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Short Communication

Enhancement of CO₂/CH₄ selectivity in metal-organic frameworks containing lithium cations

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ABSTRACT

Incorporation of Li cations into MOFs by either of two methods, chemical reduction or cation exchange, significantly improves the CO₂/CH₄ selectivity. While the selectivity enhancement by the chemical reduction seems to come from favorable displacement of catenated frameworks, the selectivity improvement by the Li cation exchange comes from enhanced solid–gas interactions.

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1. Introduction

Fixed bed adsorption processes such as pressure swing adsorption (PSA) are widely used in the separation and purification of various gas mixtures [1]. These processes are especially attractive for the separation of CO₂/CH₄ mixtures in conditions such as natural gas and landfill gas. Removal of CO₂ from these gases is needed in order to reduce pipeline corrosion as well as to produce high-purity methane [2–4]. Currently, industrial PSA processes for CO₂/CH₄ separations are operated using zeolites and carbon-based adsorbents. However, if a material with substantially higher CO₂ selectivity and capacity were developed, it could greatly improve the efficiency of the PSA processes [1].

Metal-organic frameworks (MOFs) have recently emerged as promising adsorbents for gas storage and separations [5–11]. This is due to their tailorable pore structures as well as extremely high surface areas [12–17]. Large numbers of MOFs have been synthesized, but few have been tested for their selective adsorption [18]. Among them, several MOFs have shown selective adsorption of CO₂ over CH₄ based on the molecular sieving effect [19], gas–solid interactions [20,21], and combined effects of the two [22–26].

In a few cases, post-synthesis modifications of pre-constructed MOFs have been performed to tune the pore size and provide desired surface chemistries in MOFs [25,27–33]. Incorporating lithium (Li) ions into MOFs has attracted considerable attention in theoretical studies because of the potential for producing high heats of adsorption for H₂ [34–37]. Recently, two experimental strategies for incorporating Li cations into MOFs were demonstrated by Mulfort and co-workers. One is chemical reduction of a MOF with Li metal [31,38,39], and the other is exchange of a hydroxyl proton in a MOF for a Li cation [40]. Both methods produced remarkable increases in H₂ gas uptake. In addition, Farha et al. recently applied the first method to a diimide-based porous organic polymer and showed that chemical reduction can enhance the separation of CO₂/CH₄ mixtures in an amorphous coordination polymer [41]. From a computational study, Xu et al. recently predicted that Li doping can greatly improve the CO₂/CH₄ selectivity of MOF-5, one of the most studied MOFs [42]. Nevertheless, this computational work has, as yet, not been confirmed by experimental studies on MOFs. Furthermore, it is unlikely to ever be confirmed as benzene (the main component of MOF-5's struts) is not thermodynamically reducible by lithium metal.

In this work, we experimentally investigate whether the two strategies for incorporating Li cations (chemical reduction and cation exchange) can enhance the CO₂/CH₄ selectivity in three Zn-based mixed-ligand MOFs. Two of them (**1C** and **1M**) have the same two-fold catenated structure (Zn₂(NDC)₂ (diPyNI), **1**; NDC = 2,6-naphthalenedicarboxylate and diPyNI = *N,N'*-di-(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide) but are synthesized by

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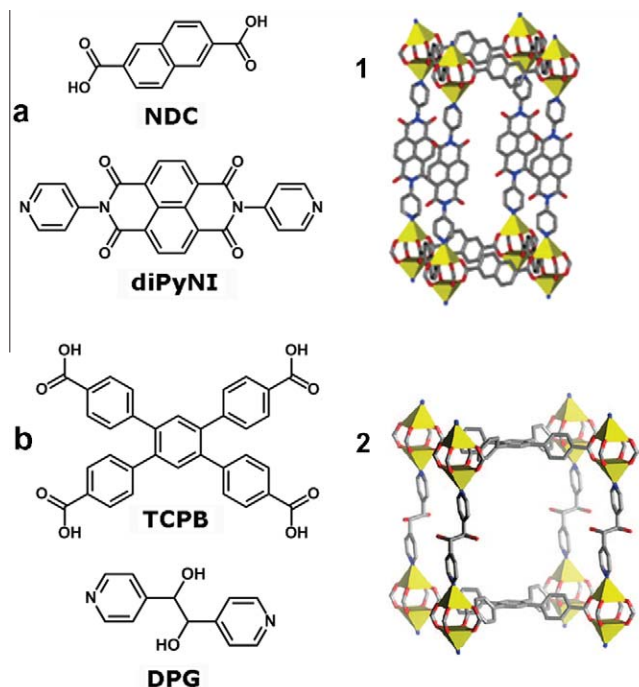


