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Communication

The competitive and synergistic effect between adsorption enthalpy and capacity in D_2/H_2 separation of M_2(m-dobdc) frameworks

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ABSTRACT

Hydrogen isotope separation is a challenging task due to their similar properties. Herein, based on the chemical affinity quantum sieve (CAQS) effect, the D_2/H_2 separation performance of M_2(m-dobdc) (M = Co, Ni, Mg, Mn; m-dobdc^{4-} = 4,6-dioxido-1,3-benzenedicarboxylate), a series of honeycomb-shaped MOFs with high stability and abundant open metal sites, are studied by gases sorption and breakthrough experiments, in which two critical factors, gas uptake and adsorption enthalpy, are taken into consideration. Among these MOFs, Co_2(m-dobdc) exhibits the longest D_2 retention time of 180 min/g (H_2/D_2/Ne: 1/1/98) at 77 K because of its second-highest adsorption enthalpy (10.7 kJ/mol for H_2 and 11.8 kJ/mol for D_2) and the best sorption capacity (5.22 mmol/g for H_2 and 5.49 mmol/g for D_2) under low pressure of 1 kPa and 77 K), which make it a promising material for industrial hydrogen isotope separation. Moreover, the results indicate that H_2 and D_2 capacities under low pressure (about 1 kPa) dominate the final D_2/H_2 separation property of MOFs.

As one of the primary nuclear fuels, deuterium (D_2) plays an irreplaceable role in controlled nuclear fusion and is also widely used in non-radioactive isotope tracing, chemical reaction mechanism tracing, as well as medicine and life sciences [1–4]. However, the separation and purification of D_2 from H_2 isotopic mixture is a challenging task due to their similar sizes and chemical properties. Conventional D_2/H_2 separation methods on industrial plant scale, such as cryogenic distillation process and Girdler sulfide process, are highly energy- and time-intensive. Furthermore, these technologies can only provide very low separation factors, making it difficult for extensive application [5–10]. Therefore, it is still an urgent and daunting task to explore new alternative methods for D_2/H_2 separation.

Recently, the strategy of separating hydrogen isotopes based on the kinetic quantum sieving (KQS) and chemical affinity quantum sieve (CAQS) effects of porous materials has attracted considerable attention. Based on KQS effect, which means that different diffusion rates can separate hydrogen isotopes in restricted pores [11], many reports have studied hydrogen isotope separation behavior of porous materials such as porous carbons [12–15], zeolites [16–18], metal-organic frameworks (MOFs) [19–23], covalent organic frameworks (COFs) [24] and porous organic cages [25]. However, the KQS effect is only obvious at extremely low temperatures (as low as 20 K), increasing separation costs dramatically. Unlike the KQS effect, CAQS effect can effectively separate hydrogen isotopes in porous materials under higher temperatures ($\geq$ 77 K) because hydrogen isotopes demonstrate different adsorption capacity and enthalpies under low pressure [26]. Based on CAQS effect, heavier D_2 preferentially adsorbed on strong active sites, achieving high D_2/H_2 selectivity. Compared to porous carbons, zeolites and COFs, MOFs exhibit more advantages for D_2/H_2 separation because their pore sizes and open metal sites (OMSs) are controllable and further optimize gas uptake and adsorption enthalpy, which are critical factors for D_2/H_2 separation based on CAQS effect. In recent years, MOFs have been widely used in gas separation [27–30]. However, very few MOFs, such as Cu(I)-MFU-4 L [31,32], Co-MOF-74 [33] and FJI-Y11 [34], are applied to D_2/H_2 separation based on obvious CAQS effect. Low-temperature thermal desorption spectroscopy indicated that Cu(I)-MFU-4 L only showed high H_2/D_2 selectivity at very low temperature (20 K). Furthermore, it is well known that Cu(I)-MOFs are always unstable in air and can be easily oxidized by oxygen, limiting its practical

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application. Therefore, we devote to screening stable materials with strong binding sites and high D_2/H_2 uptakes for D_2/H_2 separation under more mild conditions.

