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Short Communication

Enhancement of CO_2/CH_4 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 CO_2/CH_4 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.

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 CO_2/CH_4 mixtures in conditions such as natural gas and landfill gas. Removal of CO_2 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 CO_2/CH_4 separations are operated using zeolites and carbon-based adsorbents. However, if a material with substantially higher CO_2 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 CO_2 over CH_4 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 H_2 [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 H_2 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 CO_2/CH_4 mixtures in an amorphous coordination polymer [41]. From a computational study, Xu et al. recently predicted that Li doping can greatly improve the CO_2/CH_4 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 CO_2/CH_4 selectivity in three Zn-based mixed-ligand MOFs. Two of them (**1C** and **1M**) have the same two-fold catenated structure ($Zn_2(NDC)_2$ (diPyNI), **1**; NDC = 2,6-naphthalenedicarboxylate and diPyNI = *N,N′*-di-(4-pyridyl)-1,4,5,8-naphthal-enetetracarboxydiimide) but are synthesized by

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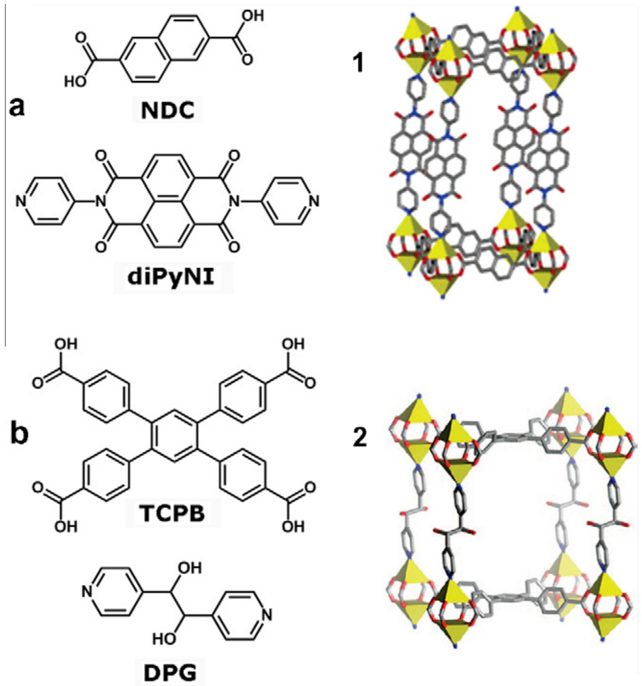

Fig. 1. (a) Chemical structures of **NDC** and **diPyNI** and the crystal structure of **1** omitting the interwoven second network. (b) Chemical structures of **TCPB** and **DPG** and the crystal structure of **2**. Hydrogens are omitted for clarity. The yellow polyhedra represent the zinc ions. Carbon: 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 (Zn_2(TCPB)(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 (napthalendide) 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 LiO*t*Bu ($Li^+[OC(CH_3)_3{}^-]$) 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 cm^3/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