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Selective Separation of Water, Methanol, and Ethanol by a Porous Coordination Polymer Built with a Flexible Tetrahedral Ligand

Akihito Shigematsu,[†,‡] Teppei Yamada,*[,†] and Hiroshi Kitagawa*[,†,‡,§]

[†]Division of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
[‡]Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan
[§]CREST, Japan Science and Technology Agency (JST), Sanban-cho 5, Chiyoda-ku, Tokyo 102-0075, Japan

S *Supporting Information*

ABSTRACT: A novel porous coordination polymer, $Cu^{II}(mtpm)Cl_2$ [mtpm = tetrakis(*m*-pyridyloxy methylene)methane], has been synthesized, and its crystal structure has been determined. Its adsorption isotherms for water, methanol, and ethanol are totally different from each other. It adsorbs water at low humidity and shows gate-open behavior for methanol, but it does not adsorb ethanol. This compound has the capacity to separate both methanol and water from bioethanol, which is a mixture of water, methanol, and ethanol.

Bioethanol is a sustainable energy source that has attracted much interest. Bioethanol is at present made by fermentation of molasses and inevitably includes some water and methanol; thus, the development of purification techniques for bioethanol is critical for its widespread use.[1] As is well-known, water and ethanol form an azeotropic mixture, and 4% of the water cannot be removed by the conventional distillation process.[2,3] Eliminating both methanol and water from bioethanol is presently desired in order to obtain highly pure ethanol; however, it is difficult to separate ethanol from the ternary mixture of water, methanol, and ethanol because the chemical properties of methanol and ethanol are similar to each other. Few examples of the elimination of both water and methanol from the ternary mixture have been reported.[4]

We intended to apply porous coordination polymers (PCPs), or metal−organic frameworks (MOFs), to separate both water and methanol from the ternary mixture. PCPs have great potential for gas storage, separation, magnetism, electrical conduction, and catalysis.[5] Compared with conventional microporous materials such as activated carbon or zeolites, PCPs have advantages for precise separation because their pore sizes and surface environments can easily be tuned by variation of the metal ions and organic ligands.[6] The pore size and shape and several types of host−guest interactions, such as hydrogen-bonding, $\pi-\pi$, and van der Waals interactions, have been applied to effect the separation with PCPs.[7] The flexibility of the frameworks, which zeolites and activated carbon do not possess, has also been used. This flexibility often causes unconventional sorption behaviors, such as gate-open behavior, because of rearrangement of the framework in response to certain guest molecules.[8,9] Although PCPs are expected to show improved separation capacity for multicomponent mixtures by adopting unique sorption behavior, the separation of both water and methanol from the ternary mixture using PCPs has not been reported to date. Here we report the first example of selective separation of water, methanol, and ethanol by a PCP.

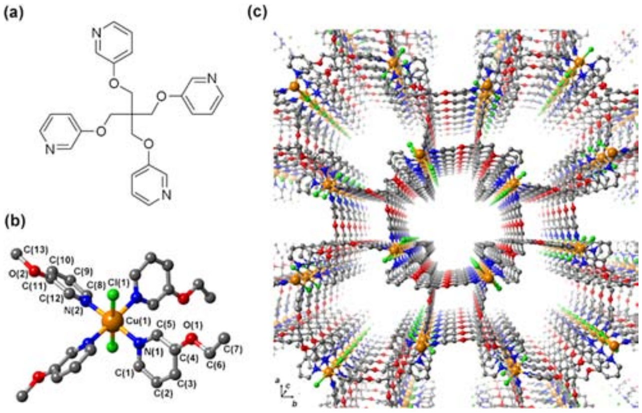

Figure 1. (a) Structure of mtpm. (b) Coordination geometry of copper ions with the labeling scheme of the building unit, $Cu(mtpm)Cl_2$. (c) View of **1** along the *c* axis. The colors red, blue, gray, green, and orange correspond to oxygen, nitrogen, carbon, chlorine, and copper atoms, respectively.