Compared to low-temperature thermal desorption spectroscopy, the breakthrough experiment used for D_2/H_2 separation is closer to simulated industrial separation processes. Recently, our group carried out breakthrough experiments to explore D_2/H_2 separation performance of the famous MOF-74 series frameworks with a high density of OMSs, especially Co-MOF-74 that exhibited a satisfying D_2 retention time of 300 min/g (H_2/D_2/Ne: 1/1/98) at 77 K [35]. As structural isomers of MOF-74, M_2(m-dobdc) (M = Co, Ni, Mg, Mn) frameworks possess a narrower pore size of 9.8 Å than that of MOF-74 (11 Å). The smaller pore size may be more conducive to mass transfer process of hydrogen isotope gas molecules in the channels. Based on the above considerations, we evaluate the D_2/H_2 separation ability of M_2(m-dobdc) frameworks by considering the competitive and synergistic effect between adsorption enthalpy and capacity during the breakthrough process.

M_2(m-dobdc) (M = Co, Ni, Mg, Mn) were synthesized by solvothermal method (Fig. S1 in Supporting information) according to previous reports [36]. M_2(m-dobdc) frameworks feature a three-dimensional honeycomb structure constructed by one-dimensional $[M(\mu-COO)(\mu-OH)]_n$ chains. The calculated pore size of M_2(m-dobdc) is 9.8 Å, smaller than that of MOF-74 (11 Å). This facilitates mass transfer process of hydrogen isotope molecules in the channels. Since the hydroxyl oxygen atom and the carboxyl oxygen atom in m-dobdc ligands are involved in coordination, this series of materials can maintain their original frameworks under high vacuum at 180 °C. The removal of coordinated solvent molecules leaves large number of OMSs, with a calculated density of 4.6 OMSs/nm^{-3} in M_2(m-dobdc), much higher than those of HKUST-1 (2.6 OMSs/nm^{-3}) [37] and PCN-16 (1.2 OMSs/nm^{-3}) [37]. The purity of prepared frameworks was confirmed by their PXRD patterns (Fig. 1a), and typical type-I N_2 sorption isotherms (Fig. 1b) at 77 K indicate their microporous characteristics.

To better understand the adsorption behavior of hydrogen isotope for M_2(m-dobdc), sorption isotherms of H_2 and D_2 at 77 K and 87 K were obtained, respectively. Among these four materials, Co_2(m-dobdc) shows the highest adsorption capacity as 9.62 mmol/g for H_2 and 10.7 mmol/g for D_2 at 800 mmHg and 77 K, higher than Ni_2(m-dobdc) (H_2: 8.24 mmol/g, D_2: 9.24 mmol/g), Mg_2(m-dobdc) (H_2: 7.97 mmol/g, D_2: 8.75 mmol/g) and Mn_2(m-dobdc) (H_2: 7.88 mmol/g, D_2: 8.56 mmol/g) (Fig. 2). As for the low-pressure part (1 kPa, a partial pressure of H_2 and D_2 during the breakthrough process) of the adsorption curve, the $D_2(H_2)$ adsorption capacity of Co_2(m-dobdc) and Ni_2(m-dobdc) sharply increase to 5.49(5.22) and 4.32(3.96) mmol/g, respectively, which are contrast to the near-flat growth of adsorption curve for Mg_2(m-dobdc) (3.07(2.70) mmol/g) and Mn_2(m-dobdc) (3.29(2.90) mmol/g), which can be attributed to the strong binding force

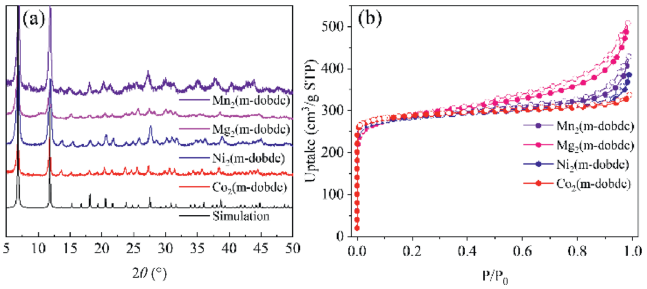

Fig. 1. (a) PXRD patterns of M_2(m-dobdc) (M = Co, Ni, Mg, Mn). (b) N_2 adsorption isotherms of M_2(m-dobdc) at 77 K (filled, adsorption; empty, desorption).

