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Published on: 01 Jan 2012 - [Chemical Science](#) (The Royal Society of Chemistry)

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CITATION:

Horike, Satoshi ...[et al]. A solid solution approach to 2D coordination polymers for CH₄/CO₂ and CH₄/C₂H₆ gas separation: equilibrium and kinetic studies. *Chemical Science* 2011, 3(1): 116-120

ISSUE DATE:

2011-10-06

URL:

<http://hdl.handle.net/2433/161792>

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

A Solid Solution Approach to 2D Coordination Polymers for CH₄/CO₂ and CH₄/C₂H₆ Gas Separation: Equilibrium and Kinetic Studies

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Gas separation properties of CH₄/CO₂ and CH₄/C₂H₆ for flexible 2D porous coordination polymers under equilibrium gas condition and mixture gas flowing condition were investigated and the gas separation efficiencies were optimized by precise tuning of flexibility in ligand-base solid solution compounds.

Introduction

The development of materials for gas separation technology has become increasingly important in recent times.¹ For example, the separation of CO₂ from CH₄/CO₂ mixtures in biogas and C₂H₆ from CH₄/C₂H₆ mixtures in natural gas exhausts is facilitated by the use of solid adsorbents. The pressure swing adsorption (PSA) process and the use of solid support membranes are well-known technologies and in both cases, the selective binding of the target gas and gas adsorption kinetics are important factors for the design of the adsorbents.^{2,3} In particular, the conditions used in the PSA process depend on the target gas produced by various industrial processes and therefore porous materials that have the appropriate separation properties for specific working conditions have been required.⁴ Porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) consist of metal ions and organic ligands that are promising candidates for CO₂ gas separation.⁵⁻²⁰ The pore surface can be designed to be either basic or acidic and the pore dimensions and diameter are readily tunable ranging from 0.3 nm to a few nm. Some compounds that exhibit a “flexible” nature in the framework have been highlighted for gas separation.²¹⁻²⁶ The flexibility affords a structure transformation from a non-porous to porous system via gas adsorption where the transformation depends on the gaseous species. This phenomenon often results in gas separation (or recognition) properties. Indeed, we have succeeded in controlling flexibility by employing a solid solution where two distinct PCP/MOFs are uniformly integrated into a single framework with an arbitrary ratio.²⁷ Considering the potential use of these materials in separation processes, we have to evaluate them not only under equilibrium conditions but also under kinetic dynamic conditions at operating temperatures and pressures employed in gas separation. Because PSA, for instance, typically runs under ambient temperature and a total pressure of 0.4–0.8 MPa, the cycle time is several minutes. This process requires quick separation ability. In this work, we evaluated CO₂ and C₂H₆ gas separation from CH₄ under both equilibrium and kinetic conditions using flexible 2D layer-type PCP/MOFs and optimized their selectivity performance. Fine tuning of structure

flexibility in the frameworks turned out to be a significant factor in the design of materials for potential application in PSA processes for CH₄/CO₂ and CH₄/C₂H₆ gas mixtures.

Results and discussion

We employed two PCP/MOF frameworks, [Zn(5NO₂-ip)(bpy)]_n (CID-5, 5NO₂-ip = 5-nitroisophthalate, bpy = 4,4'-bipyridyl) and [Zn(5MeO-ip)(bpy)]_n (CID-6, 5MeO-ip = 5-methoxyisophthalate), both of which possess microporous 2D layer stacking structures.²⁷ These can be regarded as a series of porous coordination polymers with interdigitated structures, which we denote as CIDs.²⁷⁻³⁴ We also fabricated three ligand-base solid solution compounds of CID-5 and CID-6. The formula is depicted as [Zn(5NO₂-ip)_{1-x}(5MeO-ip)_x(bpy)]_n (CID-5/6), where *x* is the ratio of 5MeO-ip ligands in the structures. In the crystal structures, two Zn²⁺ ions are connected by carboxylate groups and the axial position of the Zn²⁺ ions are coordinated to the nitrogen atoms of bpy ligands to form an octahedral coordination environment as shown in **Fig. 1**. Dicarboxylates and Zn²⁺ form ribbon-type infinite 1D chains and each chain is linked by bpy to create 2D layers. The layers are stacked to complete the interdigitated porous structure. It has been reported that the structure flexibility of CID-5 is larger than that of CID-6.²⁷ CID-5 has large flexibility that results in a significant structure transformation from totally non-porous to porous. CID-6 is regarded as a rigid (robust) type porous framework where its porosity hardly changes during guest containment or the removal phase. The origin of their flexibility could be caused by the size/shape and electron-donating/-withdrawing properties of the substituent group of ligands and the resulting packed structures. We also confirmed that the three CID-5/6 (*x* = 0.1, 0.2, 0.4) were all single-phase materials by powder X-ray diffraction (XRD) studies and elemental analysis. This means that the two different ligands (5NO₂-ip and 5MeO-ip) are evenly distributed in the crystals regardless of the ratio of the ligands. CID-5/6 (*x* = 0.1) has characteristics similar to those of pure CID-5 with regard to crystal structure. However, CID-5/6 (*x* = 0.2, 0.4) compounds are more closely related to pure CID-6 and their flexibility depends on the *x* content; as *x* increases, the flexibility decreases.

