Supporting Information

Metal-organic framework membranes with layer structure prepared within the porous support

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Experimental

1. Preparation of Cu-BTC membrane and Cu-BTC powder

The porous α-alumina tube with a diameter of 3 mm, an average pore diameter of ca. 150 nm, and a thickness of ca. 350 μm was supplied by NOK CORPORATION. The porous α-alumina support was cut into pieces ca. 50 mm in length, washed with acetone, and dried under vacuum at 60°C for 12 h.

The solutions for the preparation of the Cu-BTC membrane were prepared as follows. A 0.3 M copper(II) nitrate trihydrate aqueous solution was prepared by dissolving 7.25 g copper(II) nitrate trihydrate (Wako Chemicals, Japan) in a total volume of 100 mL DI water. A 0.2 M 1,3,5-benzenetricarboxylic acid solution in ethanol was prepared by dissolving 4.20 g 1,3,5-benzenetricarboxylic acid (Sigma-Aldrich) in a total volume of 100 mL ethanol (Wako Pure Chemical Industries). One end of the porous α-alumina tube support was sealed with molten glass to separate the inner and outer parts of the membrane. The hollow tube support was then filled with ca. 0.25 mL of 0.3 M cupper(II) nitrate trihydrate aqueous solution, followed by vacuum treatment to completely fill the pores of the porous α-alumina support. The hollow tube support was vertically placed with the sealed end down in a glass container filled with 20 mL of preheated 0.2 M 1,3,5-benzenetricarboxylic acid solution in ethanol at 75°C, while keeping the two solutions inside and outside the hollow tube support separated. The glass container was then placed in an autoclave and heated at 120°C for 2, 4, or 6 h. The

autoclave was allowed to cool to room temperature, and the hollow tube support was washed with aqueous ethanol solution (50 vol%) at 75°C for 24 h and dried at 90°C for 24 h in a vacuum oven.

Cu-BTC powder was prepared by mixing 25 mL of 0.3 M copper(II) nitrate trihydrate aqueous solution and 25 ml of 0.2 M 1,3,5-benzenetricarboxylic acid solution in ethanol. The mixture was placed in the autoclave and heated at 120°C for 6 h, i.e., the same conditions as those for the preparation of the Cu-BTC membrane. The autoclave was then allowed to cool down to room temperature. The blue powder was washed with ethanol several times and dried under vacuum at 90°C for 24 h.

2. X-ray diffraction analysis (XRD)

The crystal structure was determined by X-ray diffraction analysis with Cu-Kα radiation (Bruker, D8 Advance). Diffraction patterns were measured at room temperature with a 2θ ranging from 5° to 40° and a slow scan rate of 6 s/step. The porous α-alumina support and the Cu-BTC membrane were split into small pieces and placed on the plastic cell for measurements.

3. SEM analysis

The surface structure and internal structure of the Cu-BTC membrane was analyzed by scanning electron microscopy (SEM, Hitachi High-Technologies Corporation, S-3400N) with energy dispersive X-ray analysis (SEM-EDX).

4. Gas permeation measurements

Single-component gas permeation properties of the Cu-BTC membrane were measured using He, H_2, CO_2, O_2, N_2, and CH_4 in the increasing order of kinetic diameter, as shown in Table S1. The measurements were conducted in-house under the steady-state conditions at 25°C with a vacuum time-lag method under a pressure difference of 1 atm.[1] The membrane was vacuum-dried at 90°C for over 24 h after fixing it on the permeation test cell for removing the residual water. Both the feed and permeate sides of the membrane were evacuated prior to each measurement.

