Enhanced isosteric heat, selectivity, and uptake capacity of CO₂ adsorption in a metal-organic framework by impregnated metal ions†

Hye Jeong Park and Myunghyun Paik Suh*

We demonstrate by experimental and theoretical studies that the impregnation of various metal ions such as Li⁺, Mg²⁺, Ca²⁺, Co²⁺, and Ni²⁺ in the pores of an anionic MOF, [Zn₃(TCPT)₂(HCOO)][NH₂(CH₃)₂] (SNU-100) significantly enhances isosteric heat, selectivity, and uptake capacity of the CO₂ adsorption in the MOF. Due to the electrostatic interactions between CO₂ and the extra-framework metal ions, the isosteric heats of CO₂ adsorption are increased to 37.4–34.5 kJ mol⁻¹ and the adsorption selectivities of CO₂ over N₂ at room temperature are increased to 40.4–31.0, compared with those (29.3 kJ mol⁻¹ and 25.5, respectively) of the parent MOF (SNU-100) containing [NH₂(CH₃)₂]⁺ cations.

Introduction

Porous metal-organic frameworks (MOFs) have attracted significant interest due to their potential to be applied in hydrogen storage,¹ carbon dioxide capture,² and O₂/N₂ gas separation.³ In particular, selective and reversible capture of carbon dioxide from industrial flue gas has become one of the most important issues recently in the scientific community. Industrial flue gas contains not only carbon dioxide but also other gases, and its composition is dependent on the combustion methods. The flue gas emitted from the post-combustion chamber has a pressure of 1 atm with 15% of CO₂, 75% of N₂, 5–10% of water vapour, and other minor components such as O₂, SO₂, NO₃, and CO. To apply a MOF in capturing CO₂ from industrial flue gas that is emitted from a post-combustion chamber, its storage capacity at ambient temperatures under low pressure (0.15 atm) of CO₂ and adsorption selectivity for CO₂ over other gases should be high. For practical applications, the stability of the framework against water vapour as well as the effects of water vapour and other minor components of the flue gas on the separation of CO₂ must be also considered.

MOFs which have high surface area and pore volume show high CO₂ adsorption capacity at room temperature under high pressures.⁴ For example, MOF-177 that has a BET surface area of 4500 m² g⁻¹ can store 60.8 wt% (750 cm³ g⁻¹) of CO₂ at 298 K and 35 bar.⁵ However, under 1 atm and at 298 K, the CO₂ storage capacity of MOF-177 decreases to 3.4 wt%. In addition, the selectivity for CO₂ adsorption over N₂ in MOF-177 calculated by using the molar ratio of the CO₂ uptake at 0.15 atm and the N₂ uptake at 0.85 atm is only 4.²⁶ The isosteric heat (Qₛₜ) of CO₂ adsorption in common MOFs ranges from 25–35 kJ mol⁻¹.²⁶ It was reported that Cu-BTTri-en²⁷ and Cu-BTTri-mmen²⁸ whose metal sites were functionalized with ethylenediamine and N,N'-dimethylethylenediamine, respectively, exhibited zero-coverage Qₛₜ values of 90 and 96 kJ mol⁻¹, respectively, which were too high to reversibly release CO₂ from the amine moieties without applying heat. To increase the CO₂ adsorption capacity together with the adsorption selectivity for CO₂ over other gases at ambient temperature under the CO₂ pressure of ca. 0.15 atm, the Qₛₜ value of CO₂ adsorption should be increased to a certain extent that minimizes the energy penalty for regeneration.

Here we report for the first time based on experimental and theoretical studies that the impregnation of various metal ions such as Li⁺, Mg²⁺, Ca²⁺, Co²⁺, and Ni²⁺ in the pores of an anionic MOF significantly increases the Qₛₜ value of CO₂ adsorption in the MOF to the range of 37.4–34.5 kJ mol⁻¹ as well as the adsorption selectivity of CO₂ over N₂ to 40.4–31.0, and thus enhances the CO₂ capture ability at room temperature.

