CH₄/CO₂ and CH₄/C₂H₆ gas separation using a flexible one-dimensional copper(II) porous coordination polymer

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ABSTRACT: Porous coordination polymers (PCPs) that show a gate-type adsorption originating from structural flexibility represent a new concept for developing gas separation materials. Here, the gas adsorption and separation properties of a flexible one-dimensional (1D) copper(II) PCP, $[\text{Cu}(\text{BF}_4)_2(1,3\text{-bis}(4\text{-pyridyl})\text{propane})_2]_n$, were evaluated. The single-gas adsorption isotherms revealed different gate-opening pressures for CO_2 and $\text{C}_1\sim\text{C}_4$ linear alkanes, suggesting great possibility for the separation of mixtures of these gases. The gas separation properties were characterized by performing breakthrough experiments at ambient temperature using CH_4/CO_2 and $\text{CH}_4/\text{C}_2\text{H}_6$ mixtures. The results demonstrated the practical utility of 1D PCPs in gas separation applications. Single-crystal X-ray diffraction analysis demonstrated high structural adjustability for the incorporation of a variety of guest molecules.

Keywords: flexible porous coordination polymer, gas separation, carbon dioxide, methane, ethane

1. Introduction

In recent years, the development of gas separation materials has emerged to be of critical importance in industrial applications and environmental science. For example, solid adsorbents are used to separate CO₂ from CH₄/CO₂ mixtures in biogas, and C₂H₆ from CH₄/C₂H₆ mixtures in natural gas. The pressure swing adsorption (PSA) process is a classical technology, in which the adsorbents must have a combination of the following two properties: (1) high selectivity for the target gas, and (2) good adsorption kinetics. Porous coordination polymers (PCPs) or metal–organic frameworks that are constructed from metal ions and organic ligands are promising candidates for gas separation because of their high crystallinity, structural diversity, and flexibility [1-8]. In particular, a gate-type adsorption originating from structural flexibility in which a structural change from a closed nonporous to an open porous form takes place through gas adsorption could offer a new concept for developing gas separation materials because the positions of the pressures of gate adsorption depend on the types of gases. There are a variety of flexible three-dimensional (3D) and two-dimensional (2D) PCPs exhibiting gate adsorption for CO₂ and hydrocarbon gases [9–17]. On the other hand, to date, there are limited examples of lower-dimensional compounds, such as one-dimensional (1D) PCPs and discrete metal complexes that exhibit gate adsorption for CO₂ and hydrocarbon gases [18–24].

The 1D PCPs [M₂(bza)₄(L)]_n (M = Cu(II) and Rh(II), bza[−] = benzoate, and L = pyrazine (pyz) derivatives) have paddle-wheel [M₂(bza)₄] units that are bridged by the pyz derivatives. These PCPs show gate adsorption for several gases, while their respective crystallinities are maintained after gas adsorption. The structures of the gas-including states can then be determined by single-crystal X-ray diffraction (XRD) analysis [18]. Recently, we reported that the introduction of substituents (CH₃, F, and Cl) on the bza ligand of the 1D PCP

$[\text{Cu}_2(\text{bza})_4(\text{pyz})]_n$ affects the gate adsorption behaviour [20]. We also succeeded in the rational construction of flexible 1D **PCPs** and porous assemblies of coordination complexes showing gate adsorption using fluorinated anions such as PF_6^- and CF_3SO_3^- [21–23]. These fluorinated anions contain many fluorine atoms with low polarizability and they have a delocalized negative charge. These characteristics lead to a weakening of intermolecular interactions. Even gases with low boiling points can be adsorbed to lower-dimensional compounds decorated with fluorinated anions, changing their structures from a nonporous to a porous form. The 1D **PCP** with fluorinated BF_4^- anions, synthesized by another group, also showed gate adsorption for CO_2 gas [24]. Although these 1D **PCPs** have interesting gate adsorption properties, their separation properties for mixed gases under practical conditions remain unexplored. In this study, under practical conditions, we evaluated the gas separation properties of a flexible 1D **PCP** using mixed gases in addition to fundamental single-gas adsorption properties.