Experimental data were compared with the calculated permeances based on H_2 permeance under the Knudsen diffusion mechanism using the following equation:

$$P_{i,K} = P_{H_2} \sqrt{M_{H_2}/M_i},$$

where $P_{i,K}$ is the predicted permeance of gas molecule i, P_{H_2} is the H_2 permeance, M_{H_2}
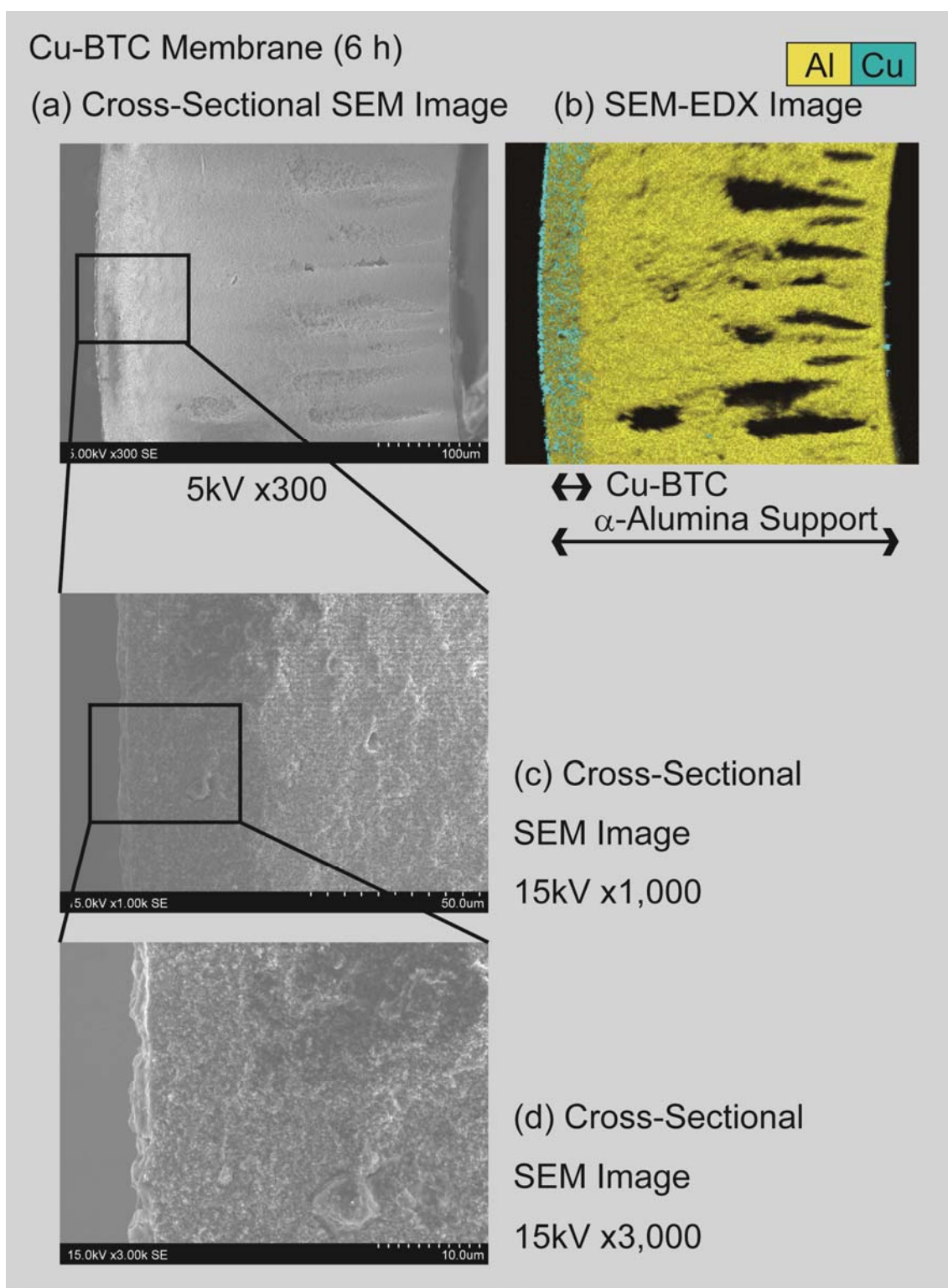
is the molecular weight of H_2, and M_i is the molecular weight of gas molecule i. The ideal H_2 selectivity, α, was obtained using the following equation:

$$\alpha = \left. P_{H_2} \middle/ P_i \right.,$$

where P_{H_2} is the permeance of H_2, and P_i is the permeance of gas molecule i.

