Technical Report

Development and Future Prospects of Energy-saving Carbon Dioxide Separation Technology Using Porous Coordination Polymer (PCP)/Metal-Organic Framework (MOF)

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Abstract

Flexible porous coordination polymer, which is a new gas separating material, adsorbs carbon dioxide by inclusion formation, which is different from the adsorption mechanism of existing solid gas adsorbents such as zeolites, etc. Since the amount of gas adsorbed changes significantly before and after the pressure of inclusion formation, it is possible to control the adsorption/desorption with a slight pressure swing. Therefore, it is expected as a new generation separating agent that enables carbon dioxide separation with energy saving and high efficiency. The development and future prospects of this flexible porous coordination polymer are described.

1. Introduction

There are various methods for lowering carbon dioxide (CO_2) emissions such as the use of natural energy and improvement of manufacturing efficiency. Among them, the method of separating and recovering CO₂ arising from manufacturing processes will be an important solution for the steelmaking and many other industries to decrease CO₂ discharge in the future.¹⁾ In the project of Development of Environment Friendly Process Technology (COURSE50) under the auspices of the New Energy and Industrial Technology Development Organization (NEDO), Nippon Steel Corporation and Research Institute of Innovative Technology for the Earth (RITE) have developed a chemical absorbents by which CO₂ is dissolved in an aqueous solution of amine and recovered by heating the solution: CO₂ separation technology using this technology are already in operation in Japan at Muroran, Hokkaido, and Niihama, Shikoku. As there are many large-scale commercial CO₂ separation plants using various chemical absorption methods besides the above two, chemical absorption is regarded as highly effective at CO₂ separation. However, since the aqueous solution has to be heated by this process, it inevitably consumes much energy. For this reason, some consider that physical adsorption methods using porous adsorbents not requiring heating of water and membrane separation methods involving virtually no moving parts are better in terms of energy consumption (see Fig. 1).²⁾

Nippon Steel has been separating and using CO_2 by a physical adsorption method since 1989 as a pioneer in the Japanese steel industry. By this method, however, the gas is blown through an adsorption tower filled with adsorbent pellets, and as a consequence, pressure loss tends to increase when the processing capacity is large, and thus there are few examples of large-scale commercial application. Membrane separation methods, on the other hand, are applied mostly to high-pressure gas, and separation membranes that can be effectively used for a large amount of CO₂ contained in gas at ambi-



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ent pressure, as is the case in the steel industry, remain under development. Considering the future where reduction of CO_2 emissions will be commonly practiced and a greater amount of CO_2 is captured than it is now, it is important to minimize the energy consumption of CO_2 separation methods even if renewable energy is widely available. In addition to further improving the energy consumption and process efficiency of chemical absorption methods, it is important to focus attention on the methods of physical adsorption and membrane separation, which are better in terms of energy saving. The present paper examines a CO_2 separation technology using flexible polymer complexes that are promising for separating CO_2 at energy consumption significantly lower than by using conventional porous adsorbents that have been widely used for various physical adsorption processes such as zeolites and activated carbon, and prospects of the technology.

2. New Porous Material: Porous Coordination Polymers

2.1 History of porous coordination polymers

Materials containing a large number of small pores are collectively referred to as porous materials. Of these, zeolite and activated carbon, which have many pores of a nanometer size, are widely used for different industrial purposes such as gas adsorption and separation and as catalysts. They are also used in our daily life as deodorizers for refrigerators and the like. While these materials have been developed for various applications through decades of technical developments, a group of new porous materials have appeared, the development of which began only recently. They are called porous coordination polymers (PCPs): they are also referred to as metal-organic frameworks (MOFs). Note here that while the word PCP covers porous polymers only, the word MOF covers non-porous ones, too, and therefore it has a broader sense. PCP will be used hereinafter to express the porous polymers that are the subject of this paper. A PCP is a polymer of complexes synthesized from metal ions and multidentate ligands that serve as cross links between the metal ions: it is sometimes referred to as a molecular jungle gym (see Fig. 2). PCPs of one-, two-, or three-dimensional structure can be synthesized by properly selecting the types of metal ions and ligands and changing the synthesis process condition.