2. Experimental section

2.1. Materials

All the reagents and solvents were commercially available and used as received. Microcrystals of the 1D **PCP**, $[\text{Cu}(\text{BF}_4)_2(\text{bpp})_2]_n$ (**1**), in which bpp is 1,3-bis(4-pyridyl)propane, were synthesized according to the literature [24].

2.2. Synthesis of $\{[\text{Cu}(\text{BF}_4)_2(\text{bpp})_2] \cdot x(2\text{-butanone})\}_n$ (**1** $\supset$ $x(2\text{-butanone})$).

Single crystals of $\{[\text{Cu}(\text{BF}_4)_2(\text{bpp})_2] \cdot x(2\text{-butanone})\}_n$ (**1** $\supset$ $x(2\text{-butanone})$) suitable for single-crystal XRD analysis were prepared by the careful diffusion of a 2-butanone solution of bpp (80 mM) into an aqueous solution of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (40 mM) via a 2-butanone/ H_2O 1:1 (vol) solution in a straight glass tube.

2.3. Physical Measurements

Attenuated total reflection infrared (ATR-IR) spectra were recorded on a Thermo Nicolet iS10 FT-IR spectrometer equipped with a GladiATR™ accessory with a resolution of 4 cm^{-1} . Thermogravimetric/differential thermal analysis (TG-DTA) measurements were performed using a Rigaku ThermoPlus2/TG-DTA8129 over the temperature range r.t.–500 °C under a N_2 flow (100 mL min^{-1}) at a heating rate of 10 °C min^{-1} . Powder XRD data of microcrystals were collected using a Rigaku RINT-Ultima III diffractometer employing $\text{Cu K}\alpha$ radiation. The high-pressure adsorption and desorption isotherms for CO_2 , CH_4 , C_2H_6 , and C_3H_8 (298 K) were measured with a BELSORP-HP volumetric adsorption equipment (BEL Japan, Inc.). The adsorption and desorption isotherms for $n\text{-C}_4\text{H}_{10}$ were measured at 298 K using a BELSORP-mini volumetric adsorption equipment (BEL Japan, Inc.). Before measurements, the sample was heated at 373 K under reduced pressure (1~2 Pa). Breakthrough curves were measured using a hand-made gas flowing system. The sample cell was filled with PCP microcrystals, and the temperature of the cell was controlled by a refrigerant circulating system. For CH_4/CO_2 mixed gas, the gas proportion was $\text{CH}_4:\text{CO}_2 = 60:40$ (vol) and the measurements were performed at the total pressure of 0.80 MPa at 298 K with a space velocity of 3 min^{-1} . The partial pressures of CH_4 and CO_2 were 0.48 and 0.32 MPa, respectively. For $\text{CH}_4/\text{C}_2\text{H}_6$ mixed gas, the gas proportion was $\text{CH}_4:\text{C}_2\text{H}_6 = 80:20$ (vol) and the measurements were carried out at the total pressure of 0.90 MPa at 298 K with a space velocity of 6 min^{-1} . The partial pressures of CH_4 and C_2H_6 were 0.72 and 0.18 MPa, respectively.

2.4. Crystallographic Data Collection and Refinement of Structure

Single-crystal XRD measurement of **1** $\supset$ x(2-butanone) was performed using a Rigaku RAXIS–RAPID imaging plate diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation (λ

= 0.71075 Å). The data were corrected for Lorentz and polarization effects. The structure was solved using SHELXS-97 and expanded using Fourier techniques [24]. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were refined using the riding model. The refinements were carried out using full-matrix least-squares techniques on F^2 using SHELXL-97 [25]. Guest 2-butanone molecules were highly disordered at 173 K. Therefore, the SQUEEZE function of PLATON was used to eliminate the contribution of the electron density in the solvent region from the intensity data [26], and the solvent-free model of $[\text{Cu}(\text{BF}_4)_2(\text{bpp})_2]_n$ was employed for the final refinement. All calculations were performed using Yadokari-XG software package [27]. The crystal data and selected bond distances/angles are summarized in Tables S1 and S2 of the Supplementary information.