(a) Porous a-Alumina Support

(b) Cu-BTC Membrane (2 h)

(c) Cu-BTC Membrane (4 h)
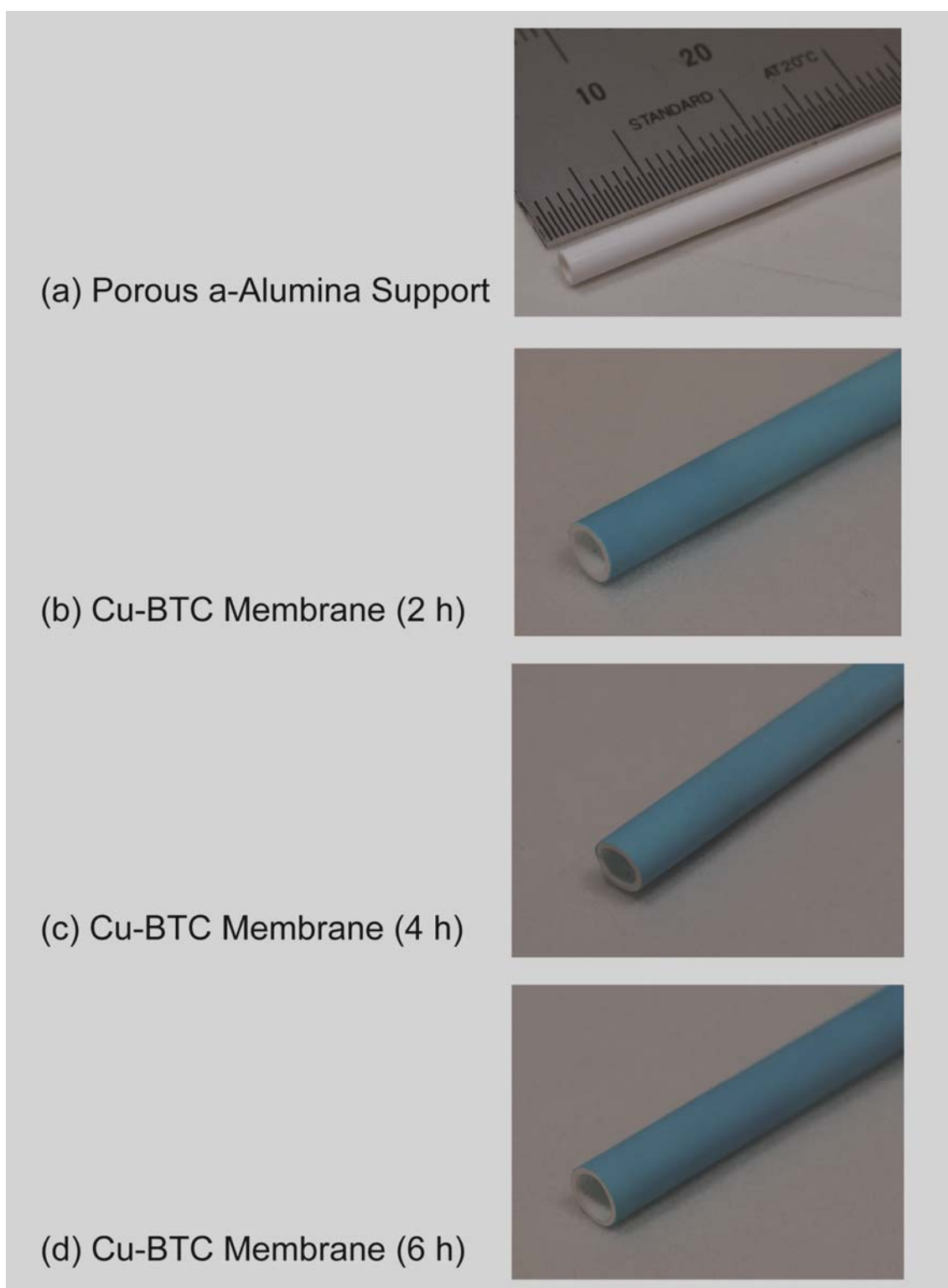
(d) Cu-BTC Membrane (6 h)

