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Single-Crystal Membrane for Anisotropic and Efficient Gas Permeation

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Microporous materials, which have pores with diameters less than 20 Å, are attractive in both industry and scientific fields because they are applicable for gas separation, gas adsorption, and catalysis.[1] In particular, microporous materials have been focused on their potential for efficient gas separation, which greatly contributes to industry, since their pore sizes are suitable for highly selective gas separation. Gas separation membranes are desirable for gas purification in industry because of their economical aspects (low energy requirements, efficient use of space, etc.). To develop microporous materials as efficient separation membranes, molecular design to achieve high selectivity and high permeability is needed. Although efficient membranes with high selectivity and permeance have been reported,[2−4] polycrystalline membranes of microporous materials[3,4] have not fulfilled the principles of molecular design for microporous membranes. Obvious contributions of defects and boundaries between individual crystals in polycrystalline membranes, which also result in low reproducibility of experimental data, prevent the precise estimation of gas permeation, especially for small-molecule gases such as H_2, He, and CO_2. One of the most reliable methods for studying gas permeation is the use of single-crystal membranes. However, gas permeation of single crystals has not been studied well, although gas diffusion has been studied for single crystals.[5,6] Although there have been pioneering works to observe the gas permeation of single-crystal zeolites,[7,8] the data for oriented crystal membranes were obtained under low permeance fluxes for only N_2 and gaseous alkanes.[8] Thus, the relationship of size and direction of channels to permeance and selectivity in porous materials has not been explained.

We previously reported a porous single crystal of the metal complex $[Cu_2(bza)_4(pyz)]_n$ (**1**) (bza = benzoate; pyz = pyrazine) (Figure 1a),[9,10] which is easily obtained as well-formed single crystals and has the potential to act as a single-crystal membrane showing moderate permeance because single-crystalline **1** easily adsorbed various gases through narrow channels with a diameter of 2−4 Å.[11−14] In this report, we succeeded in observing selective permeation and anisotropic permeation properties by using single-crystalline **1** as a single-crystal membrane. In addition, since crystal **1** has narrow channels, its membrane is expected to have high separation selectivity for small-sized gas molecules such as H_2, He, and CO_2, which are among the most significant targets for separation in industry.

A typical single crystal of **1** is shown in Figure 1b with the indexes of crystal surfaces determined by single-crystal X-ray structural analysis. Two oriented channels, which penetrate the crystal in the [110] and $[1\bar{1}0]$ directions (red and blue arrows, respectively, in Figure 1b), are layered alternatively along the *c* axis. As a result, both channels penetrate the (100) crystal surface, whereas no channel penetrates the (001) crystal surface. Two kinds of membranes with orthogonal crystal orientations of **1**, one with exposed (001) crystal surfaces (channel membrane) and the other with exposed (001) crystal surfaces (nonchannel membrane), were prepared by placing well-formed crystals in holes of aluminum plates using epoxy bond (Figure 1c,d).

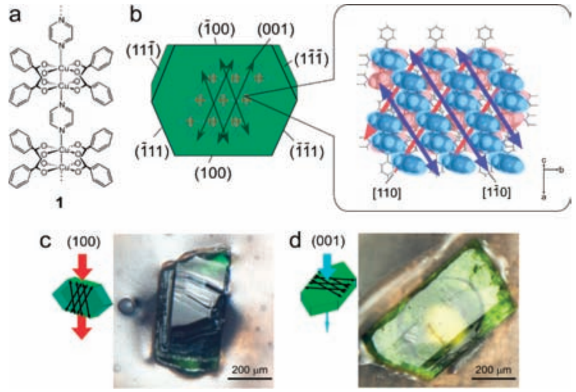

Figure 1. (a) Chemical structure and (b) crystal structure of $[Cu_2(bza)_4(pyz)]_n$ (**1**) showing the determined numbers of the crystal planes and the channel direction. (c, d) Photographs of single-crystal membranes of **1**: (c) exposed (100) crystal surface (channel membrane); (d) (001) crystal surface (nonchannel membrane).

The single-crystal membrane of **1** exhibited gas permeability along the channel direction and exhibited barrier properties perpendicular to the channel direction. The gas permeabilities of these membranes for various gases (He, H_2, N_2, CO, Ar, O_2, CH_4, and CO_2) at 293 K are shown in Figure 2a. This method gave reproducible results independent of the variation in crystal membranes. Permeability values along the channels (channel membrane) were 7−60 times greater than those perpendicular to the channels (nonchannel membrane) for corresponding gases [also see Table S3 in the Supporting Information (SI)]. The permeability along the channels was 1×10^{-12} to 6×10^{-14} mol m m^{-2} s^{-1} Pa^{-1}, which is extremely high in comparison with the reported permeability for a single-crystal membrane of ferrierite zeolite with a diameter of ~5 Å (1.0×10^{-15} mol m m^{-2} s^{-1} Pa^{-1} for CH_4).[8] In contrast, the permeability perpendicular to the channels was undetectable for N_2, Ar, CO, O_2, and CH_4 gases under the measurement conditions (the waiting time for pooling permeated gas was up to 20 min). He, H_2, and CO_2 gases permeated slightly perpendicular to the channels, probably as a result of a small number of crystal defects for H_2 and He gases and the high adsorption ability of CO_2 gas. This fact clearly indicated that the gases permeated the membrane through the channels, even though the channel neck diameter (~2 Å) was smaller than the kinetic diameters of the sample gases (2.55−3.80 Å).[15]