3. Results and discussion

The 1D **PCP** $[\text{Cu}(\text{BF}_4)_2(\text{bpp})_2]_n$ (**1**) is a material exhibiting gate adsorption for CO_2 [24]. As depicted in Fig. 1, the binding of Cu(II) ions by bent bpp ligands leads to the formation of 1D doubly linked chains. The fluorinated BF_4^- anions are weakly coordinated at the axial sites. Although the detailed assembled structure is unknown, the adsorption measurements suggest that **1** has a dense packing form without micropores. In our study of adsorption selectivity, we used two different approaches: (1) the volumetric adsorption isotherms at equilibrium using pure gas, and (2) breakthrough curves under kinetic and mixed-gas flow conditions.

Adsorption/desorption isotherms for CO_2 and alkanes at 298 K are shown in Fig. 2a and 2b, in standard and in semi-log forms, respectively, in order to highlight the low pressure steps. The individual isotherms are separately plotted in Fig. S2. As previously reported, **1** showed gate adsorption for CO_2 (gate-opening pressure of 63 kPa) [24,28]. At high-pressure, CH_4 also led to

gate adsorption (gate-opening pressure of 547 kPa). The amount of uptake at 0.93 MPa was 63 and 25 cm³ (STP) g⁻¹ for CO₂ and CH₄, respectively. Different gate-opening pressures for each gas and almost no hysteresis for CO₂ gas is a great advantage for the separation of CO₂ over CH₄ by the PSA process, particularly with regard to the regeneration energy.

For all of the alkane molecules considered in this study, steps in the isotherms can be clearly distinguished (Fig. 2). As previously mentioned, the smaller molecule CH₄ showed a negligible uptake, up to 0.5 MPa, followed by a gradual increase, leading to the adsorbed amount of approximately 25 cm³ (STP) g⁻¹ at 0.93 MPa. Saturation of the adsorbed amount is likely to be seen at higher pressure. As shown in Fig. 2 and Fig. 3, the gate-opening pressure decreased as the length of the hydrocarbon chain increased (gate-opening pressures 547, 105, 56, and 31 kPa for CH₄, C₂H₆, C₃H₈, and *n*-C₄H₁₀, respectively). This behavior can be ascribed to an increase in the van der Waals interactions between the alkane and **1**. A similar tendency has been seen in the flexible 3D PCP [14]. Different gate-opening pressures for each alkane gas indicate great possibility for the separation of an alkane mixture.

To evaluate the gas separation ability of adsorbents, it is important to study not only the single-gas adsorption properties and ideal adsorbed solution theory simulation under equilibrium conditions [29], but also mixed-gas adsorption properties under flowing (kinetic) conditions. Thus, we performed a breakthrough experiment—a typical method used to evaluate the gas separation ability of adsorbents under flowing gas conditions that are related to the PSA process. First, we measured the gas separation properties of **1** for a CH₄:CO₂ mixture of 60:40 (vol) at 298 K and under a total pressure of 0.8 MPa. In recent years, the separation of CO₂ from CH₄/CO₂ mixtures in biogas has become increasingly important. The PSA process is a well-known technology. The selective binding of the target gas and gas adsorption kinetics are

important factors in the design of adsorbent materials. Typically, PSA operates at ambient temperature and under a total pressure of 0.4–1.0 MPa, and the cycle time is several minutes. As shown in Fig. 4(a), CH₄ was first detected by gas chromatography (GC) at the outlet of the column and CO₂ flowed out about 7 minutes later, indicating high selectivity for CO₂ over CH₄ under mixed gas and flowing conditions. After the breakthrough curves reached the breakpoint, they returned to the original gas ratio. The results recorded under practical conditions suggest that **1** is a useful material for CO₂ separation.