The ligand tetrakis(*m*-pyridyloxymethylene)methane (mtpm) (Figure 1a) was synthesized according to the literature,[10] and crystals of $Cu^{II}(mtpm)Cl_2{\cdot}20H_2O$ ($\mathbf{1}{\cdot}20H_2O$) were obtained by slow diffusion of $CuCl_2{\cdot}2H_2O$ and mtpm into a mixture of water and methanol [Figure S1 in the Supporting Information (SI)]. The crystal structure of $\mathbf{1}{\cdot}20H_2O$ was determined by single-crystal X-ray diffraction (SCXRD) measurements (Figure 1b,c).[11] $\mathbf{1}{\cdot}20H_2O$ consists of one mtpm ligand, one copper ion, and two chloride ions. Each copper center is equatorially coordinated by four nitrogen atoms of four different mtpm ligands and axially coordinated by two chloride ions, resulting in a 4 + 2 Jahn−Teller-distorted octahedral environment (Figure 1b). The Cu−N bond lengths are 2.011(3) and 2.027(3) Å. The trans N−Cu−N bond angle is 174.31(13)°, and the cis N−Cu−N bond angles are in the range from 89 to 91°. Two types of one-dimensional square channels are formed along the *c* axis, with diameters of ca. 5 and 8 Å (Figure 1c). The smaller channel is constructed from two

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copper ions and four pyridyl groups of two mtpm ligands, and the larger channel is made up of four copper ions and four mtpm ligands. The void volume was estimated to be 62.8% using PLATON[12] (46.3% and 16.5% for the larger and smaller channels, respectively). Guest water molecules inside these channels were highly disordered, and it was difficult to model their positions and distribution reliably; therefore, the final framework was refined after using the SQUEEZE routine of PLATON. The water content of the obtained compound was determined by elemental analysis and thermogravimetric analysis (TGA) (Figure S2). Twenty water molecules were included in the PCPs from the elemental analysis, in good agreement with the TGA results.

As-grown **1**·20H_2O has good crystallinity. Although the peaks in the powder X-ray diffraction (PXRD) pattern shifted and broadened upon the elimination of water, the peaks recovered very well after the counteranion was exchanged with tosylate (Figure S3). The framework of **1** has flexibility in rotation of methylene and ether bonds and is reoriented by the elimination of water, causing the peak broadening. The elemental analysis[13] and TGA data for **1** after removal of guest water and exposure to air could be fitted to the composition of **1**·H_2O, which is reasonable from its water adsorption behavior (see below). The local structure around the copper atoms in **1** was evaluated by X-ray absorption fine structure (XAFS) measurements (Figure S4 and Table S2), and the main peak observed at ca. 1.8 Å was assigned to copper fourfold-coordinated by nitrogen atoms. This result shows that the local structure of copper in **1** is similar to that in **1**·20H_2O determined by SCXRD. The stability of the framework geometry was also confirmed by PXRD measurements on the ion-exchanged sample. As-grown **1**·20H_2O was evacuated to eliminate guest water and soaked in an aqueous solution of sodium tosylate. Elemental analysis after the anion exchange experiment was in good agreement with the composition of Cu^{II}(mtpm)Cl(tosyl) (**2**).[14] The PXRD pattern of **2** was quite similar to that simulated from the crystal structure of **1**·20H_2O (Figure S3) and was well-fitted with similar lattice parameters by Pawley refinement (Figure S5).[15] These results indicate that the topology of the framework is maintained during the adsorption and desorption of guests.

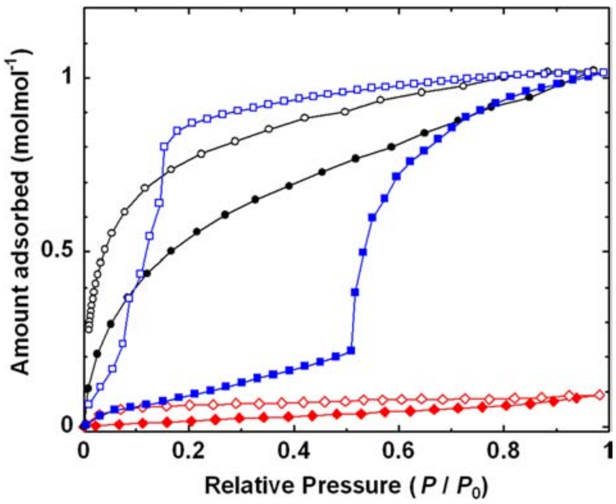

Figure 2. Adsorption (solid symbols) and desorption (open symbols) isotherms of **1** for water (black circles), methanol (blue squares), and ethanol (red diamonds) at 298 K.