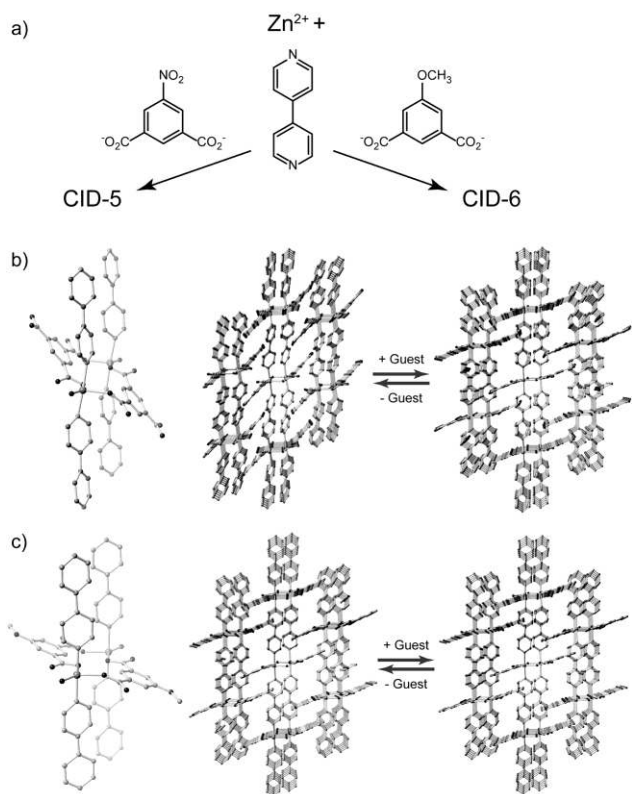


Figure 1. (a) Reaction schemes of CID-5 and CID-6. Crystal structures of the coordination environment around the Zn^{2+} ions and assembled 2D layer stacking of (b) CID-5 and (c) CID-6 before and after guest adsorption. Guests are omitted.

We then measured CO_2 and CH_4 gas adsorption isotherms for five CID compounds at 273 K as shown in **Fig. 2**. For CID-5, the total uptake of CO_2 was 57 mLg^{-1} , where the profile is not typical Type-I isotherm according to the IUPAC classification but a gate-opening-type adsorption.^{29, 35-39} Adsorption does not occur until the pressure reaches a specific point (in this case 0.10 MPa), upon which it starts abruptly and then reaches to saturation. CID-5 adsorbs less than 5 mLg^{-1} of CH_4 at 1.0 MPa and 273 K, indicating that structure transformation does not occur at this point. Interaction between CH_4 and the framework was not sufficient to open the structure under the measurement condition. On the other hand, CID-6 has permanent porosity in the deguested form and shows a Type-I adsorption isotherm in which gas uptake starts at the low-pressure region. Because of permanent microporosity, CID-6 adsorbs both CO_2 and CH_4 , and the total uptake at 1.0 MPa and 273 K is 58 mLg^{-1} (CO_2) and 45 mLg^{-1} (CH_4), respectively. We observed distinct adsorption behaviour on CID-5 and CID-6 that can be attributed to structure flexibility. Gas adsorption isotherms of CID-5/6 and the ligand-base solid solution of CID-5 and CID-6 are also shown in **Fig. 2c–2e**. As discussed before, the structure characteristics of CID-5/6 such as porosity and flexibility depend on the relative ratio of each ligand (x) in the framework. Regarding CO_2 , CID-5/6 ($x = 0.2, 0.4$) showed Type-I isotherms that were similar to CID-6 because they have permanent porosity in the deguested form. Meanwhile, CID-5/6 ($x = 0.1$) was dominated by the flexible properties of CID-5, and the CO_2 isotherm demonstrated gate-opening-type behaviour, even though the gate-opening pressure