Not only CO₂ separation from a CH₄/CO₂ mixture but also the separation of C₂H₆ from a CH₄/C₂H₆ mixture is of great importance, because of potential applications for the separation of C₂H₆ from natural gas [30]. Purified C₂H₆ is applicable for conversion to various C₂ and C₃ chemicals. As shown in Fig. 2, **1** afforded gate adsorption with the gate-opening pressure of 105 kPa for C₂H₆, which was slightly higher than that for CO₂. Given that the gate-opening pressure for CH₄ was considerably higher than that for C₂H₆ under equilibrium conditions, we evaluated the separation property of C₂H₆ over CH₄ under kinetic gas flow conditions. Fig. 4(b) shows breakthrough curves for a gas mixture of C₂H₆ and CH₄ at 298 K. The content percentages of C₂H₆ in natural gas exhausts vary depending on the area. We selected a low content percentage of C₂H₆ (CH₄:C₂H₆ = 80:20 (vol)) to evaluate the separation ability over CH₄. After injection of the CH₄/C₂H₆ gas mixture, the concentration of C₂H₆ and CH₄ detected by GC was 5% and 95%, respectively, and the retention time was around 10 min. Then the breakthrough curves reached the breakpoint and returned to the initial gas ratio. Given that the partial pressure of C₂H₆ (180 kPa) in the mixed gas was higher than the gate-opening pressure of **1** (105 kPa), derived from the equilibrium isotherm, **1** was expected to adsorb C₂H₆ with an accompanying structural change. On the other hand, the partial pressure of CH₄ was 720 kPa, and **1** showed low uptake of gas at

this pressure. Consequently, we observed a concentration effect of C₂H₆ over CH₄ under the kinetic conditions. However, the detected concentration of CH₄ was only 95%—not close to 100%. A plausible mechanism for this behavior can be explained as follows: as the mixed CH₄/C₂H₆ gas reaches the microcrystals of **1**, selective adsorption of C₂H₆ commences via a gate adsorption phenomenon. Then, the partial pressure of C₂H₆ in the column decreases rapidly, to below the gate-opening pressure, which causes the detection of 5% C₂H₆ before the breakpoint. Similar behavior has been reported for other flexible PCPs [16].

In practical applications of gas separation materials, both the gas selectivity and the adsorption kinetics at ambient temperature are important factors that determine the separation efficiency. Under mixed-gas conditions, both gases may be adsorbed to flexible PCPs after gate-opening, even if one gas is not adsorbed under pure gas conditions. These considerations mean that the separation properties of flexible PCPs should be evaluated under practical conditions, that is, under kinetic and mixed-gas conditions. Some reports have elucidated the gas separation properties of flexible 2D and 3D PCPs under practical conditions [15-17]. There are, however, only a few 1D PCPs showing practical separation performance under kinetic and mixed-gas conditions at ambient temperature. The separation performance of **1** under practical conditions proves that 1D PCPs are indeed applicable to a gas separation process.

The results of the gas adsorption properties imply that **1** has a high structural adjustability for different sized guests. To elucidate this, we tried to determine and then compare, the crystal structures of **1** with different sized guests using single-crystal XRD analysis at the same temperature. The crystal structure of {[Cu(BF₄)₂(bpp)₂]•x(acetone or EtOH)}_n (**1** ⊃ x (acetone or EtOH)) in which Cu(II) centers are bridged by bpp ligands to form the 1D doubly linked chain has been reported by another group [24,31]. We synthesized **1** ⊃ x (2-butanone)

with larger guests, i.e., 2-butanone. Although the crystal structure of **1** $\supset$ x (2-butanone) is isostructural to **1** $\supset$ x (acetone or EtOH) (see Supplementary information: Table S1, Table S2, and Fig. S1), the accessible pore volume increased by 15.5% (Supplementary information: Table S3) [32]. More specifically, the *a* and *c* axes expanded by 2.23% and 2.76%, respectively, while a slight expansion of 0.72% was observed in the *b* axis, which corresponds to the direction in which the 1D chains run. Moreover, the desolvated **1** can readsorb 2-butanone, with an accompanying structural change, when it is exposed to saturated 2-butanone vapor. This was confirmed by ATR-IR spectra, TG-DTA, and powder XRD measurements (Supplementary information: Fig. S3, Fig. S4, and Fig. S5). All adsorption and crystallographic results demonstrated the presence of high structural adjustability for a variety of guest molecules in the 1D **1**.