The research of PCPs is reported to have begun in an embryonic manner in the 1950s, and as the technique of structural determination using advanced X-rays, they quickly became the target of active studies at universities from 1990. In fact, many studies on the topology of their network structure and research on their special structures were conducted in the 1990s. In 1997, when Prof. Susumu Kitagawa of Kyoto University discovered that PCPs could adsorb gas, that is, they functioned as porous materials such as zeolite and activated carbon, they attracted a great deal of attention.³⁾ Research



Fig. 2 Schematic diagram of PCP synthesis (a) One dimensional structure, (b) Two dimensional structure

on PCPs was conducted mainly at universities as late as in the 2000s, and after 2010, many companies in and outside Japan began to study them. Regrettably, there are no large-scale practical applications yet, but taking advantage of the fact that PCPs are capable of adsorbing a large amount of gas and the gas pressure falls as a result, some PCPs have been made commercially available in cylinders for handling toxic semiconductor gases. Some venture businesses consider that PCPs will be put into practical use in the fields of gas separation and/or storage, drug delivery systems, catalysts, sensors, etc., and the size of their global market is expected to expand to 1 billion yen (roughly US\$ 9 million) by 2025 at a growth rate of 35% per annum.⁴⁾

2.2 Physical properties of PCPs

As stated earlier herein, PCPs may be likened to a molecular jungle gym in which metal ions are clamps (or joints) and ligands are bars. Ions of virtually all metal elements in the periodic table can be used as the clamps, and structural diversity of PCPs is given by the difference in the ionic radius, the valence, and the coordination structure (the number and orientation of joining hands) of the metal element. When transition metal ions are used, the PCP may exhibit catalytic properties.⁵⁾ Physical and chemical diversity can be assigned to PCPs by using different ligands having two coordination points or more to cross-link metal ions for their synthesis. Moreover, even when the same type of ligand is used, the shape and size of the pores can be changed; thus, the structure of PCPs is greatly diversified (see **Fig. 3**).

During the period of PCP research mainly at universities up to 2010, there was fierce international competition over increasing the BET numerical value, an indicator of gas adsorption capacity, and expanding the pore size. As a result, BET values far higher than those of conventional adsorbents were achieved, and expectations for PCPs soared rapidly. On the other hand, however, one of the PCPs best known in the world at that time having a very large BET value, MOF-5, which is synthesized from zinc ions and terephthalic acid, was found to be so unstable against moisture that it could not be handled in the air, and the impression that PCPs are chemically unstable spread widely.^{6,7)} As a result of later studies, however, PCPs with excellent moisture resistance and high adsorption ability that do not decrease even at boiling water tests have been discovered. For example, UiO-66-H, which has a three-dimensional network structure containing Zr(IV) ions, is renowned for its extremely high resistance to water. It is now possible to synthesize PCPs highly resistant to water without having to use somewhat exotic elements such as zirconium. Of the PCPs having a stacked structure of two-dimensional layers (to be described later) that were developed jointly by Nippon Steel and Chiba University, ELM-31, which contains Ni(II) ions and BF_4^- ions, has a low moisture resistance, but ELM-31b, which contains the same Ni(II) ions, counter ions, and



Fig. 3 Structural diversity of PCPs

(a) Different coordination structures with different metal cations, (b) Different pore structures with same-length ligands having different coordination sites

longer ligands, demonstrates excellent moisture resistance (see **Fig. 4**). The mechanism of PCP degradation by water is so complicated that it has not been elucidated yet.⁸⁾ There are very stable PCPs and unstable ones, and actually the chemical stability of PCPs differs from type to type. It should be noted in this relation that there are reports to the effect that the moisture resistance of some PCPs can be improved by measures such as surface treatment.⁹⁾