Fig. 1. (a) Chemical structures of **NDC** and **diPyNI** and the crystal structure of **1** omitting the interwoven second network. (b) Chemical structures of **TCPB** and **DPG** and the crystal structure of **2**. Hydrogens are omitted for clarity. The yellow polyhedra represent the zinc ions. Carbon: gray. Oxygen: red. Nitrogen: blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

different routes (Fig. 1a) [26,43]. The third material is a non-catenated hydroxyl-functionalized MOF ($\text{Zn}_2(\text{TCPB})(\text{DPG})$, **2**; TCPB = 1,2,4,5-tetrakis(4-carboxyphenyl)-benzene and DPG = meso-1,2-bis(4-pyridyl)-1,2-ethanediol) (Fig. 1b) [40,44].

2. Experiments

MOFs **1C**, **1M** and **2** were synthesized following previously reported methods [26,40,43]. Confirmation of the bulk material purity was done by matching the experimental powder X-ray diffraction (PXRD) patterns with patterns simulated from single crystal data (see Supporting Information). Porosity was confirmed via thermogravimetric analysis (TGA) (see Supporting Information). Lithium metal reduction of **1C** and **1M** was done as previously reported using a lithium suspension in tetrahydrofuran (THF) containing naphthalene (naphthalene) as a redox shuttle [31]. Each MOF was reacted with a lithium suspension for 10 min and rinsed with THF to remove any unreacted lithium. All manipulations with Li metal were carried out under an argon atmosphere (see safety note in Supporting Information). Lithium-reduced materials (**1C-Li** and **1M-Li**) were protected from oxygen and moisture prior to isotherm measurement. Lithium cation exchange of **2** was carried out under previously reported conditions [40]. An evacuated sample was resolvated with THF, and then reacted with 1.0 M LiOtBu ($\text{Li}^+[\text{OC}(\text{CH}_3)_3^-]$) solution in THF overnight. The Li-exchanged material (**2-Li**) is not oxygen sensitive but is slightly moisture sensitive. Care was taken in handling the sample to minimize exposure to air and water. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to measure the Li:Zn ratio within the Li-doped MOFs. It should be noted here that achieving a desired doping amount exactly is difficult for both methods. Factors such as reactant concentration, reaction duration and crystal size make the extent of lithium incorporation difficult to predict.

Single-component isotherms of CO_2 and CH_4 for each sample were measured volumetrically at 298 K and pressures up to 17 bar. For **1C**, **1M**, **1C-Li** and **1M-Li**, 45–70 mg of sample were heated at 100 °C under vacuum overnight before each measurement, to remove solvent. For **2** and **2-Li**, 35–70 mg of sample were heated at 200 °C under vacuum for 24 h. The evacuated samples are denoted as **1C'**, **1M'**, **2'**, **1C'-Li**, **1M'-Li**, and **2'-Li**. CO_2 (99.9%) and CH_4 (99%) were obtained from Airgas, Inc. (Radnor, PA). The detailed procedures for the adsorption measurements can be found elsewhere [26].

3. Results and discussion

Previously, we synthesized **1** by either of two routes, a conventional solvothermal method (**1C**) and a microwave-assisted method (**1M**) [26]. The two as-synthesized samples (**1C** and **1M**) showed similar powder X-ray diffraction patterns, but the evacuated samples (**1C'** and **1M'**) showed differences in PXRD patterns and pore volumes. Although **1M'** showed lower CO_2 and CH_4 uptake probably due to less crystallinity with partially collapsed pores, it exhibited much higher CO_2/CH_4 selectivities (~ 30) than **1C'** (~ 5). In this work, we investigate whether chemical reduction by incorporating Li cations enhances the CO_2/CH_4 selectivities of **1C'** and **1M'**.