Fig. 5 shows the pore structure of **1** $\supset$ x (2-butanone), which was traced using a probe with a radius of 1.2 Å. The PCP **1** $\supset$ x (2-butanone) has 1D bellows-type pores, where the wide space is connected by narrow passages. There are two wide spaces per formula unit. The minimum dimensions of a 2-butanone molecule are $4.2 \times 5.4 \text{ Å}^2$, and the narrow passages have the dimensions $3.3 \times 5.5 \text{ Å}^2$ and $1.4 \times 5.0 \text{ Å}^2$, indicating that a 2-butanone molecule cannot be accommodated into the narrow passage; one wide space accommodates one 2-butanone in a sort of clathration. Interestingly, the adsorbed amount of gases, except in the case of CH₄, is saturated at about two molecules per formula unit, which corresponds to the number of wide spaces (see Fig. S6 of the Supplementary information). Hence, each gas molecule can be expected to be accommodated in the wide spaces of 1D bellows-type pores as in the case of 2-butanone. These results again highlight the finding that **1** has good flexibility to fit the pore structure for not only organic vapors with high boiling points but also for gases with low boiling points.

4. Conclusions

Adsorption selectivity and separation properties of the flexible 1D PCP **1** were evaluated from single-gas adsorption measurements and mixed-gas breakthrough measurements. The positions of gate-opening pressures for alkane gases strongly depended on the length of the hydrocarbon chains. Therefore, the different affinities of **1** for the alkanes according to their chain length, might lead to applications in gas separation. The breakthrough curve for a CH₄/C₂H₆ mixture indicated a high likelihood of separating alkane gases. Furthermore, **1** showed gate adsorption for CO₂ at low pressure and exhibits good separation of CO₂ over CH₄ under kinetic and mixed-gas conditions at ambient temperature. Crystallographic characterization demonstrated high structural adjustability to accommodate a variety of guest molecules. All results emphasized that flexible 1D PCPs are promising candidates for gas separation materials.

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Footnotes

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Figure captions

Fig. 1. 1D structure of **1**.

Fig. 2. Excess adsorption/desorption isotherms for CO₂ (red circle), CH₄ (blue square), C₂H₆ (green triangle), C₃H₈ (orange rhombus), and *n*-C₄H₁₀ (black inverted triangle) at 298 K. Adsorption, closed symbols; desorption, open symbols; (a), standard coordinates; (b), semi-log plot.

Fig. 3. Variation of the gate-opening pressures at 298 K as a function of the boiling points of alkane molecules. The solid line is a guide for the eye.

Fig. 4. (a) Breakthrough curves for a CH₄/CO₂ mixture (60:40 (vol)). The red circle is CO₂ and the blue square is CH₄. Curves were measured at 298 K, total pressure 0.8 MPa, and space velocity 3 min⁻¹. (b) Breakthrough curves for a CH₄/C₂H₆ mixture (80:20 (vol)). The green triangle is C₂H₆ and the blue square is CH₄. Curves were measured at 298 K, total pressure 0.9 MPa, and space velocity 6 min⁻¹.

Fig. 5. 1D pore structure of **1** ⊃ x(2-butanone) projected along the *b* axis, in which the probe with the radius of 1.2 Å was used to trace the pore structure. The wide spaces are surrounded by green lines.

Fig 1

Fig 2

(a)

Fig 2

(b)

Fig 3

Fig 4

(a)

Fig 4

(b)

Fig 5

Graphical Abstract

One-Dimensional Gas Separation Material