When a porous material is used as a gas adsorbent, its capacity to adsorb the target gas is often lowered as water is selectively adsorbed in the pores, if it is not degraded by this. For this reason, for gas separation using zeolites, it is usually necessary to dry the gas using a dehydration tower or the like. In order to evaluate the effect of moisture on the adsorptivity of different adsorbents, I exposed specimen adsorbents to the atmosphere, pre-treated them under the condition adequate for each of them, and measured their ability to adsorb CO₂ at 0°C (see Fig. 5). The zeolite used for CO₂ separation (F-9HA made by Tosoh Corporation) had a high polarity, its adsorptivity rapidly decreased owing to moisture adsorption, and was almost completely lost in 30 minutes. MOF-5 behaved similarly presumably because its water resistance was low, its structure changed as a result of moisture adsorption, and its adsorptivity was lost. HKUST-1 having a low water resistance also behaved likewise. The relative adsorption amount of highly hydrophobic activated carbon fiber, A-20, decreased to around 60%, but after that, it remained substantially unchanged. The adsorptivity of 3D-OTf,¹⁰⁾ a type of PCP the composition of which is expressed as [Cu(bpy)₂(OTf)₂]₂, did not decrease to below a certain value, like that of the activated carbon fiber. This is presumably because it contains highly hydrophobic counter ions (CF₂SO₂⁻=OTf). Studies are currently being conducted on the application of PCPs whose CO, adsorption ability does not fall even in the presence of moisture to systems to directly capture CO₂ in the atmosphere (direct air capture (DAC)).^{11, 12)} 2.3 Synthesis and Price of PCP

MOF-5 described above, which has attracted attention worldwide, is synthesized through reactions in dimethylformamide at



Fig. 4 Water and heat resistance test of PCPs (Aliquot sample of PCP was sealed with water and heated for a predetermined time.)



Fig. 5 Changes in CO₂ (273 K) adsorptivity of various adsorbents due to atmospheric exposure at room temperature

100°C or higher, but this is relatively hard to practice on a large scale. It is undeniable that this has made PCPs appear to be a special kind of material difficult to put into commercial use. With the advance of research, however, methods have been established whereby PCPs are synthesized within a short time at a high yield by simply mixing metal salt and a ligand material at room temperature, and the obtaining of PCPs in pellets has been enabled by having the raw materials react by mixing them in a kneader without using a solvent. Such synthesis methods in a short process time or at room temperature facilitate the production of composite materials in which a PCP is supported on a base material, and will expand the applications of PCPs.¹³⁾ In addition, PCPs made from inexpensive aluminum or iron ions, and those synthesized from economical ligand materials such as terephthalic or fumaric acid are also popular. The price of waterresistant PCPs that are being studied for application to heat pumps and the like is expected to be 300 yen(US\$ 2.8)/kg when produced on an industrial scale.

3. CO₂ Adsorptivity of PCPs

Since PCPs adsorb gas in large quantities, they have attracted attention as storage materials for hydrogen and methane, but against the background of decarbonization in recent years, the interest in PCPs has shifted to that of them being CO₂ separators. **Figure 6** shows the CO₂ adsorption isotherms (at 298 K) of PCPs that have particularly large CO₂ adsorptivity, or uptake, and that of the zeolite actually used for CO₂ separation. The uptake of either of the two PCPs is higher than that of the zeolite: some researchers regard HKUST-1 as the most promising CO₂ separator in consideration of its various properties.¹⁴

It should be noted, however, that the adsorption isotherm of either of these PCPs is similar to that of the zeolite with the uptake increasing as the pressure rises. This is because the CO_2 adsorption mechanisms of all these adsorbents are the same: pore adsorption. **Figure 7** shows schematic diagrams of the cases where gas is adsorbed and recovered by the pressure swing method^{*1} using these types of adsorbents.