Results and discussion

We have prepared a new anionic MOF including dimethylammonium cations in the 1D channels, [Zn₃(TCPT)₂(HCOO)] [NH₂(CH₃)₂]·5DMF (SNU-100, TCPT = 2,4,6-tris-(4-carboxyphenoxy)-1,3,5-triazine), by heating the DMF solution of Zn(NO₃)₂·6H₂O and H₃TCPT at 90 °C for 24 h. In the X-ray structural determination of SNU-100, there exist crystallographically independent two Zn(Ⅱ) centers (Zn1 and Zn2) and they are linked in the sequence of Zn1–Zn2–Zn1 to form a Zn₃ cluster unit (Fig. S1†).
Zn1 and Zn2 show a tetrahedral- [\(\angle O-Zn-O\), av. 116.88(3)\)] and an octahedral-coordination geometry, respectively. Three Zn₃ cluster units are connected by two TCPT³⁻ linkers infinitely to form 2D layers, which run parallel to the ab plane (Fig. S2†). The triazine rings of the two TCPT³⁻ are nearly coplanar and form a \(\mathcal{D}_2\)-Piedfort unit.† The 2D layers are linked by formate species along the c axis, which gives rise to a 3D anionic framework. In SNU-100, two 3D frameworks are mutually interpenetrated to generate 1D channels where dimethylammonium cations are included (Fig. 1). The solvent accessible volumes of SNU-100 with and without dimethylammonium are 14.5 and 38.1%, respectively, as estimated by PLATON.† The guest solvent molecules included in the pores could not be refined, and they were characterized by the IR, elemental analysis (EA), and thermogravimetric analysis (TGA) data (Fig. S3†).

When the single crystals of SNU-100 were immersed in MeOH for 2 days, the guest solvent molecules were exchanged to provide \([\text{Zn}_3(\text{TCPT})_2(\text{HCOO})][\text{NH}_2(\text{CH}_3)_2] \cdot 6\text{MeOH}\) (SNU-100m). When SNU-100 was activated at 60 °C under vacuum for 2 h, the desolvated solid \([\text{Zn}_3(\text{TCPT})_2(\text{HCOO})][\text{NH}_2(\text{CH}_3)_2]\) (SNU-100') was resulted. The powder X-ray diffraction (PXRD) patterns of SNU-100m and SNU-100' were coincident with that of SNU-100, indicating that the framework structure could be retained during the guest-solvent exchange and guest-removal processes (Fig. S8†). Interestingly, the framework structure of SNU-100' was retained even after the exposure to water vapor for 7 days or immersion in water for 7 days, as evidenced by the PXRD patterns (Fig. S9†). The stability of the framework that contains tetrahedral Zn²⁺ ions against water may be attributed to the interpenetrated nature and/or the anionic charge of the framework, in addition to the coordinated formate that links secondary building units.† To explain this better, we will further conduct simulation works.

To verify the porosity of SNU-100', sorption isotherms were measured for \(\text{N}_2, \text{O}_2, \text{H}_2, \text{CO}_2\), and \(\text{CH}_4\) gases (Table S2†). The \(\text{N}_2\) sorption isotherm measured at 77 K showed typical Type-I sorption behaviour, characteristic for the microporosity (Fig. S10†). The BET surface area and the pore volume estimated by applying the Dubinin–Radushkevich (DR) equation are 814 m² g⁻¹ and 0.315 cm³ g⁻¹, respectively. SNU-100' adsorbs \(\text{H}_2\) gas up to 1.81 wt% at 77 K and 1 atm, and 1.30 wt% at 87 K and 1 atm (Fig. S11 and S12†). The \(Q_{st}\) values of \(\text{H}_2\) adsorption in SNU-100' are 8.17–7.11 kJ mol⁻¹ depending on the degree of \(\text{H}_2\). loading (Fig. S13†), as estimated by fitting the \(\text{H}_2\) isotherms at 77 K and 87 K to the virial equation (Fig. S14†). The zero-coverage \(Q_{st}\) (8.17 kJ mol⁻¹) is significantly higher than those of the common MOFs such as MOF-5 (4.8 kJ mol⁻¹),† because of the small pore size resulting from the interpenetration as well as the dimethylammonium cations included in the channels. The CO₂ gas adsorption isotherms of SNU-100' indicate that the material stores a large amount of CO₂, up to 3.20 mmol g⁻¹ (71.6 cm³ g⁻¹ at STP, 14.1 wt%) at 298 K and 1 atm (Fig. 2a). After SNU-100' was exposed to water vapor for 7 days or immersed in water for 7 days, or after water vapor sorption was measured at 293 K (Fig. S15†), the CO₂ uptake capacity of SNU-100' was still maintained once the sample was reactivated at 60 °C under vacuum for 12 h (Fig. S16†). The \(Q_{st}\) of CO₂ adsorption in SNU-100' is 29.3–27.7 kJ mol⁻¹ (Fig. 2b), as calculated by the Clausius–Clapeyron equation using dual-site Langmuir parameters at 231, 273, and 298 K (Fig. S20 and Table S8†). The selectivity for CO₂ adsorption over \(\text{N}_2\) is 25.5, as estimated from the ratios of Henry constants obtained by the
Langmuir equation (Fig. S21†). These values are comparable to those of ZIF-799 and higher than BPL carbon that is widely used in the industry for gas separations.11

