine-appended metal-organic frameworks for post-combustion CO₂ capture by vacuum swing adsorption. *Sep. Purif. Technol.* **211**, 540–550 (2019).
- Jo, H. et al. Fine-tuning of the carbon dioxide capture capability of diamine-grafted metal-organic framework adsorbents through amine functionalization. *ChemSusChem* **10**, 541–550 (2017).
- Milner, P. J. et al. Overcoming double-step CO₂ adsorption and minimizing water co-adsorption in bulky diamine-appended variants of Mg₂(dobpdc). *Chem. Sci.* **9**, 160–174 (2018).
- Inagaki, F., Matsumoto, C., Iwata, T. & Mukai, C. CO₂-selective absorbents in air: reverse lipid bilayer structure forming neutral carbamic acid in water without hydration. *J. Am. Chem. Soc.* **139**, 4639–4642 (2017).
- Milner, P. J. et al. A diaminopropane-appended metal-organic framework enabling efficient CO₂ capture from coal flue gas via a mixed adsorption mechanism. *J. Am. Chem. Soc.* **139**, 13541–13553 (2017).
- Lee, W. R. et al. Diamine-functionalization of a metal-organic framework adsorbent for superb carbon dioxide adsorption and desorption properties. *ChemSusChem* **11**, 1694–1707 (2018).
- Siegelman, R. L. et al. Water enables efficient CO₂ capture from natural gas flue emissions in an oxidation-resistant diamine-appended metal-organic framework. *J. Am. Chem. Soc.* **141**, 13171–13186 (2019).
- Choe, J. H. et al. Revealing an unusual temperature-dependent CO₂ adsorption trend and selective CO₂ uptake over water vapors in a

- polyamine-appended metal-organic framework. *Mater. Chem. Front.* **3**, 2759–2767 (2019).
31. Kang, M. et al. A diamine-grafted metal-organic framework with outstanding CO₂ capture properties and a facile coating approach for imparting exceptional moisture stability. *J. Mater. Chem. A* **7**, 8177–8183 (2019).
  32. Liu, X., Xie, L. & Wu, Y. Recent advances in the shaping of metal-organic frameworks. *Inorg. Chem. Front.* **7**, 2840–2866 (2020).
  33. Mallick, A. et al. Advances in shaping of metal-organic frameworks for CO₂ capture: understanding the effect of rubbery and glassy polymeric binders. *Ind. Eng. Chem. Res.* **57**, 16897–16902 (2018).
  34. Carne-Sanchez, A., Imaz, I., Cano-Sarabia, M. & Maspoch, D. A. spray-drying strategy for synthesis of nanoscale metal-organic frameworks and their assembly into hollow superstructures. *Nat. Chem.* **5**, 203–211 (2013).
  35. Kang, M., Kang, D. W. & Hong, C. S. Post-synthetic diamine-functionalization of MOF-74 type frameworks for effective carbon dioxide separation. *Dalton Trans.* **48**, 2263–2270 (2019).
  36. Siegelman, R. L. et al. Controlling cooperative CO₂ adsorption in diamine-appended Mg₂(dobpdc) metal-organic frameworks. *J. Am. Chem. Soc.* **139**, 10526–10538 (2017).
  37. Luz, I., Soukri, M. & Lail, M. Synthesis of fluidized CO₂ sorbents based on diamine coordinated to metal-organic frameworks by direct conversion of metal oxides supported on mesoporous silica. *Chem. Eur. J.* **24**, 10612–10616 (2018).
  38. Darunte, L. A. et al. Monolith-supported amine-functionalized Mg₂(dobpdc) adsorbents for CO₂ capture. *ACS Appl. Mater. Interfaces* **9**, 17042–17050 (2017).
  39. Bou, M., Martin, J. M. & Le Mogne, T. Chemistry of the interface between aluminium and polyethyleneterephthalate by XPS. *Appl. Surf. Sci.* **47**, 149–161 (1991).
  40. Sun, Z. et al. A facile fabrication of mesoporous core-shell CaO-based pellets with enhanced reactive stability and resistance to attrition in cyclic CO₂ capture. *J. Mater. Chem. A* **2**, 16577–16588 (2014).
  41. Knight, A., Ellis, N., Grace, J. R. & Lim, C. J. CO₂ sorbent attrition testing for fluidized bed systems. *Powder Technol.* **266**, 412–423 (2014).
  42. Wang, J. et al. Hydration energetics of a diamine-appended metal-organic framework carbon capture sorbent. *J. Phys. Chem. C* **124**, 398–403 (2019).
  43. Kujawa, J. et al. Efficiency of grafting of Al₂O₃, TiO₂ and ZrO₂ powders by perfluoroalkylsilanes. *Colloids Surf. A Physicochem. Eng. Asp.* **420**, 64–73 (2013).
  44. Martell, J. D., Milner, P. J., Siegelman, R. L. & Long, J. R. Kinetics of cooperative CO₂ adsorption in diamine-appended variants of the metal-organic framework Mg₂(dobpdc). *Chem. Sci.* **11**, 6457–6471 (2020).
  45. Forse, A. C. et al. Elucidating CO₂ chemisorption in diamine-appended metal-organic frameworks. *J. Am. Chem. Soc.* **140**, 18016–18031 (2018).
  46. Bemrose, C. R. & Bridgwater, J. A. Review of attrition and attrition test methods. *Powder Technol.* **49**, 97–126 (1987).

Acknowledgements

This work was supported by a Korea CCS R&D Center (KCRC) grant funded by the Korean Government (the Ministry of Science, ICT, & Future Planning (MSIP)) (NRF-2012-0008901), the Basic Science Research Program (NRF-2018R1A2A1A05079297), and the Priority Research Centers Program (NRF-2019R1A6A1A11044070).

Author contributions

C.S.H. conceived the project. J.H.C. conducted experiments including sample synthesis and characterizations by PXRD, gas isotherms, SEM, and XPS data with assistance of H.K. and M.K.; J.R.P., Y.S.C., and D.S.C. fabricated MOF beads under the guidance of H.S. and Y.-K.P.; D.W.K. prepared and characterized the ligand. J.H.C. and C.S.H. wrote the paper. All authors contributed to discussions and finishing the paper.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this paper at <https://doi.org/10.1038/s43246-020-00109-8>.

Correspondence and requests for materials should be addressed to C.S.H.

Peer review information Primary handling editor: John Plummer.

Reprints and permission information is available at <http://www.nature.com/reprints>

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) 2021