

## CO<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> Adsorptions in Flexible Metal-Organic Framework: Combination of Periodic Boundary Calculation with post-Hartree-Fock Correction

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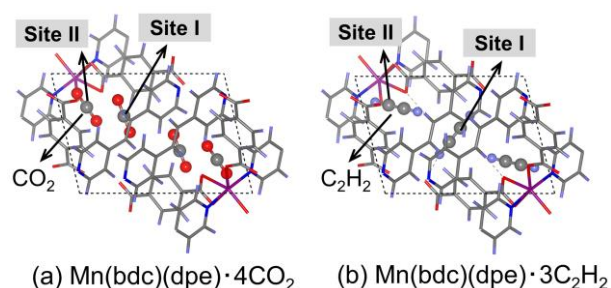
**[Abstract]** We theoretically investigated adsorptions of CO<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> in a flexible metal-organic framework (MOF) [Mn(bdc)(dpe)]<sub>n</sub> (H<sub>2</sub>bdc = 1,4-benzenedicarboxylic acid, dpe = 1,2-di(4-pyridyl)ethylene) which shows gate-opening adsorption for C<sub>2</sub>H<sub>2</sub> but via usual non-gate-opening adsorption for CO<sub>2</sub>. The adsorption positions and enthalpies of CO<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> were reproduced well using a hybrid method combining DFT (PBE-D3) for infinite system and post-Hartree-Fock method (SCS-MP2 and CCSD(T)) for cluster model. The difference in adsorption behavior between C<sub>2</sub>H<sub>2</sub> and CO<sub>2</sub> arises from their different adsorption structures; C<sub>2</sub>H<sub>2</sub> adsorption induces a larger structural transformation than CO<sub>2</sub> adsorption. It is concluded that the crystal deformation energy and interaction energy of gas molecule with MOF play crucial roles in determining the adsorption behavior.

**[Introduction]** Flexible metal-organic frameworks (MOFs), which undergo structural transformation in response to external stimuli such as gas adsorption and desorption, attract great attention as potential materials for gas storage and gas separation. However, the influence of such structural transformation on the adsorption behavior is still unclear. Recently, a flexible Mn(II)-based MOF, [Mn(bdc)(dpe)]<sub>n</sub>, was synthesized and demonstrated to exhibit structural expansion upon C<sub>2</sub>H<sub>2</sub> and CO<sub>2</sub> adsorptions. However, the adsorption isotherms differ very much between C<sub>2</sub>H<sub>2</sub> and CO<sub>2</sub>; for instance, the gate-opening adsorption occurs for C<sub>2</sub>H<sub>2</sub> but does not for CO<sub>2</sub>, leading to excellent gas-separation ability<sup>[1]</sup>.

Theoretical study on gas adsorption in such flexible MOF is important to understand the different adsorption behavior between gas molecules with similar properties. However, it is challenging to estimate accurately the interaction energy of gas molecule with MOF, because the post-Hartree-Fock (HF) method must be employed to evaluate dispersion interaction, which is important in gas adsorption in MOFs, but its application to MOFs is difficult.

In this work, we theoretically investigated CO<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> adsorptions in this flexible MOF using a hybrid method combining DFT (PBE-D3) for infinite system and SCS-MP2 and CCSD(T) for cluster model to disclose the reasons for the difference in adsorption behavior between CO<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> and factors that govern the gate-opening adsorption.

**[Methods and Computation]** Geometry optimization was carried out using PBE+D3 functional with periodic boundary conditions as implemented in the VASP program. Binding energy of



**Fig. 1.** Optimized adsorption structures of CO<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>.

gas molecule was calculated with Eqs. (1) and (2).

$$\text{BE}^{\text{Final}} = E(\text{H-G})_{\text{eq}} - E(\text{H})_{\text{eq}} - E(\text{G})_{\text{eq}} = \text{BE}^{\text{PBE-D3}} + \text{INT}(\text{H-G})^{\text{SCS-MP2}} - \text{INT}(\text{H-G})^{\text{PBE-D3}} + \text{INT}(\text{G-G})^{\text{SCS-MP2}} - \text{INT}(\text{G-G})^{\text{PBE-D3}} + \Delta\text{CCSD}(\text{T}) \quad (1)$$

$$\text{INT}^{\text{SCS-MP2 or PBE-D3}}(\text{H-G}) = E(\text{H-G})_{\text{eq}}^{\text{SCS-MP2 or PBE-D3}} - E(\text{H})_{\text{dis}}^{\text{SCS-MP2 or PBE-D3}} - E(\text{G})_{\text{dis}}^{\text{PBE-D3 or PBE-D3}} \quad (2)$$