To recover 90% of the gas adsorbed at 1 atm by a material that





¹ The method whereby gas is adsorbed at a high pressure and desorbed (recovered) at a low pressure (pressure swing adsorption), or it is adsorbed at a high or ambient pressure and desorbed at a low pressure (vacuum swing adsorption). Either is widely employed for gas production such as oxygen production from the atmosphere and separation of methane and hydrogen.



Fig. 7 Virtual CO₂ adsorption isotherms (a) Typical adsorption isotherm, (b) Three types of adsorption isotherms with different adsorptivities

exhibits the adsorption isotherm given in Fig. 7(a), it is necessary to change the pressure across a range as wide as 0.97 atm (from 1.0 to 0.03 atm, orange arrow in the figure); therefore, it takes much energy and a long time to change the pressure across such a wide range. In addition, decompression to a such a low pressure as this requires a high-performance blower, which increases the equipment cost. When CO₂ is recovered by a pressure change from high to medium pressure (for example, from 1.0 to 0.5 atm as given by the green arrow in Fig. 7(a)) to avoid the above problem, the amount of recovered CO₂ is only 22% of what is adsorbed at 1 atm, and the efficiency is dissatisfactory. When the affinity of the adsorbent with CO_{2} is enhanced to increase the adsorption amount, it increases at low pressures in most cases as shown by the blue isotherm in Fig. 7(b), and the recovery tends to be difficult. If the affinity with CO, is lowered to avoid this, in contrast, the uptake will decrease (the green curve), and the amount of recovery will also decrease. That is to say, with adsorbents having a typical CO₂ adsorption isotherm based on the pore adsorption mechanism as given in Fig. 7(a), it is not easy to recover the gas even when the adsorption amount is increased, and this applies also to PCPs. For this reason, some consider that, from the viewpoint of engineering CO₂ recovery systems on a large scale, PCPs of a particularly high CO, adsorptivity are not necessarily better than zeolites.15)

4. Gas Adsorption Characteristics of Flexible PCPs

It is possible to synthesize PCPs using various types of metal ions and ligands, give them different physical and chemical properties, and make them capable of adsorbing larger amounts of gas than any existing porous materials do. It has been stated earlier, however, that high-efficiency CO_2 separation cannot always be achieved by simply increasing adsorptivity or strengthening interaction with CO_2 . This means that to develop an innovative CO_2 separation system far more efficient than the conventional ones using existing adsorbents, it is important to introduce a CO_2 adsorption mechanism different from pore adsorption.

4.1 Strategies of biomaterials enabling easy adsorption and desorption of gas

There are some materials in nature that can recover large quantities of gas with only a small pressure change. Hemoglobin consists of four subunits that contain heme having the ability to bond with oxygen. Oxygen is bonded to heme iron at a site within a living body where the partial pressure of oxygen is high (a lung, for example), it is detached at sites where the oxygen partial pressure is low (peripheral parts), and thus oxygen is supplied to peripheral tissues; this way hemoglobin functions as an oxygen carrier within a living body. Four oxygen atoms can be bonded to it, and the structure of an entire hemoglobin changes at the time of bonding with a first oxygen atom, and as a result, bonding with a second and subsequent oxygen atoms is accelerated. For this reason, a curve drawn by plotting oxygen partial pressure along the horizontal axis and its bonding amount along the vertical axis has an S shape (sigmoid) by which the oxygen bonding amount rises sharply in a partial-pressure range above a certain value. Thus, because it absorbs and desorbs oxygen easily even though the difference in oxygen concentration is very small between a lung and peripheral tissues, hemoglobin functions as a highly efficient oxygen carrier. Such S-shaped oxygen bonding behavior does not occur with myoglobin consisting of monomers, but takes place as a result of a cooperative structural change of tetramers like hemoglobin.

4.2 Structure and functionality of flexible PCPs

Although many PCPs do not show flexibility like zeolites,^{*2} the crystal structure of a very small number of PCPs changes markedly when they adsorb and desorb gas; they are called flexible PCPs, soft PCPs, soft porous crystals, etc. **Figure 8** illustrates typical modes of the structural change of flexible PCPs.