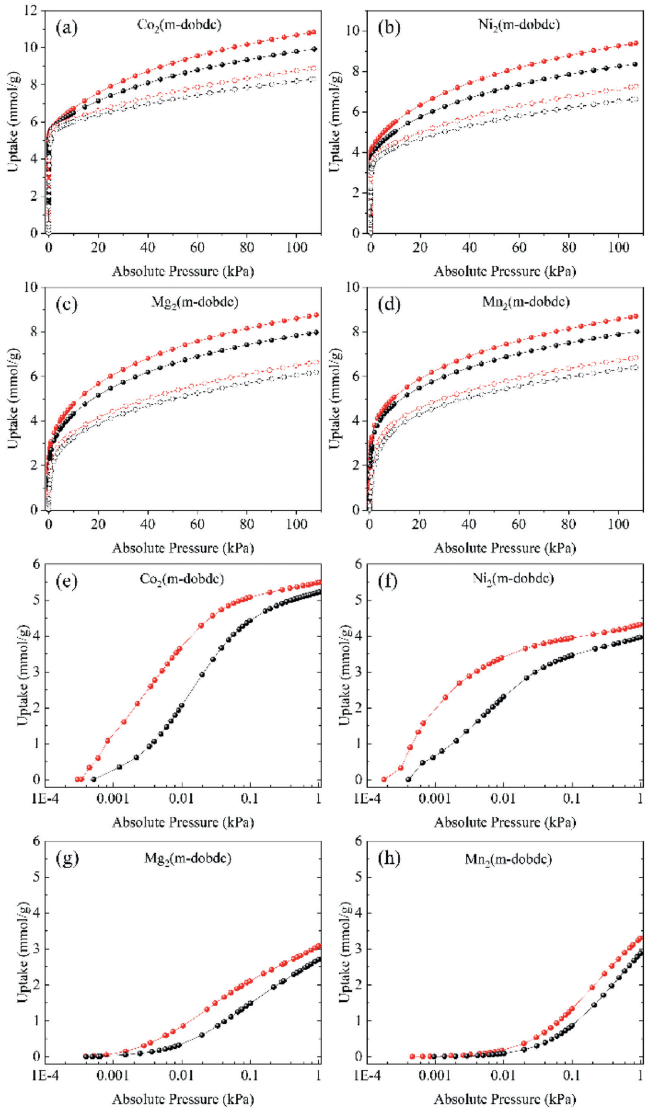

Fig. 2. (a-d) D_2 (red) and H_2 (black) sorption isotherms for M_2(m-dobdc) at 77 K (filled) and 87 K (empty). (e-h) Adsorption isotherms of D_2 (red) and H_2 (black) for pressure in the range of 0–1 kPa (77 K).

between OMSs and hydrogen isotope molecules in the framework. The results further indicate their great potential for D_2/H_2 separation. The results demonstrate that metal centers significantly influence host-guest interactions, resulting in different performance in the selective adsorption of H_2 and D_2.

Adsorption enthalpy contributes towards understanding the interaction strength between gas molecules and adsorbates. Herein, the adsorption enthalpies of H_2 and D_2 are calculated through the Clausius-Clapeyron equation. As shown in Fig. 3a, among these four materials, Ni_2(m-dobdc) shows the highest adsorption enthalpy of H_2 and D_2 at zero coverage (H_2: 11.5 kJ/mol, D_2: 13.0 kJ/mol), slightly higher than Co_2(m-dobdc) (H_2: 10.7 kJ/mol, D_2: 11.8 kJ/mol). Such high adsorption enthalpy implies that Co_2(m-dobdc) and Ni_2(m-dobdc) may be good candidates for D_2/H_2 separation.