To investigate the effect of the impregnated metal ions in the pores of the MOF on the gas sorption properties, the dimethylammonium included in SNU-100m was post-synthetically exchanged with Li⁺, Mg²⁺, Ca²⁺, Co²⁺, and Ni²⁺ ions, which afforded SNU-100-Li, SNU-100-Mg, SNU-100-Ca, SNU-100-Co, and SNU-100-Ni, respectively. In the experiments, crystals of SNU-100m (ca. 0.10 mmol) were immersed in the MeOH solutions of various hydrated metal salts, such as LiCl·xH₂O, Mg(NO₃)₂·6H₂O, Ca(NO₃)₂·4H₂O, Co(NO₃)₂·6H₂O, and Ni(NO₃)₂·6H₂O (concentration, 0.0970–0.126 M) for 10 days. Some of the SNU-100-M samples maintained the single crystalinity, but they provided poor X-ray diffraction data. After drying SNU-100-M at 60 °C under vacuum for 12 h, the degree of metal ion impregnation was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The ICP-AES data indicate that 84.4–95.4% of the dimethylammonium cations were exchanged with Li⁺, Mg²⁺, Ca²⁺, Co²⁺, and Ni²⁺. Unexpectedly, however, with Fe³⁺ and Cu²⁺ ions, even the intra-framework Zn²⁺ ions as well as the extra-framework ammonium cations were substituted with the metal ions. The trivalent metal ions such as Al³⁺ and Fe³⁺ could not be included because the framework was dissociated in the MeOH solutions of the trivalent metal salts even when the concentrations were low (1.0 mM). The chemical formula of the frameworks impregnating various metal ions, SNU-100-M, which were activated by heating at 60 °C under vacuum for 12 h, were determined based on the relative mass ratios of M/Zn, together with the elemental analysis data. The results suggested that the introduced metal ions still bound 4–6 water molecules. These water molecules are also evidenced by the IR spectra of SNU-100-M, which show OH stretching and HOH bending modes at 3641–3647 cm⁻¹ and 1629 cm⁻¹, respectively (Fig. S22†). These coordinated water molecules must be originated from the metal salts used in the cation exchange process. The PXRD patterns indicate that the series of SNU-100-M have the same structure as that of SNU-100 (Fig. S8†). Even after exposure to water vapor for 7 days, the framework of SNU-100-M remained stable as evidenced by PXRD patterns (Fig. S9†).

The N₂ sorption isotherms of SNU-100-M measured at 77 K showed typical Type-I sorption behavior with no hysteresis upon desorption (Fig. S10†). The BET surface areas ranged from 924 m² g⁻¹ for SNU-100-Li to 1000 m² g⁻¹ for SNU-100-Co, slightly higher than that of SNU-100. Since there are relatively few anionic MOFs that can retain their porosity after cation exchange,12† the present results are significant.