was 0.02 MPa, which was smaller than that for pure CID-5. The reason for the lowering of the gate-opening pressure is that the thermodynamic stability of the deguested porous framework of CID-5/6 ($x = 0.1$) was lower than pure CID-5 because of partial doping of the CID-6 domain. For CH_4 , the adsorption isotherms were more sensitive to the ligand ratio in CID-5/6. As the content of 5MeO-ip ligand (x) decreases, the adsorption profiles became more gradual and the total amount of adsorption was low. Although the adsorption isotherms of CID-5/6 ($x = 0.2, 0.4$) were Type-I, the isotherm of CID-5/6 ($x = 0.1$) was not Type-I but appeared to be Type-III isotherm³⁵ because the compound was more closely related to pure CID-5 with high flexibility and a non-porous structure. Because of the decrease of cooperativity in the framework of CID-5/6 ($x = 0.1$) for gate-opening behaviour, the structure transformation from non-porous to porous became gradual, which resulted in the apparent Type-III isotherm. As a result, we observed a strong dependency on gas adsorption isotherms for CO_2 and CH_4 in the ambient temperature and pressure region as the ratio of ligand in the ligand-base solid-solution-type CID compounds was changed.

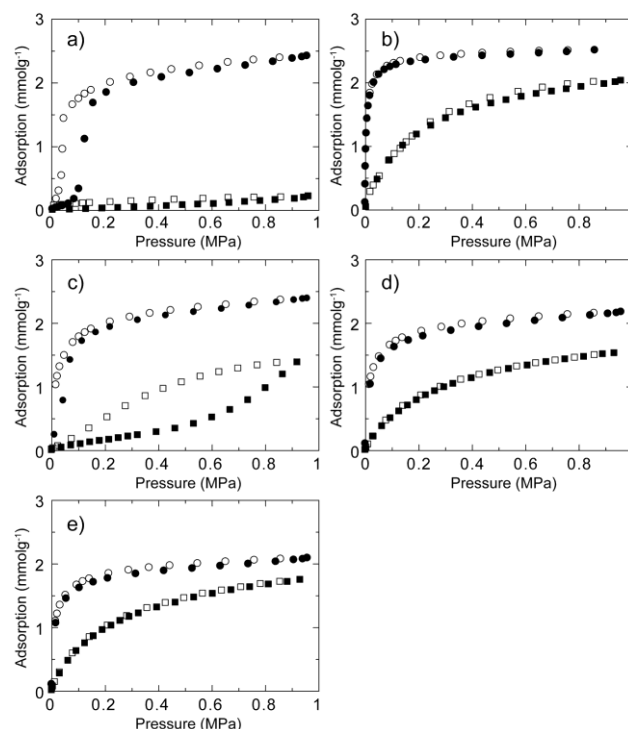


Figure 2. CH_4 (square) and CO_2 (circle) sorption isotherms for (a) CID-5, (b) CID-6, (c) CID-5/6 ($x = 0.1$), (d) CID-5/6 ($x = 0.2$) and (e) CID-5/6 ($x = 0.4$) at 273 K. Adsorption: closed characters; desorption: open characters.

We also studied the gas separation properties under kinetic gas flowing conditions at ambient conditions. The breakthrough curve is a typical way of evaluating gas separation ability for adsorbents under flowing gas conditions that are related to the PSA process. We measured the gas separation properties of CID-5, 6, CID-5/6 ($x = 0.1, 0.4$) (**Fig. 3**) for the CH_4/CO_2 mixture at 273 K and a total pressure of 0.80 MPa. The breakthrough curve of CID-5 is shown in **Fig. 3a**. After injection of the gas mixture, the concentration of CO_2 detected by gas chromatography (GC) was 10% and 90% for CH_4 and the retention time was around 10