To predict the D_2/H_2 separation ability of M_2(m-dobdc), the separation performance for D_2/H_2(50/50) mixtures was evaluated through ideal adsorbed solution theory (IAST) [38] (Figs. 3b-e). At 77 K, the D_2/H_2(50/50) selectivity of Co_2(m-dobdc) and Ni_2(m-dobdc) can reach 4.3 and 5.5 at zero coverage, respectively, higher than some famous reported porous materials such as CuBOTf (1.3)

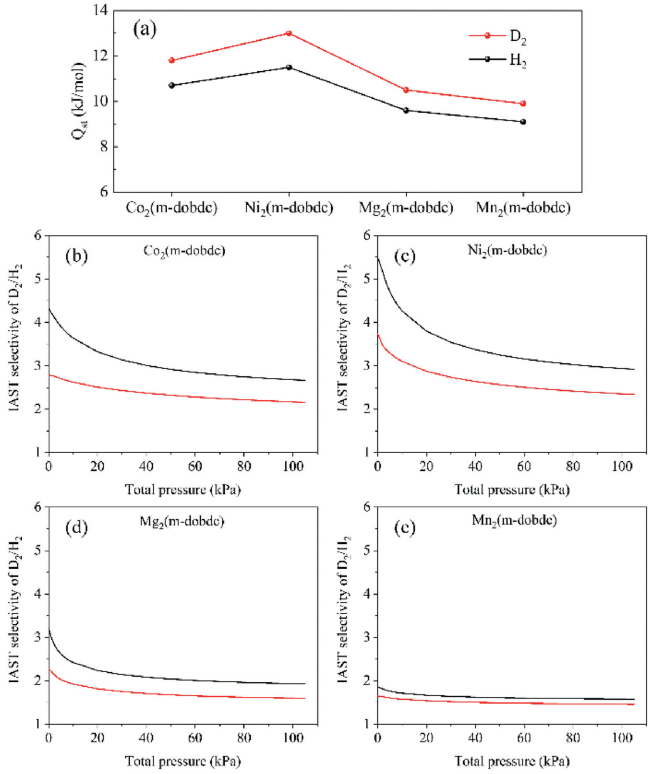

Fig. 3. (a) H_2 and D_2 adsorption enthalpies of M_2(m-dobdc) at zero coverage. (b-e) H_2/D_2(50/50) IAST selectivity of M_2(m-dobdc) at 77 K (black) and 87 K (red).

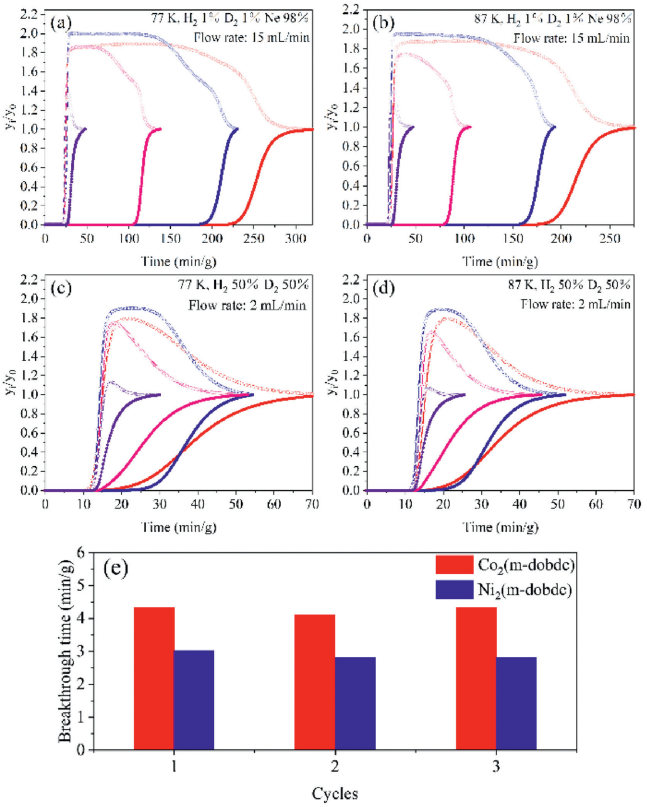

Fig. 4. (a–d) Breakthrough curves for D_2/H_2 separation on Co_2(m-dobdc) (red), Ni_2(m-dobdc) (blue), Mg_2(m-dobdc) (pink), Mn_2(m-dobdc) (violet). The hollow circle represents H_2, and the solid circle represents D_2. (e) Breakthrough time of D_2 in cycling tests on Co_2(m-dobdc) and Ni_2(m-dobdc) for H_2/D_2 (50:50) mixture.

[39], Fe-MOF-74 (2.5) [26] and Co-MOF-74 (3.2) [26]. When the pressure rises to 1 kPa, these two values still maintain at 4.22 and 5.39, respectively. According to previous reports, materials with such high IAST selectivity at 77 K were rarely reported, meaning the potential ability of Co_2(m-dobdc) and Ni_2(m-dobdc) for separating hydrogen isotopes.