The H₂ storage capacities at 77 K and 87 K under the pressure of up to 1 atm for the series of SNU-100-M increased compared with that of SNU-100 (Table 1, Fig. S11 and S12†), which must be attributed to the increased accessible surface areas and pore volumes of SNU-100-M. The zero-coverage Q̄₁ values of H₂ sorption isotherms at 77 K and 87 K by using the virial equation (Fig. S23–S27†), ranged from 8.40–7.01 kJ mol⁻¹ (Fig. S13†), indicating that the impregnated metal ions exert rather minor effects on the interaction energy between H₂ and the MOF. We assume that the coordinated aqua ligands prevent direct access of H₂ molecules to the metal site. If metal ions were bare without coordinated solvent molecules, zero-coverage Q̄₁ values of the H₂ adsorption should be increased by ca. 4–5 kJ mol⁻¹.14,16,17 To improve Q̄₁ of the H₂ adsorption in MOFs, various strategies18 have been employed such as creation of accessible metal sites,13 incorporation of polarizing organic functional groups,14 impregnation of metal nanoparticles15 or metal ions15 in the pores, and the exchange of metals within the metal nodes.16 The post-synthetic exchange of dimethylammonium or protonated piperazine included in the MOFs with other metal ions such as Li⁺ or Mg²⁺ only slightly (0.2–1.1 kJ mol⁻¹) increased Q̄₁ values of the H₂ adsorption due to the solvent molecules still bound to the extra-framework metal ions.12† Similarly to our findings, the exchange of the guest Mn²⁺ ions in Mn₃[(Mn₄Cl)₃(BTT)₈(CH₃OH)₁₀] with Li⁺, Cu⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ resulted in a difference of only 2 kJ mol⁻¹ between the weakest and the strongest zero-coverage Q̄₁ values for the samples since the metal ions bound solvent molecules.12b

As for the CO₂ adsorption, SNU-100 shows the highest CO₂ capacity at 195 K (Fig. S17†) among the present samples. However, at higher temperatures, SNU-100-M with larger BET surface area adsorbs a larger amount of CO₂ than SNU-100 (Table 1, Fig. 2a, Fig. S18 and 19†). At 298 K and 1 atm, SNU-100-Co can store 16.8 wt% of CO₂, which is the next highest value to the best data in the MOF-74 series (25.7±1.6 wt%)17 and HKUST-1 (19.8 wt%).18 For better understanding, we calculated Q̄₁ values of CO₂ adsorption for SNU-100-M by using the Clausius–Clapeyron equation based on dual-site Langmuir parameters at 231, 273, and 298 K (Fig. S28–S32 and Table S8†). Contrary to Q̄₁ of H₂ adsorption, the low coverage Q̄₁ values of the CO₂ adsorption in the SNU-100-M series are increased to 37.4–34.5 kJ mol⁻¹, compared with that (29.3 kJ mol⁻¹) of SNU-100 (Table 1, Fig. 2b). These high Q̄₁ values must be primarily attributed to the electrostatic field provided by the extra-framework metal ions19† as well as the strong interaction of CO₂ with the water molecules coordinated at the metal ions.18 The low coverage Q̄₁ values of CO₂ adsorption in SNU-100-M are higher than those in common MOFs (25–35 kJ mol⁻¹), but lower than the MOF-74 series (Mg-MOF-74, 47 kJ mol⁻¹; Ni-MOF-74, 42 kJ mol⁻¹)17 and MIL-100 (62 kJ mol⁻¹),20 which contains open metal sites, and Cu-BTTri that is amine-functionalized at the metal site (90 kJ mol⁻¹).3 On cation exchange with Co³⁺, colorless crystals of SNU-100m changed to pink to form SNU-100-Co, which turned to purple on activation at 60 °C under vacuum for 12 h (Fig. S33†), suggesting that the coordination number of Co³⁺ changed from 6 to 4 upon activation. To see the effect of coordinated water molecules on CO₂ uptake, we attempted to remove the coordinated water molecules at Co³⁺ from SNU-100-Co. For this, the sample was activated at 60, 100, 150, 200, 250, 300, 350, and 400 °C, respectively, and the CO₂ gas sorption isotherms were measured at 298 K. When the sample was activated at the temperatures lower than 350 °C under vacuum, the CO₂ uptake capacities were nearly the same as that of the sample activated at 60 °C under vacuum (Fig. S34†). However, the sample activated at 400 °C under vacuum showed much
lower CO2 storage capacities, and the measured PXRD pattern reveals the collapse of the framework (Fig. S35†). This means that the coordinated water molecules could not be partially removed by heating the sample up to 350 °C under vacuum.