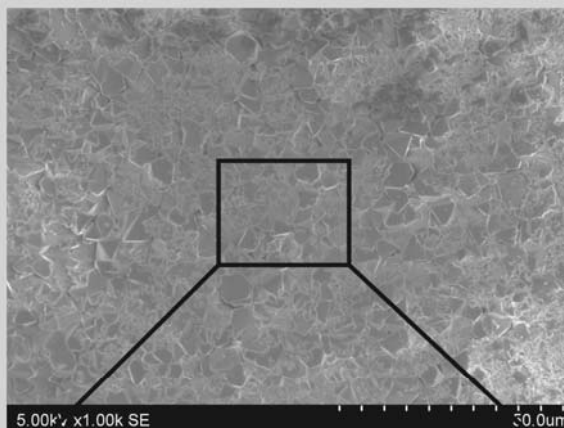**Fig. S1** Photographs of (a) porous α-alumina support, (b) Cu-BTC membrane (2 h preparation time), (c) Cu-BTC membrane (4 h preparation time) and (d) Cu-BTC membrane (6 h preparation time).
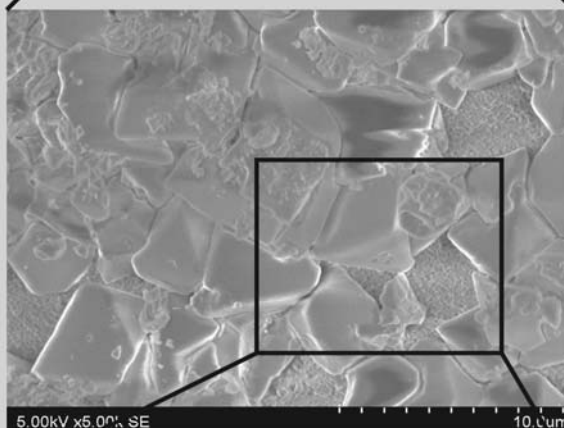
Cu-BTC Membrane (6 h)

Al Cu

(a) Cross-Sectional SEM Image   (b) SEM-EDX Image

5kV x300

↔ Cu-BTC
α-Alumina Support

(c) Cross-Sectional
SEM Image
15kV x1,000

(d) Cross-Sectional
SEM Image
15kV x3,000

Fig. S2 (a) Cross-sectional SEM image of the Cu-BTC membrane (6 h preparation time) at the magnification of ×300, and (b) the SEM-EDX mapping image for the same area as in (a). Cross-sectional SEM images at the magnification of (c) ×1,000, (d) ×3,000.