For this purpose, we measured the single-component isotherms of CO_2 and CH_4 for **1C'**, **1M'**, **1C'-Li** and **1M'-Li** at 298 K and pressures up to 17 bar (Fig. 2). Fig. 2a shows that the chemical reduction of **1C** ($3.7\% = 3.7$ Li per 100 diPyNI struts) produces considerable increases in CO_2 and CH_4 adsorption throughout the entire pressure range. This agrees well with a previous result that showed a remarkable enhancement in H_2 uptake by the chemical reduction of **1C** [38]. However, the enhanced H_2 adsorption was not attributed to the creation of special metal-based adsorption sites, but to a favorable displacement of the interwoven frameworks [31]. We hypothesize that the significant increases in CO_2 and CH_4 adsorption by the chemical reduction of **1C** can be also explained by the same mechanism. In the interwoven network of **1C**, two catenated frameworks are located in close proximity to each other. When Li cations are incorporated into **1C**, it is energetically favorable for them to be positioned between the interwoven frameworks [36], facilitating a displacement of the frameworks. At 18 atm, the enhancement in CO_2 uptake is 17 CO_2 molecules per added Li^+ . Direct CO_2/Li binding cannot explain such a large increase in CO_2 uptake in **1C'-Li**. This provides circumstantial evidence for the framework displacement. This Li-driven displacement of **1C'-Li** networks leads to increased adsorption of CO_2 and CH_4 . Interestingly, Li doping produces large increases (52% at 1 bar; 13% at 17 bar) in CO_2 adsorption but gives only minor increases (33% at 1 bar; 1% at 17 bar) in CH_4 adsorption (Fig. 2a). If we extrapolate the CO_2 and CH_4 isotherms to higher pressures, the CO_2 and CH_4 uptake in **1C'-Li** becomes lower than those in **1C'**. This is tentatively attributed to pore volume reduction resulting from the addition of Li cations into the pores of **1C'**.

Fig. 2b shows that chemical reduction of **1M** by Li doping decreases both the CO_2 and CH_4 uptake. This is contrary to the results for **1C**. The decrease in uptake seems to be related to the smaller micropore volume of **1M'** (0.064 cm^3) compared to that of **1C'** ($0.34 \text{ cm}^3/\text{g}$) [26]. The decreases of CO_2 and CH_4 uptake observed in **1M'-Li** may come from additional pore volume reduction by incorporating Li cations into the pores of **1M'**, especially because the level of Li doping is somewhat higher ($8.0\% = 8.0$ Li per 100 diPyNI). However, it was previously reported that **1C** doped with potassium shows little difference in H_2 uptake despite various levels of K doping (6% and 26%) [31]. At low pressures, almost no difference in uptake is observed in the CO_2 isotherms of **1M'** and **1M'-Li**. On the other hand, the CH_4 isotherm clearly shows a