The \( Q_{st} \) values of CH4 adsorption were calculated by applying Langmuir–Freundlich parameters at 231, 273, and 298 K (Fig. S41–S46 and Table S9†) to the Clausius–Clapeyron equation because the Langmuir–Freundlich equation afforded a better fit to CH4 adsorption data than the dual-site Langmuir equation (Fig. S47†). The low coverage \( Q_{st} \) values of CH4 adsorption are also increased by the impregnated metal ions, but the enhancement (by 4.26–0.16 kJ mol\(^{-1}\)) is much smaller (Fig. S40†) than those (by 8.1–5.3 kJ mol\(^{-1}\)) for the CO2 adsorption. Due to the significantly greater quadrupole moment and polarizability of CO2, the interaction of CO2 molecules with the anionic framework and extra-framework metal ions must be much stronger than that of CH4 molecules.

The selectivities of CO2 adsorption over N2 for the series of SNU-100'-M, estimated from the ratios of Henry constants derived from the Langmuir equation (Fig. S48–S52 and Table S10†), are also significantly increased to 37.8, 32.6, 40.4, 31.0, and 37.4 for SNU-100'-Li, SNU-100'-Mg, SNU-100'-Ca, SNU-100'-Co, and SNU-100'-Ni, respectively, compared to 25.5 of SNU-100'. The enhanced selectivity of CO2 over N2 must be attributed to the increased interaction of CO2 molecules with impregnated metal ions in the channels. It should be noted here that the selectivity calculations may have a large error since a single-site Langmuir equation does not fit well the Henry region of these relatively steep isotherms.

The selective and reversible capture of CO2 at 298 K in SNU-100'-M as well as in SNU-100' was verified by the gas cycling experiment using a gas stream of 15% (v/v) CO2 in N2, which approximately mimics flue gas, followed by a pure N2 gas stream (Fig. S53†). Reversible changes of 2.1 wt% in SNU-100'-M and 2.0 wt% in SNU-100' were observed over the cycles, and the material was regenerated by the N2 gas flow.

To test the cyclability of CO2 adsorption in SNU-100'-Ca, which exhibited the highest zero-coverage \( Q_{st} \) (37.4 kJ mol\(^{-1}\)) of CO2 adsorption among the present samples, the CO2 gas sorption isotherms at 298 K and the values in parenthesis are selectivities estimated by using the molar ratio at 298 K of the CO2 uptake at 0.15 atm and the N2 uptake at 0.85 atm.