Gas adsorption studies for water, methanol, and ethanol were carried out on **1**, which was dried at 373 K. As shown in Figure 2, significant differences can be observed among these three isotherms. Water was gradually adsorbed onto **1** in the low-pressure region, and the water uptake increased as the vapor pressure increased. Finally, one water molecule per formula unit was adsorbed at saturated vapor pressure, and a slight hysteresis between the adsorption and desorption isotherms was observed. In contrast, methanol was adsorbed with a clear step at P/P_0 = 0.5 and the desorption isotherm displayed a steep decrease at P/P_0 = 0.15, with a large hysteresis between them. Ethanol was adsorbed least. These differences in the adsorption behaviors result from the interaction between the framework and the guest. Water adsorption occurs in the low-pressure region because water produces a large adsorption energy by forming hydrogen bonds to the framework, and the rearrangement energy is small. In contrast, the adsorption isotherm for methanol is attributed to typical "gate-open behavior".[8] Miyahara and co-workers modeled this type of adsorption behavior by adsorption-induced lattice rearrangement, which is affected by the extent of rearrangement of the PCP framework and the affinity between the host and guest.[16] A structural rearrangement of **1** was observed with uptake of water and methanol, and the adsorption energy for methanol is smaller than that for water, compensating for the rearrangement of the framework; therefore, the gate-open adsorption occurred for the methanol adsorption. Ethanol requires a larger rearrangement energy and is not adsorbed until the saturated vapor pressure is reached. As a result, **1** can selectively recognize water, methanol, and ethanol. Thus, **1** has the potential to separate both methanol and water from a water−methanol−ethanol mixture and open a novel route for applying bioethanol as an alternative energy source.

In summary, a novel porous coordination polymer, Cu(mtpm)Cl_2·20H_2O, was synthesized and characterized by SCXRD and adsorption measurements. Compound **1** adsorbs water and methanol but not ethanol, and the adsorption characteristics for water and methanol are different from each other. This compound has the capacity to separate both methanol and water from water−methanol−ethanol mixtures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Procedures for the syntheses of mtpm and **1**, details of the ion exchange experiment, PXRD patterns, Pawley refinement, TGA curves, XAFS spectrum, and a CIF for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

teppei343@gmail.com; kitagawa@kuchem.kyoto-u.ac.jp

Notes

The authors declare no competing financial interest.

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(11) Crystal data for **1**·20H$_2$O: M = 578.94, T = 100 K, λ = 0.71069 Å, tetragonal, $P4_22_12$, a = 23.485(5) Å, c = 8.995(5) Å, V = 4961(3) Å^3, Z = 4, ρ_{calcd} = 0.775 g cm^{-3}, R_1 [$I > 2\sigma(I)$] = 0.0575, R (all data) = 0.0613, wR_2 (all data) = 0.1672, GOF = 1.064. The structure refinement was carried out after using the SQUEEZE procedure of the program PLATON. The crystallographic data are available from the Cambridge Crystallographic Data Centre (CCDC 886221).

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(13) Anal. Calcd for **1**·H$_2$O (CuC$_{25}$H$_{26}$O$_5$N$_4$Cl$_2$): C, 50.30; H, 4.39; N, 9.39. Found: C, 50.30; H, 4.18; N, 9.44.

(14) Anal. Calcd for **2**·(H$_2$O)$_{2.5}$ (CuC$_{32}$H$_{36}$O$_{9.5}$N$_4$SCl): C, 50.59; H, 4.78; N, 7.38. Found: C, 50.63; H, 5.14; N, 7.39.

(15) Triclinic, a = 23.904(3) Å, b = 23.187(4) Å, c = 9.229(1) Å, α = 84.597(9)°, β = 87.949(7)°, γ = 90.538(8)°, R_p = 0.0420, R_{wp} = 0.0637.

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