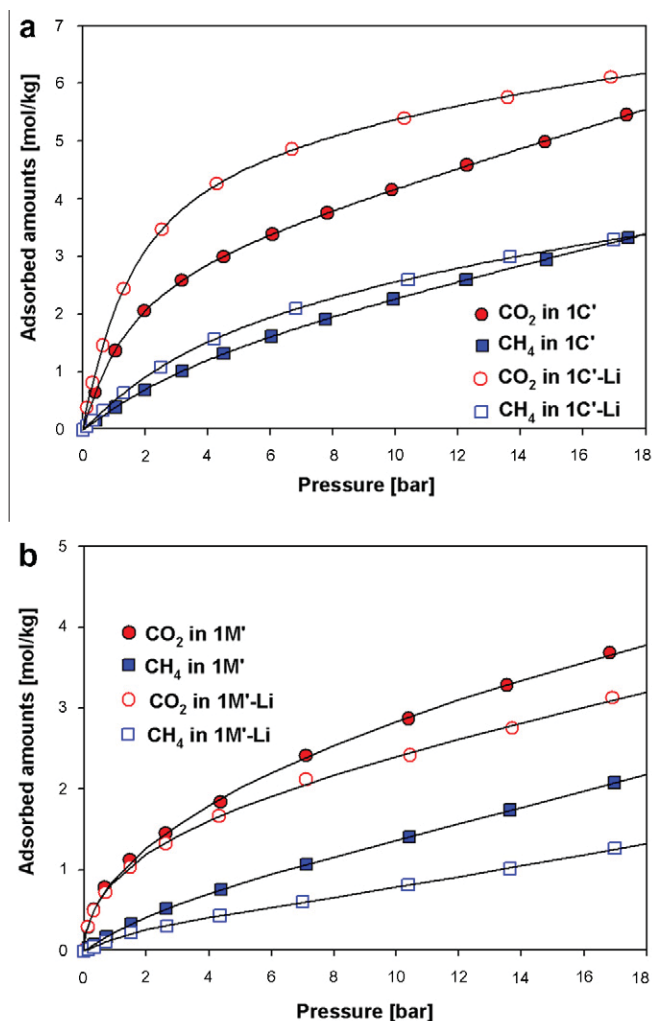


Fig. 2. Effect of chemical reduction on the CO₂ and CH₄ isotherms in (a) **1C** and (b) **1M** at 298 K. Solid lines are fits from the dual-site Langmuir Freundlich model.

decrease in uptake after Li doping. This may result in an increase in CO₂/CH₄ selectivity after incorporating Li cations into **1M**.

In Fig. 2a and b, the difference between CO₂ and CH₄ uptake, especially at low pressures, becomes larger after Li doping. From this, we can infer that Li doping in **1C** and **1M** may increase CO₂/CH₄ selectivities at the mixture conditions. To check whether this is true, we estimated CO₂/CH₄ selectivities from the experimental pure isotherms using the ideal adsorbed solution theory (IAST). The IAST method has been shown to predict well simple mixed gas behavior in MOFs from single-component isotherms [26,45,46]. For consistent comparisons, all selectivities were calculated at equimolar mixture conditions. Fig. 3a and b reveal significant increases in CO₂/CH₄ selectivities after chemical reduction of **1C** and **1M** and incorporation of Li cations. For **1C'-Li**, the selectivity improvement stems from the increase in CO₂ adsorption as shown in Fig. 2a. For **1M'-Li**, however, the increases in the selectivities seem to originate from decreases in CH₄ adsorption as shown in Fig. 2b. As mentioned above, the selective behavior is believed to come from the favorable displacement of catenated frameworks as well as from the pore volume reduction that accompanies Li doping. **1M'-Li** shows very high CO₂/CH₄ selectivities (~50), especially at low pressures. These selectivities are considerably higher than experimental reports for other adsorbents under similar conditions: a mixed-ligand MOF (~30) [26], a carborane-based MOF with