min. Then it reached the breakpoint and smoothly went back to the initial ratio of the gas mixture. Considering that the relative pressure of CO₂ (0.32 MPa) in the gas mixture was higher than the gate-opening pressure of CID-5 (0.10 MPa) studied by an equilibrium isotherm, the compound adsorbed CO₂ and was accompanied by a structure transformation. On the other hand, the relative pressure of CH₄ was 0.48 MPa and CID-5 did not show uptake of gas at this pressure and consequently we observed a concentration effect of CO₂ over CH₄ from the flowing gas. Even though we observed a concentration effect of the target gas under flowing conditions, the detected concentration of CH₄ was 90% and not close to 100%, which is not sufficient for purification of the target gas. A plausible mechanism for this behaviour is the following. As the CH₄/CO₂ gas mixture reaches the powder of CID-5 at the first point of adsorption, it starts to adsorb selectively CO₂ with a gate-opening phenomenon. Then, the relative pressure of CO₂ in the column of CID-5 decreases quickly, with the result that the relative pressure is now below the gate-opening pressure. The gas mixture of CH₄/CO₂ in which the relative pressure of CO₂ detected at the outlet is below the gate-opening pressure caused the detection of ca. 10% of CO₂ before the breakpoint was reached.

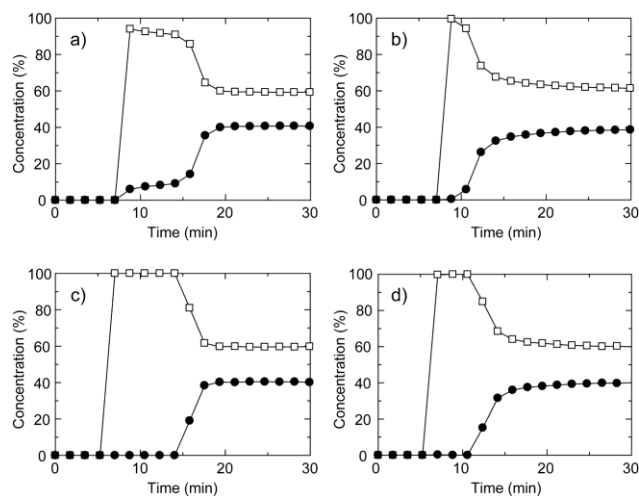


Figure 3. Breakthrough curves of CH₄/CO₂ mixture (60:40 (vol)) for (a) CID-5, (b) CID-6, (c) CID-5/6 ($x = 0.1$) and (d) CID-5/6 ($x = 0.4$). The open square is CH₄ and the closed circle is CO₂. These were measured at 273 K, the total pressure was 0.80 MPa and the space velocity was 6 min⁻¹.

The breakthrough curve of CID-6 had a short retention time for separation of CO₂ and CH₄ even though it possesses permanent microporosity in the deguested form (Fig. 3b). It reached the breakthrough point in minutes and then returned to the initial gas ratio where negligible separation was observed. This is because CID-6 adsorbs both CO₂ and CH₄ with a Type-I isotherm and under kinetic gas flowing conditions, co-adsorption of both gases occurred and no clear separation from the breakthrough curve was observed. This indicates that CID-6 could not effectively capture CO₂ over CH₄ under the investigated gas flowing condition because of the absence of specific binding sites or flexibility for selective CO₂ adsorption in the framework.

To improve the separation properties, we tried optimizing performance with a solid solution of CID-5/6 ($x = 0.1, 0.4$). As shown in Fig. 3d, CID-5/6 ($x = 0.4$) having similar properties to

