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Evaluation of CO_2 Sorption Characteristics of Metal-Organic Frameworks

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Growing concern over the impact on global climate change of the buildup of greenhouse gases in the atmosphere has resulted in proposals to carbon dioxide capture and storage. Although many investigations of new candidate materials with the unique CO_2 sorption behavior focus on equilibrium sorption data, it is also critical to consider sorption kinetic properties when evaluating sorbent performance.

In this work, CO_2 sorption kinetic data at various temperatures were collected for Mg_2(dobpdc) before and after appended diamine using the volumetric sorption system. The purpose of this work is to demonstrate the effectiveness of dynamic characterization techanique for materials with strong CO_2 sorption sites using the volumetric sorption system, through discussion of MOFs with difference CO_2 sorption mechanism.

The samples studied in this investigation is a commercially manufactured 3 types of MOFs supplied by Atomis Inc.. These Mofs, known as Mg_2(dobpdc), mmen-Mg_2(dobpdc) and mm2-Mg_2(dobpdc).

Fig.1 shows typical CO_2 sorption isotherms at 25 °C for Mg_2 (dobpdc) before and after appended diamine. Mg_2(dobpdc) showed normal Langmuir-type physisorption behaviour, mmen-Mg_2(dobpdc) and mm2-Mg_2(dobpdc) showed sharp isotherm steps at 0.02 kPa and 6 kPa, respectively. The step-shaped CO_2 sorption isotherms results from cooperative chemisorption process to form ammonium carbamate chains.

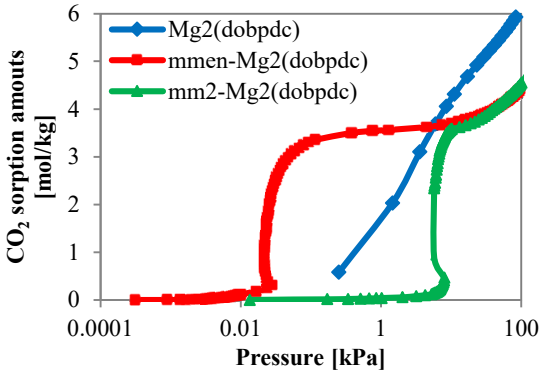

Fig.1 CO_2 sorption isotherms at 25 °C for Mg_2(dobpdc), mmen-Mg_2(dobpdc) and mm2- Mg_2(dobpdc)

Based on Liner Driving Force model considering the volumetric sorption system, CO_2 transfer coefficient (k_{LDF}) was estimated from sorption kinetic data at various temperature. Fig.2 shows Arrhenius plots of CO_2 transfer coefficient for Mg_2(dobpdc) with 1.0, 1.5, 2.0 mol/kg sorption amounts. Here, CO_2 transfer coefficient at the particular equilibrium sorption amounts estimated from CO_2 sorption amounts vs logarithmic CO_2 transfer coefficient by linear interpolation. The CO_2 transfer coefficient significantly increases with increasing temperature, indicating that CO_2 diffusivity increasing in the pore of Mg_2(dobpdc). The activation energy was determined from the logarithmic dependence of CO_2 transfer coefficient on reciprocal temperature. Obtained activation energy of 30 kJ/mol was equal to the energy barrier of 30 kJ/mol for CO_2 to hop from a metal site to a neighboring unoccupied metal site from DFT calculations of CO_2 diffusion pathways in a similar MOF known as Mg_2(dobdc).

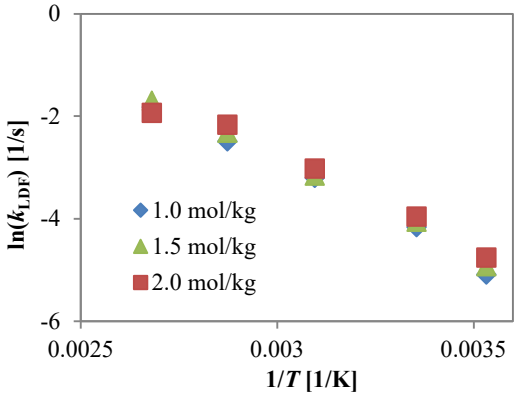

Fig.2 Arrhenius plots of CO_2 transfer coefficient (k_{LDF}) for Mg_2(dobpdc) with 1.0, 1.5, 2.0 mol/kg sorption amounts

Table1 Isosteric adsorption heat and activation energy for Mg_2(dobpdc), mmen-Mg_2(dobpdc) and mm2- Mg_2(dobpdc)

	$-\Delta H$ [kJ/mol]	ΔE [kJ/mol]
Mg_2(dobpdc)	42	30
mmen- Mg_2(dobpdc)	76	88
mm2- Mg_2(dobpdc)	61	61

Table1 shows Isosteric adsorption heat ($-\Delta H$) and activation energy (ΔE) for Mg_2(dobpdc), mmen-Mg_2(dobpdc) and mm2- Mg_2(dobpdc). Here, $-\Delta H$ was calculated based on Clausius-Clapeylon equation from CO_2 equilibrium sorption amounts at various temperature. Since the ΔE estimated from the CO_2 transfer coefficient is close to $-\Delta H$, suggesting that the diffusion was suppressed by the stabilization of the sorption CO_2 with the increase of $-\Delta H$ even in the cooperative CO_2 sorption process.

Based on these results, the dynamic sorption characterization technique by the volumetric method is considered to be widely effective for materials with strong CO_2 sorption sites.