Contribution ID: **24** Type: **Oral Presentation**

Framework-dependent kinetics of adsorption-induced structural transition in flexible metal-organic frameworks

Tuesday, May 21, 2024 5:50 PM (20 minutes)

Flexible metal–organic frameworks (MOFs) exhibit a guest-induced structural transition upon gas adsorption, called “gate opening”or “breathing,”and are expected to be applied to gas separation processes due to their high selectivity and stepwise change in the amount adsorbed. [1] While the mechanism of the adsorption-induced structural transition has been explained by thermodynamics, [2] the kinetic nature of the structural transition has not been fully investigated. In this study, we aimed to elucidate the dynamics of the structural transition on ELM-11 ([Cu(BF4)2(4,4’-bipyridine)2]n) induced by CO2 adsorption using time-resolved in situ X-ray powder diffraction (TRXRD) measurements.

The TRXRD patterns of ELM-11 during CO2 gate opening were continuously obtained with 0.5 s exposure for each data at SPring-8, Japan. During the measurements, the CO2 pressure was increased with constant pressurization rates at 0.005, 0.08, 0.32, and 0.8 kPa/s, and the temperature was controlled at 223, 248, and 273 K.

Fig. 1a shows the TRXRD patterns at 248 K and 0.80 kPa/s. All of the patterns have peaks belonging to the closed state (cl) and/or peaks belonging to the open state (op), which indicates the absence of an intermediate phase. Thus, the fraction transformed α was determined from the intensity ratio of op to cl (Fig. 1b). A detailed analysis of the measured data revealed that the transition rate could be expressed as the difference between the gas pressure and the gate-opening pressure (P –Pg) multiplied by the autocatalytic reaction model ((k1α + k2)(1 –α)), which is in good agreement with the experimental results. (solid lines in Fig. 1b). The autocatalytic reaction model of ELM-11 was found to reflect the existence of two pathways for CO2 penetration in the framework. Moreover, the same analysis was conducted for CO2 breathing in MIL-53(Al) ([Al(OH)(1,4-benzendicarboxylate)]n) and CO2 gate opening in CuFB ([Cu(fumarate)(trans-bis(4-pyridyl)ethylene)0.5]n), revealing that their structural transition rates are modeled by first-order model and zero-order model. This result confirmed that the adsorption kinetics of flexible MOFs is highly dependent on their framework structure. [3]

References:

1. S. Hiraide et al., Nat. Commun. 11, 3867 (2020).
2. F. X. Coudert et al., J. Am. Chem. Soc. 130, 14294 (2008).
3. Y. Sakanaka et al., Nat. Commun. 14, 6862 (2023).

Primary authors: HIRAIDE, Shotaro (Kyoto University); Dr SAKANAKA, Yuta (Department of Chemical Engineering, Kyoto University); Mr SUGAWARA, Iori (Department of Chemical Engineering, Kyoto University); Mr UEMATSU, Hajime (Department of Chemical Engineering, Kyoto University); Dr KAWAGUCHI, Shogo (Japan Synchrotron Radiation Research Institute, SPring-8); MIYAHARA, Minoru (Department of Chemical Engineering, Kyoto University); WATANABE, Satoshi (Department of Chemical Engineering, Kyoto University)

Presenter: HIRAIDE, Shotaro (Kyoto University)

Session Classification: Tuesday

Track Classification: Oral Presentations