pure CID-6 demonstrated improved separation behaviour because of more favourable characteristics for CO₂ capture. The gas detected first by GC was CH₄ only, with no detection of CO₂ indicating high selectivity for CO₂ over CH₄ under flowing conditions. After a few minutes, it reached the breakpoint and then returned to the original gas ratio. CID-5/6 ($x = 0.1$), whose structure is close to pure CID-5 but doped with a small amount of CID-6, demonstrated improved separation properties (Fig. 3c). The gate-opening pressure of CO₂ for CID-5/6 ($x = 0.1$) was 0.04 MPa, which was lower than the relative pressure of CO₂ in the gas mixture. These characteristics afforded an appropriate condition for breakthrough measurement of CH₄/CO₂ and it selectively adsorbed CO₂ over CH₄ with a retention time of 8 min. In this period, there was no detection of CO₂ through the column and almost 100% selectivity of CO₂ over CH₄ was achieved. Consequently, the ligand-base solid solutions of a CID framework made it possible to tune the gate-opening pressure, which contributed to the optimization of gas separation properties under both equilibrium and kinetic adsorption conditions. Not only is CO₂ separation from a CH₄/CO₂ mixture of interest, but so also is separation of C₂H₆ from a CH₄/C₂H₆ mixture because of the potential application of separation of C₂H₆ from natural gas.⁴⁰ C₂H₆ is subsequently applicable for conversion to various C2 and C3 chemicals. A physical property such as the boiling point of C₂H₆ (184 K) is similar to CO₂ (195 K) and we investigated the separation performance of CID compounds for CH₄/C₂H₆ separation. Gas adsorption and desorption isotherms of C₂H₆ for CID-5, 6, 5/6 ($x = 0.1, 0.2, 0.4$) at 273 K are shown in Fig. 4. Similar to CO₂, CID-5 afforded gate-opening-type adsorption with a gate-opening pressure of 0.13 MPa, which was slightly higher than that of CO₂. The saturated amount of uptake was 59 mLg⁻¹. The gate-opening pressures of CID-5 for CO₂ and C₂H₆ were similar because the adsorbent-adsorbate interactions were similar in both cases. CID-6 demonstrated a Type-I isotherm and adsorbed 50 mLg⁻¹ of C₂H₆ at 0.95 MPa. Adsorption behaviours of ligand-base solid solutions, CID-5/6, were also similar to CO₂. CID-5/6 ($x = 0.2, 0.4$) had Type-I isotherms because the crystal structure and flexibility were comparable with those of pure CID-6. CID-5/6 ($x = 0.1$) demonstrated gate-opening type behaviour even though the pressure point was very low (0.04 MPa). Given that the CH₄ adsorption isotherm of CID-5/6 ($x = 0.1$) was Type-III, the apparent separation of CH₄ and C₂H₆ was investigated under ambient equilibrium conditions.

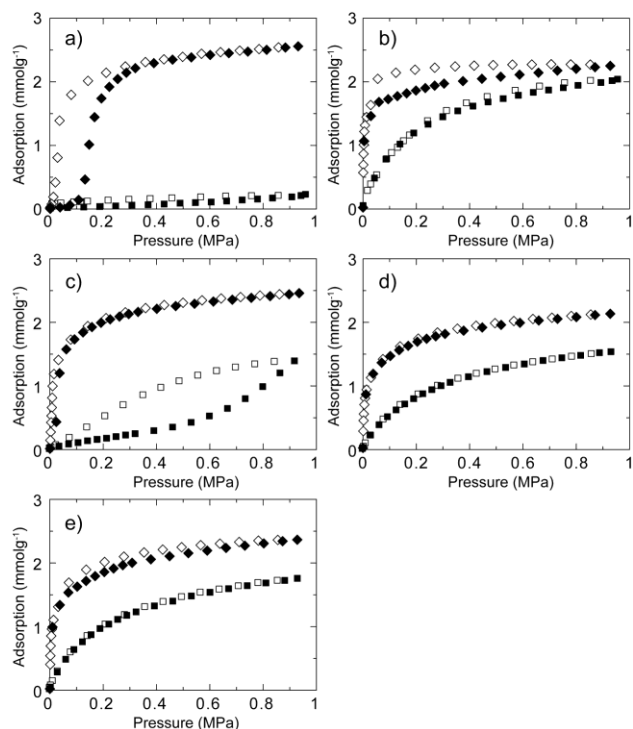


Figure 4. CH₄ (square) and C₂H₆ (diamond) sorption isotherms for (a) CID-5, (b) CID-6, (c) CID-5/6 ($x = 0.1$), (d) CID-5/6 ($x = 0.2$) and (e) CID-5/6 ($x = 0.4$) at 273 K. Adsorption: closed characters; desorption: open characters.