Cu-BTC Membrane (6 h)
SEM Image of the outer surface

(a) 1kV x1,000

5.00kV x1.00k SE 50.0um
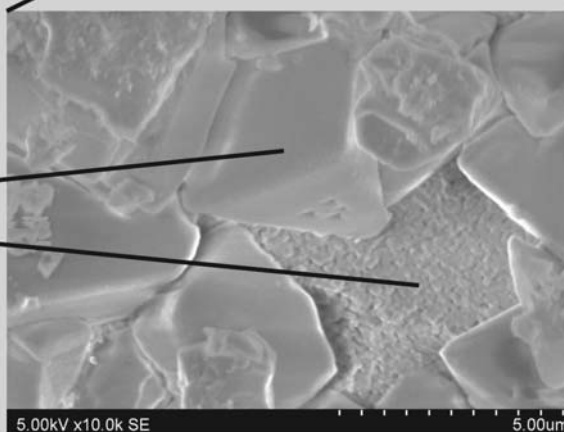
(b) 5kV x5,000
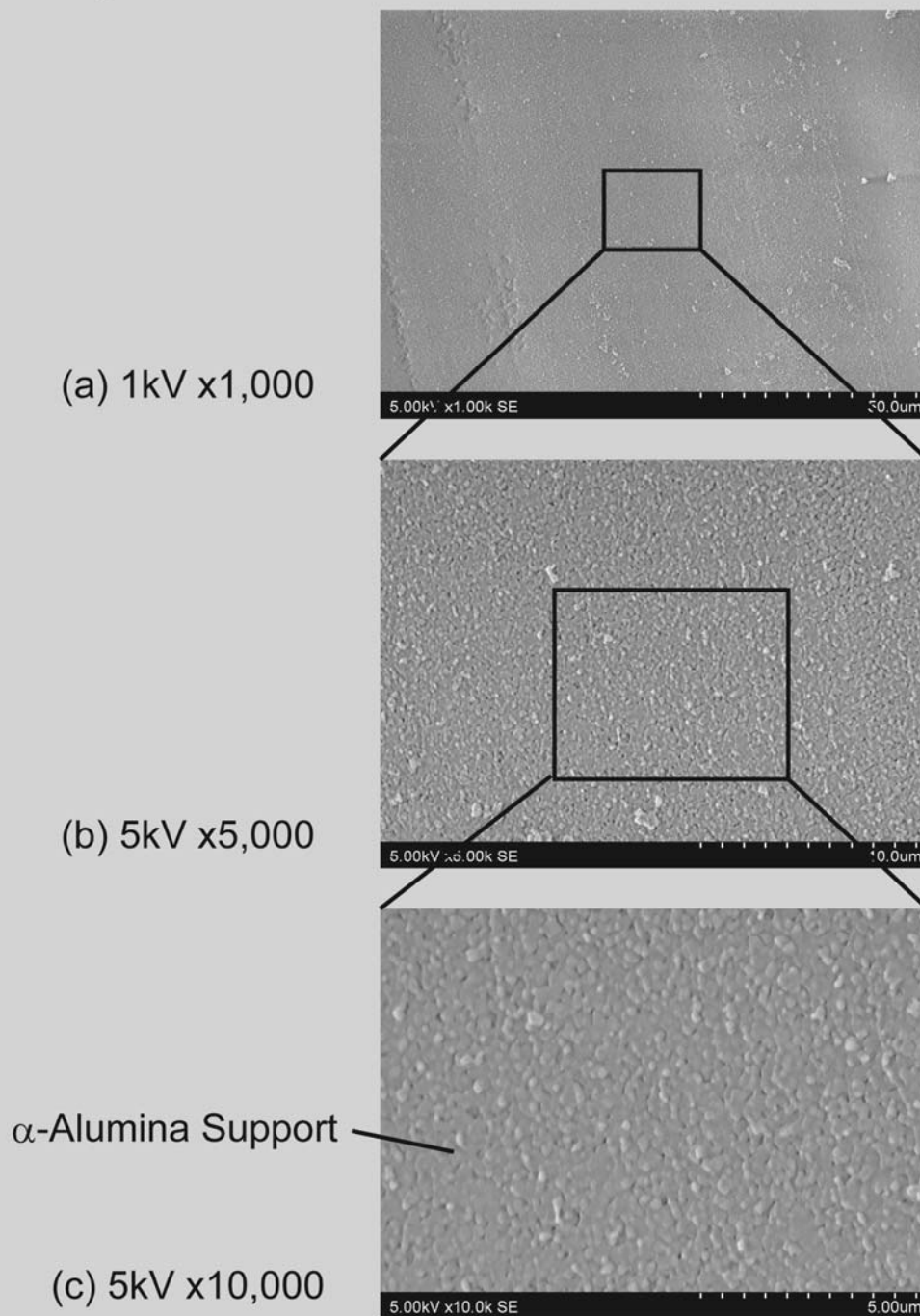
5.00kV x5.00k SE 10.0um

Cu-BTC
α-Alumina Support

(c) 5kV x10,000

5.00kV x10.0k SE 5.00um

Fig. S3 SEM images of the outer surface of the Cu-BTC membrane (6 h preparation time) at the magnification of (a) ×1,000, (b) ×5,000, (c) ×10,000.