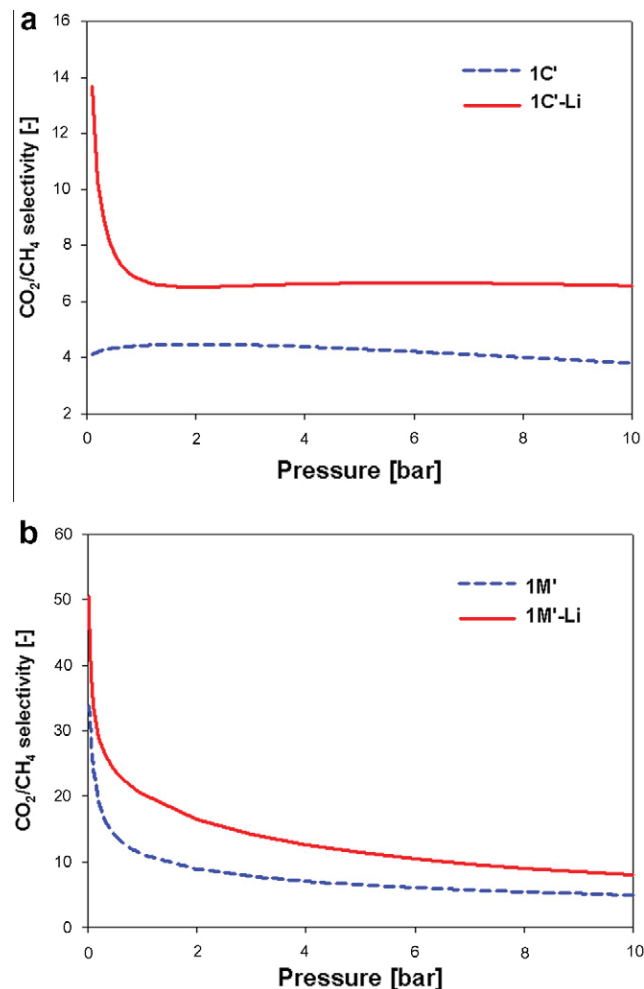


Fig. 3. Effect of chemical reduction on the CO₂/CH₄ selectivities in (a) **1C** and (b) **1M** at 298 K.

open metal sites (~17) [21], a 2-D MOF with open metal sites (~13) [47], ZIF-78 (~10) [48], and zeolite β (~28) [3].

In **1C** and **1M**, we incorporated Li cations into the pores of catenated MOFs through chemical reduction. However, for **2**, the Li cations are incorporated by a different route: **2-Li** is obtained by exchanging the hydroxyl protons within **2** for Li cations. Furthermore, since **2** is a non-catenated MOF, the effect of the displacement of catenated frameworks is eliminated. Using **2'** and **2'-Li**, we investigated the effect of the Li cation exchange on the CO₂ and CH₄ isotherms, as well as the CO₂/CH₄ selectivity. We measured the pure isotherms of CO₂ and CH₄ for **2'** and **2'-Li** at 298 K and pressures up to 17 bar. In Fig. 4a, **2'-Li** shows considerably higher CO₂ and CH₄ adsorption than **2'**. At 18 atm, the increase in CO₂ uptake is 4 CO₂ molecules per added Li⁺. This can be reasonably explained by direct CO₂/Li binding. Also, the isotherm trends in Fig. 4a suggest that the pore volume of **2'** is slightly increased or, at least, not reduced by the incorporation of Li cations (12.5% = 12.5 Li per 100 OH). This is clearly different from the cases of **1C'-Li** and **1M'-Li** (Fig. 2a and b). These distinctions can be explained by the differing methods of Li incorporation used in **1** and **2**. For the chemical reduction method, Li doping should diminish the pore volume because the Li cations are added to the pores without losing any other framework components. However, for the cation exchange method, the incorporation of Li cations should not yield appreciable changes in the pore volume since the