To investigate the separation of C₂H₆ over CH₄ under gas flowing conditions, we measured breakthrough curves for a gas mixture of C₂H₆ and CH₄ at 273 K (**Fig. 5**). The relative pressures of C₂H₆ in natural gas exhausts are variable depending on the situation and we set a low relative pressure of C₂H₆ to evaluate the separation ability over CH₄. The relative pressure of C₂H₆ is 0.07 MPa, which is smaller than that for CO₂ gas in the CH₄/CO₂ mixture gas studied in above. As shown in **Fig. 5a**, the breakthrough curve for CID-5 showed negligible separation properties and quickly reached the breakpoint without any retention time. This behaviour is different from the case of CH₄/CO₂. This is because the relative pressure of C₂H₆ (0.07 MPa) was smaller than the gate-opening pressure (0.13 MPa) determined by the equilibrium adsorption measurement. The small fraction of C₂H₆ in the flowing gas was not able to promote the structure transformation of CID-5 from non-porous to porous. CID-6 also did not demonstrate separation of C₂H₆ because of co-adsorption of CO₂ and C₂H₆ at the low-pressure region and the obtained breakthrough curve was similar to CID-5. As a result, the two pure CID frameworks did not demonstrate appropriate separation properties under the gas flowing conditions. We also investigated the solid solution compounds. CID-5/6 ($x = 0.4$) in **Fig. 5d** afforded an almost identical breakthrough curve compared with CID-6 because of similar characteristics with CID-6, and we also did not observe an efficient retention time for separation. On the contrary, the profile for CID-5/6 ($x = 0.1$) was obviously different from the other three breakthrough curves: 100% selectivity of C₂H₆ over CH₄ was observed and the retention time reached 25 min under the measurement conditions. Although the volumetric percentage of C₂H₆ in the gas mixture was only 10%, CID-5/6 ($x = 0.1$) could selectively adsorb C₂H₆.

The retention time was sufficient for the PSA process and we succeeded in optimizing the separation performance by the solid solution approach. With the systematic control of the intrinsic flexibility of soft PCP/MOFs, we can design various adsorbents for separation under specific conditions.

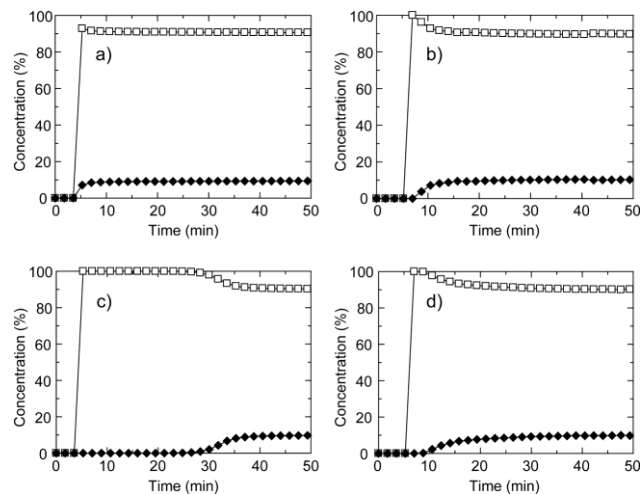


Figure 5. Breakthrough curves of CH₄/C₂H₆ mixture (90:10 (vol)) for (a) CID-5, (b) CID-6, (c) CID-5/6 ($x = 0.1$) and (d) CID-5/6 ($x = 0.4$). The open square is CH₄ and the closed diamond is C₂H₆. These were measured at 273 K, the total pressure was 0.80 MPa and the space velocity was 6 min⁻¹.

Conclusions

The separations of gases such as CO₂ or C₂H₆ from biogas or natural gas have so far been significant challenges and will remain so in the near future. The design of porous adsorbents that show high separation performance with low energy consumption is required for purification of the target gas. In this work, we evaluated the CO₂ and C₂H₆ gas separation properties of flexible type 2D PCP/MOF compounds under equilibrium and gas flowing conditions. Equilibrium gas sorption isotherms and kinetic breakthrough curves indicated a significant contribution from the flexibility of porous frameworks. To improve gas separation under kinetic conditions, we succeeded in employing the solid solution approach for precise tuning of the gate-opening pressure. We observed improved gas separation properties for both equilibrium and kinetic conditions. The flexible frameworks also have the advantage that they could release adsorbed gas by a moderate treatment such as a gas purging procedure and this property is under investigation. The solid solution synthesis is achievable even on the large scale via a one-pot reaction and the optimization of adsorbents could contribute to the development of separation technologies including the PSA process for various target gases.

Notes and references

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- [†] Electronic Supplementary Information (ESI) available: Synthesis of compounds. See DOI: 10.1039/b000000x/
[‡] This work was supported by New Energy and Industrial Technology Development Organization (NEDO) and Grants-in-Aid for Scientific Research, Japan Society for the Promotion of Science (JSPS).
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