Time-resolved *in situ* X-ray powder diffraction measurements to clarify the kinetic nature of adsorption-induced structural transition on metal-organic frameworks

For a dozen years, metal-organic frameworks (MOFs) that consist of metal ions and organic ligands have been extensively studied as promising porous materials. Some flexible MOFs have attracted significant attention owing to their unique ‘gate adsorption’ behavior, a structural transition phenomenon induced by guest adsorption (Fig. 1). The gate adsorption leads to a stepwise change in the amount adsorbed at a specific gas pressure, which provides larger working capacities and higher selectivities than do conventional adsorbents. Therefore, flexible MOFs have the potential to be breakthrough materials for high-throughput separation processes and may help to ensure a sustainable future. In this study, we focused on the kinetic nature of CO_2 gate adsorption on ELM-11 ($[Cu(BF_4)_2(4,4'\text{-bipyridine})_2]_n$) [1] and revealed that time-resolved *in situ* X-ray powder diffraction (XRPD) measurements indicate CO_2 gate adsorption on ELM-11 to be significantly fast in response to the change in CO_2 pressure.

Time-resolved *in situ* XRPD measurements of ELM-11 during CO_2 gate adsorption were conducted using a large Debye–Scherrer-type diffractometer with a multimodular system constructed with six MYTHEN detectors at SPring-8 **BL02B2** [2]. The ELM-11 sample was placed at the end of a 0.3-mm-diameter borosilicate glass capillary attached to a stainless-steel tube with an epoxy adhesive. The sample was evacuated for 10 h at 373 K, and the sample temperature was then controlled at 273 K using a nitrogen gas blower. The *in situ* XRPD patterns were continuously obtained by exposing the sample for 1 s at intervals of 50 ms. After 4.15 s from starting the XRPD measurements, CO_2 gas in a gas manifold of a gas-handling system was introduced into the glass capillary in which the ELM-11 sample was maintained in a vacuum.

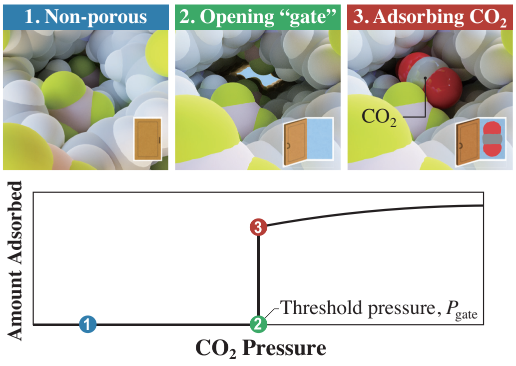

Fig. 1. Schematic illustration of the gate adsorption behavior on ELM-11. ELM-11 has no pores when the ambient CO_2 pressure is low (closed state). When the CO_2 pressure reaches the threshold pressure P_{gate}, the framework structure of ELM-11 and CO_2 molecules are adsorbed into the pores generated (open state).

Figure 2 shows time-resolved *in situ* XRPD patterns of ELM-11 during CO_2 gate adsorption together with the crystal structures of ELM-11 in closed and open states [3]. The color map showing the time development of peak intensities indicates that the structural transition of ELM-11 started immediately after the introduction of CO_2 at 40.8 kPa and was accomplished in approximately 10 s. Peak intensities of the 002 reflection at 6.1° for the open phase of ELM-11 were then obtained by the nonlinear least-squares fitting of the pseudo-Voigt function. The fractions of phases transformed as a function of time were determined by normalizing the peak intensities by that after the completion of the transition for the open phase. Figure 3(a) shows the time development of the fraction of the open phase by introducing approximately 41 kPa of CO_2 at 273, 264, and 241 K. It can be seen that the rate of phase transition increases as the temperature decreases under the same CO_2 pressure. We also investigated the dependence of the rate of phase transition on the pressure at 227 K. As shown in Fig. 3(b), the rate of structural transition increased with CO_2 pressure, and the phase transition was completed within a few seconds at the highest gas pressure. Furthermore, as drawn with solid lines in Figs. 3(a) and 3(b), these data were found to obey the following Kolmogorov–Johnson–Mehl–Avrami (KJMA) equation [4],

$$\alpha = 1 - \exp(-kt^n)\,, \qquad (1)$$

where α is the fraction transformed at time t, k is the rate constant, and n is the number of dimensions at which the transition occurs. Figure 3(c) shows the relationship between the rate constant of the KJMA equation and the pressure difference P–P_{gate}, where P is the CO_2 pressure introduced into the glass capillary with ELM-11 and P_{gate} is the gate-opening pressure. We found that, as shown by the solid line in Fig. 3(c), the following characteristic curve could be drawn for all the rate constants of the open phase investigated:

$$k(P,T) = k_0\{P - P_{gate}(T)\}\,, \qquad (2)$$

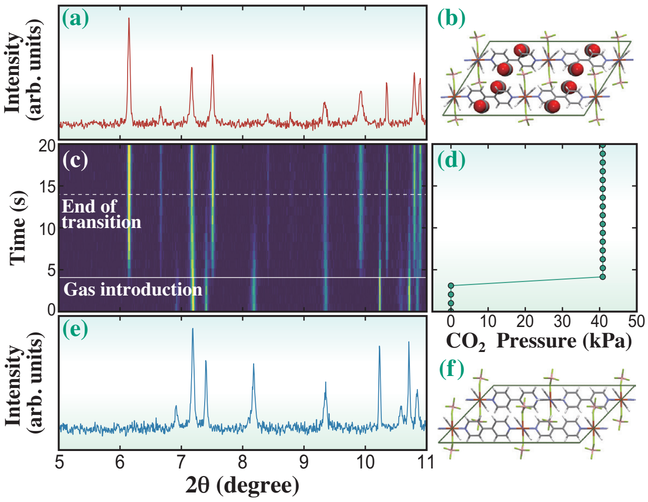

Fig. 2. **(a)** XRPD pattern and **(b)** crystal structure of ELM-11 in the open state. **(c)** Color map of time-resolved *in situ* XRPD patterns of ELM-11 at 273 K corresponding to **(d)** stepwise CO_2 pressure change from 0 to 40.8 kPa. **(e)** XRPD pattern and **(f)** crystal structure of ELM-11 in the closed state. The wavelength of the incident X-rays was 0.099899 nm.

where k_0 is a constant, which was determined to be 12.0 ± 0.5 $s^{-1/n}$ MPa^{-1} by least-squares fitting of Eq. (2). Note that the gate opening pressure at the corresponding temperature T is evaluated using the relationship obtained from the experimental adsorption isotherms over a wide temperature range of 195–298 K [3]:

$$\ln P_{\mathrm{gate}}\,[\mathrm{kPa}] = -3064.5/T\,[\mathrm{K}] + 14.683 \qquad (3).$$

This suggests that the rate constant only depends on the CO_2 gas pressure and temperature, which controls the gate-opening pressure, and that the gate-opening rate is amplified by the CO_2 pressure exerted on ELM-11. Equation (3) tells us that it takes only 1.5 s for ELM-11 to achieve 95% structural transition when CO_2 gas of 250 kPa is introduced at 298 K, which corresponds to a model case of the gas separation process for landfill gas (500 kPa of an equimolar mixture of CO_2 and CH_4). Note that the exponent of the KJMA equation, n, obtained from all the data for the open phase was 1.2–1.3, which indicates the quasi-one-dimensional growth of the open phase of ELM-11 [4]. This is indeed consistent with the mechanism of gate opening predicted in the previous study [3]: one-dimensional channels composed of stacked two-dimensional square grid layers are formed in ELM-11 once the interlayer distance is increased, and simultaneously, CO_2 molecules penetrate through one-dimensional channels, i.e., the formation of the open phase encapsulating CO_2 proceeds along the one-dimensional direction.

This fast gating of ELM-11 is a desirable feature for high-throughput separation processes, particularly for pressure swing adsorption processes with a short cycle time (rapid PSA), to increase the flow rate of the gas without increasing the system size. We therefore evaluated the separation performance of a rapid PSA system using ELM-11 for landfill gas separation and demonstrated that the proposed system can produce the same amount of production with a 69% smaller column size and a 62% lower feed than a system using a conventional adsorbent [5].

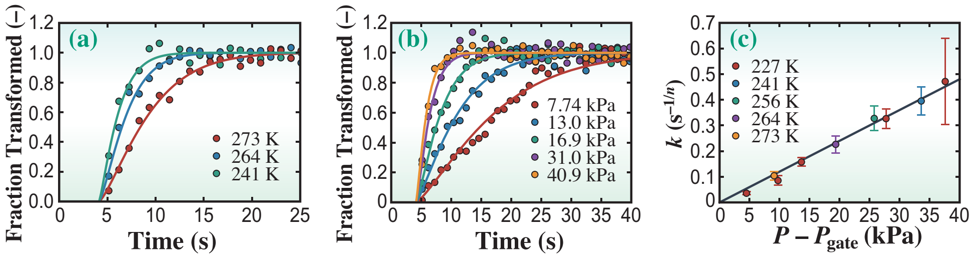

Fig. 3. **(a)** Normalized peak intensities (fractions of the phase transformed) from the 002 reflection ($2\theta = 6.1°$) of the open phase at CO_2 pressure of 41 kPa as a function of temperature and **(b)** normalized peak intensities from the 002 reflection for the open phase at 227 K as a function of CO_2 pressure. The solid lines were obtained by fitting the KJMA equation. **(c)** Relationship between the rate coefficient k and the pressure difference between the CO_2 gas pressure P and the gate-opening pressure P_{gate}.

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