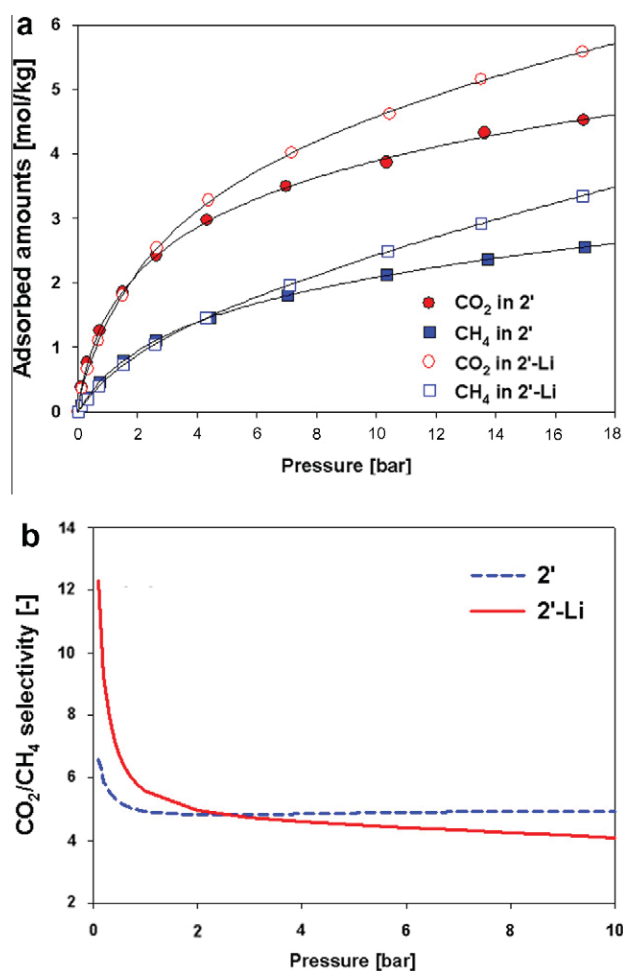


Fig. 4. Effect of Li cation exchange in (a) CO₂ and CH₄ isotherms in 2' and 2'-Li at 298 K (solid lines are fits from the dual-site Langmuir Freundlich model). (b) CO₂/CH₄ selectivities in 2' and 2'-Li at 298 K.

hydroxyl protons are exchanged for Li cations. Note that the extent of doping for 2'-Li (12.5%) is higher than for 1M'-Li (8%).

When we estimated CO₂/CH₄ selectivities from pure isotherms using IAST, 2'-Li showed considerably higher selectivities than 2' at low pressures. However, at higher pressure 2' and 2'-Li showed similar selectivities, with 2'-Li dipping below 2' at pressures above 3 bar (Fig. 4b). Since the increased selectivities at low pressures for 2'-Li do not come from the displacement of catenated frameworks, they are reasonably attributed to enhanced solid–gas interactions due to the presence of unsolvated Li cations. To investigate this idea further, we measured isosteric heats of adsorption (Q_{st}) from CO₂ isotherms collected at 273 and 298 K. A clear increase in Q_{st} is observed in 2'-Li relative to 2', especially at low coverage as shown in Fig. 5. At higher coverage, there is less enhancement in Q_{st} . We interpret the findings as indicating that at increased coverage the Li cations are surrounded by adsorbate molecules and only lower energy adsorption sites (smaller Q_{st}) remain available. This would account for the increased CO₂/CH₄ selectivities of 2'-Li over 2' at low pressures and the similar selectivities at higher pressures.

4. Conclusions

Our experiments and IAST calculations have shown that two Li incorporation methods, strut reduction and cation exchange, can significantly improve CO₂/CH₄ sorption selectivity in three Zn-based mixed-ligand MOFs. For the cases entailing framework-strut

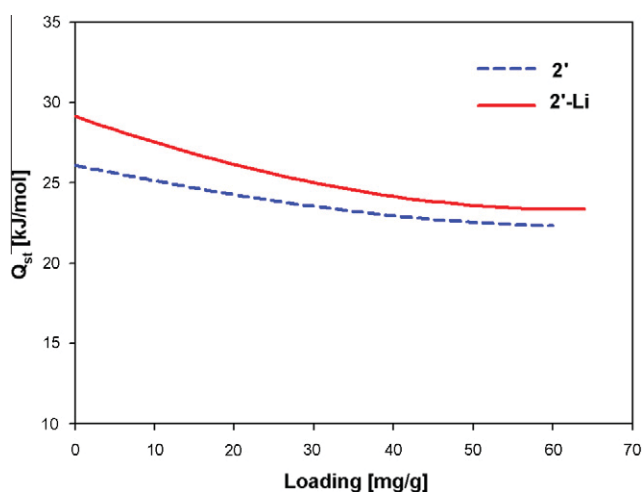


Fig. 5. Isosteric heat of adsorption (Q_{st}) of CO₂ in 2' and 2'-Li.

reduction and charge-compensating Li⁺ incorporation, the increases in selectivity can be explained by the favorable displacement of catenated frameworks, as well as pore-volume diminution. Conversely, the selectivity enhancement seen in the Li cation exchanged material seems to come from enhanced MOF–gas interactions – specifically, desolvated-Li(charge)/CO₂(quadrupole) interactions. To our knowledge, this is the first experimental report showing an improvement in CO₂/CH₄ selectivity by Li doping in MOFs.

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Appendix A. Supplementary data

Structural characterization (PXRD, TGA, ICP), low pressure CO₂ isotherms for 2' and 2'-Li, CO₂ heat of adsorption isotherm fitting for 2' and 2'-Li, and safety note for Li metal. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.micromeso.2010.10.048.

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