### Table 1
Gas sorption properties of SNU-100' and SNU-100'-M and comparison with other MOFs

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>( M/Zn ) ratio</th>
<th>( S_{BET} ) (m(^2) g(^{-1}))</th>
<th>( H_2 ) uptake (wt%)(^b)</th>
<th>( Q_{st} ) of H2 (kJ mol(^{-1}))</th>
<th>( CO_2 ) uptake (wt%)(^c)</th>
<th>( Q_{st} ) of CO2 (kJ mol(^{-1}))</th>
<th>Selectivity of CO2/N2(^d)</th>
</tr>
</thead>
</table>
| SNU-100' | \([Zn_3(TCPT)_4(HCOO)]\) [NH$_2$(CH$_3$)$_2$]
| — | 814 | 1.81 | 8.14–7.08 | 14.1 | 29.3–27.7 | 25.5 (26.5) |
| SNU-100'-Li | \([Zn_3(TCPT)_4(HCOO)]\) [Li(H$_2$O)$_2$]$_{0.44}$[NH$_2$(CH$_3$)$_2$]$_{0.116}$ | 0.281 | 924 | 1.93 | 8.40–5.91 | 15.3 | 35.7–34.3 | 37.8 (31.9) |
| SNU-100'-Mg | \([Zn_3(TCPT)_4(HCOO)]\) [Mg(H$_2$O)$_2$]$_{0.44}$[NH$_2$(CH$_3$)$_2$]$_{0.116}$ | 0.147 | 959 | 1.99 | 7.20–6.02 | 15.1 | 36.3–34.9 | 32.6 (28.7) |
| SNU-100'-Ca | \([Zn_3(TCPT)_4(HCOO)]\) [Ca(H$_2$O)$_2$]$_{0.42}$[NH$_2$(CH$_3$)$_2$]$_{0.146}$ | 0.142 | 935 | 1.88 | 8.10–6.65 | 15.1 | 37.4–34.6 | 40.4 (33.6) |
| SNU-100'-Co | \([Zn_3(TCPT)_4(HCOO)]\) [Co(H$_2$O)$_2$]$_{0.47}[NH$_2$(CH$_3$)$_2$]$_{0.046}$ | 0.159 | 1000 | 2.16 | 7.59–7.20 | 16.8 | 36.0–34.6 | 31.0 (27.0) |
| SNU-100'-Ni | \([Zn_3(TCPT)_4(HCOO)]\) [Ni(H$_2$O)$_2$]$_{0.44}[NH$_2$(CH$_3$)$_2$]$_{0.110}$ | 0.148 | 982 | 1.98 | 7.01–5.56 | 16.6 | 34.5–33.3 | 37.4 (29.6) |
| Mg-MOF-74$^{16}$ | Mg(dobdc) | — | 1495 | — | — | 26.0 | 47 | 44 |
| HKUST-1$^{17}$ | Cu$_4$(BTC)$_4$ | — | 1400 | — | — | 19.8 | 35 | 101 |
| Cu-BTTri-en$^5$ | H$_2$[(Cu$_4$Cl)$_3$(BTTri)$_6$(en)$_3$]$_{0.75}$ | — | 345 | — | — | 5.5 | 90 | 44 |
| Cu-BTTri-mmnen$^6$ | H$_2$[(Cu$_4$Cl)$_3$(BTTri)$_6$(mmen)$_{12}$] | — | 871 | — | — | 15.4 | 96 | 165 |
| MOF-177$^{24,26}$ | Zn$_2$(BTC)$_2$O | — | 4508 | — | — | 3.4 | — | 4 |

\footnote{a The number of the coordinated water molecules (n) is 4–6, as estimated by ICP-AES, EA data, and theoretical calculation. \footnote{b} Measured at 77 K and 1 atm. \footnote{c} Obtained at 298 K and 1 atm. \footnote{d} Selectivities were calculated from the ratios of Henry constants for CO2 and N2 adsorption isotherms at 298 K and the values in parenthesis are selectivities estimated by using the molar ratio at 298 K of the CO2 uptake at 0.15 atm and the N2 uptake at 0.85 atm.}

![Fig. 3](https://example.com/fig3.png) Ten cycles of CO2 uptake of SNU-100'-M at 298 K and 1 atm without the reactivation process between the cycles.
affects gas sorption properties (Fig. S55†). In this respect, we may assume that the type of metal ions has a rather minor effect (<20% change) on the CO₂ sorption properties because the sizes of metal aqua complexes are not so different.

During the introduction of metal ions, the quality of the single-crystal became unsuitable for single-crystal X-ray diffraction analysis, and thus the precise position of the incorporated metal ions in the pores could not be determined. Therefore, we conducted a “locate simulation” by using a sorption module of Materials Studio to determine the location sites of the extra-framework cations (see Experimental Section in the ESI†). The results indicate that [NH₂(CH₃)₃]⁺ cations in SNU-100 locate near the center of the 1D channels, similarly to its single crystal X-ray structure (Fig. S28†). The metal ions coordinated with water molecules also locate near the centre of the 1D channels (Fig. S36–S62†), although bare metal ion should reside beside the benzene rings of the TCPT ligand. The divalent cations occupy half sites of the monovalent cations and should reside beside the benzene rings of the TCPT ligand. In addition, the fact that the activated sample of SNU-100 showed a purple color, characteristic of the four coordinated channel, the same length as the 1D channels (Fig. S4), by using a locate simulation module of Materials Studio (see also Experimental Section in the ESI†). The calculations were performed with the assumption that 100% [NH₂(CH₃)₃]⁺ cations were exchanged with M(H₂O)₄⁺⁺ ions. To elucidate the effects of electrostatic interaction on \( Q_{as} \), additional simulations were conducted by eliminating the contribution of electrostatic interaction. The simulated \( Q_{as} \) values (26.7–25.3 kJ mol⁻¹) of CO₂ adsorption in SNU-100, considering only the dispersion interaction, are comparable to those (29.3–27.7 kJ mol⁻¹) derived from the measured CO₂ adsorption isotherms. The simulated \( Q_{as} \) values for SNU-100’⁻M are remarkably increased when the electrostatic model was applied. The results clearly indicate that the enhanced interaction would be a result of the generation of narrower pockets within the pores, but this does not seem to be happening in the present case as evidenced by increased porosity on metal ion impregnation. Among various metal ions, the Ca²⁺ ion must be the best for increasing \( Q_{as} \) of the CO₂ adsorption, as seen in Table 1 and Table 2. For the CH₄ adsorption, \( Q_{as} \) values simulated by using the electrostatic model are very similar to the experimental data but they are higher just by ca 8–10 kJ mol⁻¹ than those simulated with the non-electrostatic model. The results demonstrate that CO₂ has a much stronger tendency to have electrostatic interactions than CH₄ due to its higher polarizability and quadrupole moment.