The gas permeation in membrane **1** fit well with the calculated permeability based on the Knudsen diffusion mechanism (see Table

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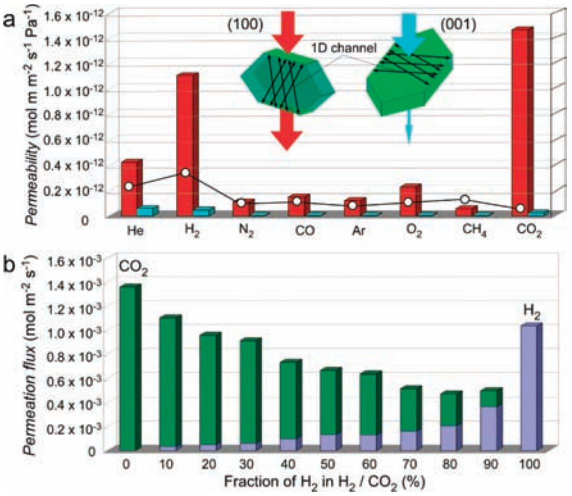

Figure 2. (a) Comparison of the permeabilities of crystal membrane **1** for various gases: (red) along the channels (channel membrane); (light-blue) perpendicular to the channels (nonchannel membrane). The inset plot (○) is the calculated permeability based on the Knudsen model. (b) Comparison of the permeation fluxes of H_2 and CO_2 along the channels of gas mixtures for various mixing ratios (H_2, purple; CO_2, green). Detailed permeability values are summarized in Table S3 for (a) and Table S6 for (b).

S4),[16] although **1** can handle a crystalline diffusion mechanism based on its narrow channel structure, which would give a much lower value. In an extreme case of H_2 and CO_2 gas permeation, the experimental permeability was much faster than the calculated permeability. This result suggested that the easy gas permeation through the narrow channels was supported by the structural flexibility of **1**.[13]

Selectivity in gas separation with a membrane can be estimated on the basis of the difference in the gas permeabilities of the component gases. For the gas selectivity along the channels, the permselectivity (F_α), which is the ratio of the permeabilities of the pure gases, shows high selectivity for H_2 and CO_2. The permselectivities of H_2 gas versus other gases were 3 (He), 10 (N_2), 7 (CO), 9 (Ar), 5 (O_2), and 19 (CH_4). These values were sufficiently large for a practical membrane (Table S5; also see the references in the SI).[2,4,17] In particular, this membrane shows high selective factors for H_2 versus CO and CH_4 gases, suggesting the high possibility of H_2 purification from reformed gas, which is required in facing the coming hydrogen society. The membrane also shows highly selective factors for CO_2 gas (10 for CO_2/CO, 25 for CO_2/CH_4). Although the permeabilities were relatively low, the order of the permeabilities perpendicular to the channels was the same as the order of the kinetic diameters of the sample gases (He $> H_2 > CO_2$) in contrast to that along the channels ($CO_2 \geq H_2 >$ He), showing that permselectivity can also be controlled by crystal orientation.

Since the gases are considered to be unable to pass each other in a narrow channel of **1** (less than ~4 Å), the gas permeation behavior in a gas mixture should deviate from that expected from single-gas permeation if the gases actually diffuse in the isolated narrow channels. Surprisingly, in gas permeation of a H_2/CO_2 gas mixture, the permeation flux of H_2 gas decreased more than the H_2 fraction in a H_2/CO_2 gas mixture did, while the flux of CO_2 gas decreased in a linear fashion with respect to the CO_2 gas fraction in a H_2/CO_2 gas mixture; this means that the permeability of H_2 was decreased by the presence of CO_2 gas while that of CO_2 gas remained unchanged (Figure 2b). This prevention of H_2 gas permeation was not observed in combination with other gases (He, CH_4), suggesting that the small molecules of CO_2 in the narrow channel make it difficult for the extremely small H_2 gas to pass. Thus, not only CO_2 but also even small gases such as H_2 are considered to dominantly permeate through the same narrow channel. Interestingly, the selective factor for CO_2 gas versus H_2 gas is considerably high compared with the permselectivity (~1.3) (see Table S6). This reverse selectivity for CO_2 gas versus H_2 gas is rare[4b,17] and useful for removing CO_2 gas from a CO_2/H_2 mixture to concentrate H_2 gas at or near feed pressure.

In conclusion, we succeeded in preparing a single-crystal membrane with high permeance and high permselectivity for H_2 and CO_2 gases that demonstrated anisotropic gas permeation behavior. The results clearly suggest that various gases permeate through one-dimensional penetration channels even though the diameter of the narrow channel neck is smaller than the kinetic diameter of the sample gases. Flexible ultramicroporous materials have great potential for the development of membranes as crystal devices in gas purification techniques.

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Supporting Information Available: Details of gas permeation experiments and preparation and characterization of the single-crystal membrane of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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