where H and G represent host (MOF) and guest (gas molecule), respectively, superscripts “PBE-D3” and “SCS-MP2” represent computational methods, subscripts “eq” and “dis” mean equilibrium structure and distorted one in H-G.  $\text{BE}^{\text{PBE-D3}}$  is the binding energy,  $\text{INT}(\text{H-G})^{\text{SCS-MP2 or PBE-D3}}$  and  $\text{INT}(\text{G-G})^{\text{SCS-MP2 or PBE-D3}}$  are interaction energies of gas molecule with cluster models and those among gas molecules, respectively. The CCSD(T) calculation was carried out to make further correction of SCS-MP2-calculated binding energy. Adsorption enthalpy was evaluated by considering zero-point energy, thermal correction, and PV term. Adsorption isotherm was calculated against  $\theta = (kp)^{\nu} / [1 + (kp)^{\nu}]$ , where  $\theta$  is the coverage at given pressure ( $p$ ),  $k$  is the adsorption equilibrium constant, and  $\nu$  is the global parameter that depends on the coverage and crystal deformation energy.

**[Results and Discussion]** In  $[\text{Mn}(\text{bdc})(\text{dpe})]_n$ , two asymmetrical adsorption sites (I and II) were found for both  $\text{CO}_2$  and  $\text{C}_2\text{H}_2$  (Fig. 1), which show different adsorption structures. The PBE-D3-calculated adsorption enthalpies are considerably larger than the experimental values for both  $\text{CO}_2$  and  $\text{C}_2\text{H}_2$  but post-HF-corrected value agrees well with the experimental results (Table 1), indicating that the post-HF correction is of considerable importance to investigate correctly the adsorption behavior. The BE of  $\text{C}_2\text{H}_2$  is smaller than that of  $\text{CO}_2$  because of the larger crystal deformation energy ( $\Delta E_{\text{def}}$ ), suggesting that  $\text{CO}_2$  and  $\text{C}_2\text{H}_2$  adsorptions induce

**Table 1.** Binding energies (BE, in kcal mol<sup>-1</sup>) and adsorption enthalpies ( $\Delta H_{\text{ads}}$ ) of  $\text{CO}_2$  and  $\text{C}_2\text{H}_2$  with  $\text{Mn}(\text{bdc})(\text{dpe})$  at different sites.

| Adsorption Sites                                | $\text{CO}_2$ |       |                     | $\text{C}_2\text{H}_2$ |       |                     |
|---|---------------|-------|---------------------|------------------------|-------|---------------------|
|   | I             | II    | full <sup>[a]</sup> | I                      | II    | full <sup>[a]</sup> |
| Number of Molecules                             | 2             | 2     | 4                   | 1                      | 2     | 3                   |
| $\text{BE}^{\text{PBE-D3}}$                     | -9.57         | -8.22 | -9.04               | -6.87                  | -7.25 | -9.02               |
| $\Delta E_{\text{def}}$                         | 1.25          | 2.23  | 2.67                | 5.31                   | 1.81  | 6.35                |
| $\text{BE}^{\text{Final}}$                      | -8.59         | -7.95 | -8.17               | -4.74                  | -6.05 | -7.25               |
| $\Delta H_{\text{ads}}$ (PBE-D3) <sup>[b]</sup> | -8.87         | -7.48 | -8.32               | -5.81                  | -6.50 | -8.19               |
| $\Delta H_{\text{ads}}$ (Final)                 | -7.88         | -7.22 | -7.43               | -3.71                  | -5.31 | -6.42               |
| $\Delta H_{\text{ads}}$ (Exp.) <sup>[c]</sup>   | -6.98 ~ -7.21 |       |                     | -6.21 ~ -6.60          |       |                     |

<sup>[a]</sup> all sites were occupied. <sup>[b]</sup>  $T = 240$  K. <sup>[c]</sup> Experimental values of  $\Delta H_{\text{ads}}$ .

different structural transformation of  $[\text{Mn}(\text{bdc})(\text{dpe})]_n$ , dependent mainly on their adsorption structures at the site I (Fig. 1). In the  $\text{C}_2\text{H}_2$  adsorption, the proton-like H atoms of  $\text{C}_2\text{H}_2$  approach the negatively charged O atoms of organic linker. In such adsorption structure,  $\text{C}_2\text{H}_2$  is almost perpendicular to the one-dimensional channel of  $[\text{Mn}(\text{bdc})(\text{dpe})]_n$ . On the other hand,  $\text{CO}_2$  molecules take a parallel orientation along the channel direction to interact better with the phenyl rings on the channel wall. The difference in adsorption structure leads to larger crystal deformation energy in  $\text{C}_2\text{H}_2$  adsorption than in  $\text{CO}_2$ .

Based on the calculated adsorption energetics, we simulated the adsorption isotherms via a revised Langmuir model. It was found that the shape of adsorption isotherm (gate-opening or non-gate-opening) depends on the delicate balance between crystal deformation energy and interaction energy of gas molecule with MOF; details will be discussed in the presentation.

## [References]

[1] M. L. Foo et al. *J. Am. Chem. Soc.* **138**, 3022 (2016).