Of the three types, the structural change of the breathing type (Fig. 8(a)) often proceeds gradually as the amount of adsorbed gas increases. In contrast, that of the stacked-layer type takes place quickly in some cases as the structure without adsorbed gas (the upper part of Fig. 8(c)) changes abruptly into the one with adsorbed gas (the lower part) as a result of only a slight pressure change. **Figure 9** shows the nitrogen adsorption isotherm (at 77 K) of ELM-



Fig. 8 Three types of structural changes of PCPs (a) Breathing type, (b) Interdigitated type, and (c) Stacked layer type (The yellow spheres indicate the adsorption space created by the structural change.)



Fig. 9 Adsorptivity and structure of flexible PCP, ELM-13 (a) N_2 adsorption isotherm (77 K), (b) Top view, and (c) Side view of network structure(s) (Cu, red; C, gray; N, purple) (Acetone (guest molecule) and H atoms are omitted for clarity.)

²² Since PCPs are more flexible than zeolites or activated carbon, the crystal structure of PCPs is deformed to a certain extent by stress, or gas adsorption causes deformation of ligands such as the rotation of benzene rings contained in them. ¹⁶ The present paper deals only with significant structural changes that cause large changes in gas adsorption characteristics.

13¹⁷⁾, a typical PCP that exhibits structural change of the stackedlayer type. In the low-pressure range (<33 kPa), two-dimensional lattices, or network structures, are stacked closely to each other, and gas is not adsorbed, but as the gas pressure rises to surpass a certain value (called a gate pressure, 33 kPa in this case), they change their relative positions to increase the interlayer distance, and gas molecules are introduced therein (adsorbed). Here, gas is adsorbed not by pore adsorption, which is the adsorption mechanism of conventional adsorbents, but by a phenomenon in which gas molecules are included in the space between the lattice layers; this occurs as a result of the cooperative change of many units that compose a PCP, and for this reason the structural change of flexible PCPs takes place abruptly.¹⁸)

It was only four years after gas adsorption by a PCP was first reported in 1997 that Prof. Katsumi Kaneko of Chiba University (at that time) and colleagues reported the peculiar adsorption behavior as described above of a PCP for the first time in the world.¹⁹⁾ This PCP, the composition of which is expressed as $[Cu(bpy)(H_2O)]_2$ $(BF_4)_2$ (bpy) (bpy=4,4'-bipyridine), had a one-dimensional structure. This structure had already been reported in 1997,²⁰⁾ but Kaneko et al. stated that this PCP exhibited a peculiar gas adsorption behavior that could not be classified by the method for classifying gas adsorption modes of the International Union of Pure and Applied Chemistry (IUPAC), and it was named the gate adsorption or the gate phenomenon. Because the PCPs that demonstrated the gate adsorption behavior adsorbed gas in spite of the fact that they proved to be non-porous at X-ray crystal analysis, they were called latent porous crystals (LPCs) at that time. Since there were a great number of networks of hydrogen bonds via water molecules in the structure of the LPC, it was suspected that hydrogen bonds were involved in the manifestation of the gate phenomenon. Later, however, the PCP of the above composition was found not to be adsorptive, but it was a precursor of another PCP that was adsorptive, that is to say, it was clarified through later studies that during the pretreatment of decompression heating for adsorption measurement, the precursor PCP underwent a dehydration reaction, its one-dimensional component units changed into two-dimensional, and as a consequence, the precursor turned into another PCP having a composition of [Cu(bpy), $(BF_{4})_{2}$; thus, this was identified as the very PCP that exhibited adsorptivity by the gate phenomenon.²¹⁾ The PCP that formed as a result of the dehydration reaction had a structure of stacked two-dimensional lattice layers, and although it was crystalline, the interlayer distance greatly increased when it adsorbed gas. Based on this finding, the PCPs that adsorb gas by this type of mechanism were named the elastic layer-structured metal-organic frameworks (ELMs). After that, Nippon Steel and Chiba University continued joint research into ELMs, and various new types of them were synthesized during the course of the research: these include isostructures containing Co(II) and Ni(II) ions in addition to copper ions, those having CF₂BF₂ ions instead of BF₄ ions, and those comprising ligands longer than bpy. Each ELM capable of gate adsorption is given a specific name, and is classified as given in Fig. 10.