Cu-BTC Membrane (6 h)
SEM Image of the inner surface

(a) 1kV x1,000

5.00kV x1.00k SE   50.0um

(b) 5kV x5,000

5.00kV x5.00k SE   10.0um

α-Alumina Support

(c) 5kV x10,000

5.00kV x10.0k SE   5.00um

Fig. S4 SEM images of the inner surface of the Cu-BTC membrane (6 h preparation time) at the magnification of (a) ×1,000, (b) ×5,000, (c) ×10,000.

Table S1 Results of single-component gas permeation measurements at 25°C.

Gas Molecule		He	H_2	CO_2	O_2	N_2	CH_4
Properties of Gas Molecules							
Kinetic Diameter [nm]		0.26	0.29	0.33	0.35	0.36	0.38
Knudsen diffusion selectivity of H_2 [-]		1.41	1	4.67	3.98	3.73	2.82
Experimental Results							
Cu-BTC membrane (2 h)	Permeance [mol m^{-2} s^{-1} Pa^{-1}]	7.46×10^{-8}	9.98×10^{-8}	2.04×10^{-8}	1.87×10^{-8}	2.03×10^{-8}	2.49×10^{-8}
	Ideal H_2 selectivity [-]	1.34	1	4.90	5.34	4.92	4.01
Cu-BTC membrane (4 h)	Permeance [mol m^{-2} s^{-1} Pa^{-1}]	1.69×10^{-8}	2.05×10^{-8}	5.36×10^{-9}	1.48×10^{-9}	7.16×10^{-10}	8.31×10^{-10}
	Ideal H_2 selectivity [-]	1.21	1	3.82	13.9	28.6	24.6
Cu-BTC membrane (6 h)	Permeance [mol m^{-2} s^{-1} Pa^{-1}]	7.67×10^{-9}	9.03×10^{-9}	2.45×10^{-9}	5.57×10^{-10}	7.34×10^{-11}	5.90×10^{-11}
	Ideal H_2 selectivity [-]	1.12	1	3.69	16.2	123	153
Reference Data of Single Gas Permeance for Previous Cu-BTC membranes							
Zhou et al. [2] (40°C)	Permeance [mol m^{-2} s^{-1} Pa^{-1}]	-	7.25×10^{-8}	5.50×10^{-9}	-	1.01×10^{-8}	1.25×10^{-8}
	Ideal H_2 selectivity [-]	-	1	13.18	-	7.18	5.80
Nan et al. [3] (25°C)	Permeance [mol m^{-2} s^{-1} Pa^{-1}]	-	7.48×10^{-7}	1.48×10^{-7}	-	2.00×10^{-7}	2.57×10^{-7}
	Ideal H_2 selectivity [-]	-	1	5.1	-	3.7	2.9
Guerrero et al. [4] (25°C)	Permeance [mol m^{-2} s^{-1} Pa^{-1}]	-	1.09×10^{-6}	5.0×10^{-7}	-	5.0×10^{-7}	8.0×10^{-7}
	Ideal H_2 selectivity [-]	-	1	2.2	-	2.2	1.4
Guo et al. [5] (25°C)	Permeance [mol m^{-2} s^{-1} Pa^{-1}]	-	1.27×10^{-6}	2.81×10^{-7}	-	2.76×10^{-7}	1.63×10^{-7}
	Ideal H_2 selectivity [-]	-	1	4.52	-	4.60	7.80

References
1.   M. Yoshimune, I. Fujiwara and K. Haraya, *Carbon*, 2007, **45**, 553-560.
2.   S. Y. Zhou, X. Q. Zou, F. X. Sun, F. Zhang, S. J. Fan, H. J. Zhao, T. Schiestel and G. S. Zhu, *J. Mater. Chem.*, 2012, **22**, 10322-10328.
3.   J. P. Nan, X. L. Dong, W. J. Wang, W. Q. Jin and N. P. Xu, *Langmuir*, 2011, **27**, 4309-4312.
4.   V. V. Guerrero, Y. Yoo, M. C. McCarthy and H. K. Jeong, *J. Mater. Chem.*, 2010, **20**, 3938-3943.
5.   H. L. Guo, G. S. Zhu, I. J. Hewitt and S. L. Qiu, *J. Am. Chem. Soc.*, 2009, **131**, 1646-1647.