Conclusions

Our experimental and theoretical studies clearly demonstrate that the impregnation of various metal ions such as Li⁺, Mg²⁺, Ca²⁺, Co²⁺, and Ni²⁺, which are coordinated with water molecules, in the pores of an anionic MOF, [Zn₃(TCPT)₂(HCOO)] [NH₂(CH₃)₃] (SNU-100), significantly enhances isosteric heat, selectivity, and uptake capacity of the CO₂ adsorption in the MOF at room temperature, while it affects rather slightly on H₂ and CH₄ adsorptions. The frameworks with impregnated metal ions, the SNU-100’⁻M series, reversibly adsorb and desorb CO₂ at 298 K. Due to the electrostatic interactions between CO₂ and the impregnated extra-framework metal ions, the isosteric heats of CO₂ adsorption in the SNU-100’⁻M series are increased

### Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Free volume</th>
<th>Surface area</th>
<th>( Q_{as} ) of CO₂ (kJ mol⁻¹)</th>
<th>( Q_{as} ) of CH₄ (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Non-electrostatic</td>
<td>Electrostatic</td>
</tr>
<tr>
<td>SNU-100'</td>
<td>0.188</td>
<td>842</td>
<td>26.7–25.3</td>
<td>55.6–49.9</td>
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<tr>
<td>SNU-100’⁻Li</td>
<td>0.153 (0.146)</td>
<td>736 (649)</td>
<td>25.7–25.0</td>
<td>76.4–66.6</td>
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<tr>
<td>SNU-100’⁻Mg</td>
<td>0.283 (0.252)</td>
<td>972 (876)</td>
<td>25.8–25.0</td>
<td>80.8–70.2</td>
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<tr>
<td>SNU-100’⁻Ca</td>
<td>0.270 (0.230)</td>
<td>939 (846)</td>
<td>24.8–25.6</td>
<td>85.4–72.6</td>
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<tr>
<td>SNU-100’⁻Co</td>
<td>0.253 (0.238)</td>
<td>912 (858)</td>
<td>25.2–24.4</td>
<td>68.3–52.4</td>
</tr>
<tr>
<td>SNU-100’⁻Ni</td>
<td>0.243 (0.230)</td>
<td>1000 (869)</td>
<td>25.3–24.5</td>
<td>72.4–66.4</td>
</tr>
</tbody>
</table>

* Calculated by the assumption that 100% [NH₂(CH₃)₃]⁺ cations in SNU-100’ are exchanged with metal ions. * Calculated for the tetraqua metal ion complexes. The values in the parentheses are the values calculated for the hexaqua complexes.
to 37.4–34.5 kJ mol$^{-1}$, and the effective adsorption selectivities of CO$_2$ over N$_2$ at room temperature are increased to 40.4–31.0, compared with 29.3 kJ mol$^{-1}$ and 25.5 of the parent MOF (SNU-100$^{10}$). Among various metal ions, the Ca$^{2+}$ ion seems to be the best for increasing the isosteric heat of CO$_2$ adsorption. The present MOFs with impregnated metal ions must be good candidates as the materials for post-combustion CO$_2$ capture from industrial flue gas.

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**Notes and references**


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