All PCPs of the ELM type having names as given in Fig. 10

ELM-@@

 \rightarrow Counter ion: 1 = BF4, 2 = CF3SO3, 3 = CF3BF3

→ Metal ion: 1 = Cu, 2 = Co, 3 = Ni²⁺

e. g. ELM-11= [Cu(bpy)2(BF4)2], ELM-22 =[Co(bpy)2(CF3SO3)2] bpy = 4,4'-bipyridine

Fig. 10 Nomenclature of flexible PCPs, ELMs

demonstrate gate-type adsorption characteristics, whereby the gas adsorption amount increases rapidly in a gas pressure range higher than the gate pressure. The gate pressure is greatly influenced mainly by metal ions, and the shape of the isotherm by counter ions. However, it should be noted in this relation that, judging from the fact that the gate pressure of ELM-12/3,*3 which contains two types or more of counter ions, is markedly lower than that of ELM-12,²²⁾ counter ions can also exert significant influence on gate pressure.

5. High-efficiency CO₂ Separation Using Flexible PCP, ELM-11

5.1 Ease of CO, recovery with ELM-11 and its CO, selectivity

Figure 11 shows the CO_2 adsorption isotherm of ELM-11, which has a two-dimensional stacked structure and has copper ions, BF_4^- ions, and bpy as ligands, and zeolite, which is used for CO_2 separation.

With ELM-11 it is possible to recover 70 mL (STP)/g of CO, by a pressure change of only 20 kPa (adsorption at 40 kPa and desorption at 20 kPa) because its gas adsorption behavior changes abruptly in the pressure range above the gate pressure. With the zeolite, in contrast, although the adsorption amount at 100 kPa is far greater than that of ELM-11, a pressure reduction of as large as 89 kPa (from 100 to 11 kPa) is required to recover the same amount of CO₂ as with ELM-11. It should also be noted that while the lowest pressure with ELM-11 is 20 kPa, the same with the zeolite is 11 kPa, which means higher power costs and longer operation time with the zeolite. The reason for this big difference in the recovery efficiency is that ELM-11 adsorbs CO₂ thanks to its clathrate structure formation mechanism due to cooperative structural changes of component units, totally different from the pore adsorption of zeolite and other conventional adsorbents; it is a characteristic feature unique to flexible PCPs. In addition to this easy gas recovery, ELM-11 is better than zeolite also in CO₂ selectivity. Figure 12 compares ELM-11, some PCPs that are not flexible but are attracting attention as CO₂ separators, and zeolite (F-9HA) in terms of CO₂ selectivity.*4

The overwhelmingly higher CO_2 selectivity of ELM-11 than those of the other separators is considered to be because its CO_2 ad-



Fig. 11 Adsorption isotherms of ELM-11 (red) and zeolite (F-9HA, blue) (CO₂, 273 K)

*3 Although the details have not been clarified yet, ELM-12/3 is considered to contain CF₃BF₃ and CF₃SO₃ ions, have a composition of [Cu(bpy)₂ (CF₃BF₃)(CF₃SO₃)], and an ELM-type network structure.

*4 The value obtained by dividing the CO₂ uptake of an adsorbent by its N₂ uptake, both at 298 K and 95 kPa. The adsorption amounts are measured here using pure gases separately, not mixed gas.