Breakthrough experiments were performed to check the actual separation performance of M_2(m-dobdc). Herein, we simulated two hydrogen isotope mixtures with different compositions (H_2/D_2/Ne: 1/1/98) and (H_2/D_2: 50/50) and evaluated the actual separation ability of M_2(m-dobdc) adsorbents through breakthrough experiments at 77 K and 87 K, respectively. For these four M_2(m-dobdc) adsorbents, when the gas mixture (H_2/D_2/Ne: 1/1/98) flowed over the packed column with a flow rate of 15 mL/min at 77 K, H_2 always flowed out first due to its lower adsorption capacity and weaker binding force with adsorbent than D_2. After the hydrogen broke up, D_2 can still be retained in the packed column filled with Co_2(m-dobdc) for 180 min/g, higher than those of Ni_2(m-dobdc) (150 min/g), Mg_2(m-dobdc) (80 min/g) and Mn_2(m-dobdc) (3 min/g) (Fig. 4). When breakthrough experiments were conducted with H_2/D_2(50:50), effective separation of D_2/H_2 can still be achieved with a breakthrough time of 4.5 min/g for Co_2(m-dobdc) and 3 min/g for Ni_2(m-dobdc), while Mg_2(m-dobdc) and Mn_2(m-dobdc) showed no obvious separation ability. Surprisingly, although Ni_2(m-dobdc) has the highest D_2 and H_2 adsorption enthalpy, Co_2(m-dobdc) showed the longest D_2 retention time. As for Mg_2(m-dobdc) and Mn_2(m-dobdc), they have similar adsorption capacity, but Mn_2(m-dobdc) has inferior separation effect due to its low adsorption enthalpy. The similar rule can also be found in our previous D_2/H_2 separation research on MOF-74. On the other hand, although M_2(m-dobdc) (M = Co, Ni, Mg) exhibit similar hydrogen isotope adsorption enthalpies with M_2(dobdc) (M = Co, Ni, Mg), M_2(m-dobdc) always showed shorter breakthrough time due to their narrower pore sizes and lower adsorption capacities of D_2 and H_2. Based on the above comparison, although adsorption enthalpy and adsorption capacity are both important to breakthrough experiment performance, adsorption capacity seems to play a more decisive role in D_2/H_2 separation because D_2/H_2 separation conducted by breakthrough experiments requires MOFs to display high D_2/H_2 uptakes as well as significant difference of D_2/H_2 uptakes to extend D_2 retention time. The regeneration of adsorbents is also an important evaluation criterion in industrial applications, and cyclic experiments revealed that during three cycles, the breakthrough times of D_2 in Co_2(m-dobdc) and Ni_2(m-dobdc) remained (Fig. 4e), indicating their excellent cycling stability for D_2/H_2 separation.

In conclusion, D_2/H_2 separation performance of M_2(m-dobdc) is explored by breakthrough experiments, in which two critical factors, including gas uptake and adsorption enthalpy, are considered to investigate the competitive and synergistic effect between adsorption enthalpy and capacity in D_2/H_2 separation ability of M_2(m-dobdc) frameworks. The results showed that for MOF materials with approximate adsorption enthalpies, MOF with higher gas uptake exhibits greater D_2/H_2 separation performance. Therefore, among these materials, Co_2(m-dobdc) exhibits the second-highest hydrogen isotope adsorption enthalpy and the highest gases uptake (5.22 mmol/g for H_2 and 5.49 mmol/g for D_2) under 1 kPa, making it the best material for D_2/H_2 separation with D_2 retention time of 180 min/g for (H_2/D_2/Ne: 1/1/98) at 77 K. Compared to Co-MOF-74 (Table S1 in Supporting information), Co_2(m-dobdc) has lower adsorption enthalpy and capacity, resulting in shorter retention time of D_2. The results demonstrate that the adsorption capacity shows a more significant impact than adsorption enthalpy on D_2/H_2 separation performance. This work

demonstrates a noteworthy design consideration to develop materials with excellent hydrogen isotope separation ability.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cclet.2021.02.063.

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