Fig. 12 Comparison of adsorption ratio of CO₂ and N₂ (273 K) (The adsorption amount ratio was calculated from the adsorption amount at 95 kPa of the adsorption isotherm measured using pure CO₂ and N₂ separately. Left-hand scale applies only to ELM-11, and right-hand scale to all the others).

sorption mechanism is based on the formation of a clathrate structure rather than pore adsorption: it is considered that in the case where N₂ molecules are included in the clathrate structure of ELM-11, it becomes unstable, and CO₂, which enhances the structural stability, is selectively adsorbed. Note here that the values of Fig. 12 were calculated from the isotherms obtained through the tests using pure CO₂ and N₂ separately instead of mixed gas, but at the tests of ELM-11 and ELM-13 using mixed gas of CO₂ and N₂, the former demonstrated very high CO₂ selectivity.^{23, 24)} Therefore, the ELM is expected to exhibit high CO₂ selectivity because it is less prone to co-adsorption even in the case of mixed gas.

5.2 Applicability of CO₂ separation with ELM-11 to large-scale commercial facilities

Materials that adsorb gas by pore adsorption such as activated carbon, zeolites, and PCPs generate heat during gas adsorption. Generally speaking, however, the adsorption amount decreases as the temperature rises, and accordingly, the effective adsorption amount decreases as heat is generated by adsorption. In order to lower the heat generation, measures such as mixing pellets of a heat storage material (e.g., Thermo Pele, of Osaka Gas Chemicals Co., Ltd.) with the adsorbent have been proposed.²⁵⁾ However, when the equipment size is increased for CO₂ separation in large amounts, heat removal may become insufficient, and the adsorption amount may decrease. In gas separation by the pressure swing method, it is possible to increase the separation amount by accelerating the adsorption/desorption cycles, but if the heat generation is large, the problem of poor heat removal will remain, and the high-cycle operation to raise separation efficiency will become difficult. The flexible PCP, ELM-11, generates heat during gas adsorption as other adsorbents do, but because its structural change for CO₂ adsorption is endothermic, the net heat generation tends to be smaller than that with conventional adsorbents. ELM-11 is, therefore, considered highly compatible with large-scale equipment or operation in quick adsorption/desorption cycles, and is expected to be suitable for large-quantity CO₂ emission sources.^{26, 27)}

There are only a limited number of PCPs that can separate CO_2 by the gate adsorption in a normal temperature range. However, when amine is supported in some PCPs, it reacts with CO_2 in a cooperative manner, and gate adsorption occurs.²⁸⁾ A CO_2 separation method using a solid adsorbent in which amine is supported is known as a solid absorption method. It is attracting attention as an energy-saving CO_2 separation technology because, different from chemical absorption methods using an aqueous solution of amine,

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heating of water is not required for CO₂ recovery.²⁹⁾ PCPs in which amine is supported are in principle energy-saving like above, it is anticipated that they will be more energy-saving and efficient in CO₂ separation than conventional adsorbents owing to the gate adsorption characteristics. Such materials are expected to be used in a wide range of conditions because they show extremely high water resistance and their properties are not degraded even by high temperature steam.

6. Conclusion

The present paper has provided an overview of porous coordination polymers (PCPs), which are attracting attention as new CO_2 separators, especially of flexible PCPs, which are capable of changing their crystal structure during CO_2 adsorption and desorption, and for this reason, enable CO_2 separation at high efficiency.

According to the declaration by Prime Minister Yoshihide Suga on October 26, 2020 for Japan to attain carbon neutrality by 2050, the trend of decarbonization will be accelerated in the steel industry as well as in many other industries. Decarbonization requires various measures such as increased use of renewable energy and further energy saving, and CO₂ separation technology is expected to play an important role in years to come. As demonstrated by studies of phase-changing liquid absorbents being promoted in the field of chemical absorption of CO₂, the importance of developing new technologies will increase that lead to more energy saving and cost reduction than by existing methods. In this situation, flexible PCPs introduced in the present paper are expected to bring about energy saving and high efficiency in CO₂ separation beyond what has been attained with conventional solid CO₂ separators.

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