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Effect of pendant isophthalic acid moieties on the adsorption properties of light hydrocarbons in HKUST-1-like tbo-MOFs: application to methane purification and storage†

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Equilibrium adsorption of methane (CH₄), C₂ gases (ethane (C₂H₆), ethylene (C₂H₄)), propane (C₃H₈), and propylene (C₃H₆), and carbon dioxide (CO₂) was measured on a series of tbo-MOFs (topological analogues of the prototypical MOF, HKUST-1, correspondingly dubbed tbo-MOF-1), which were developed via the supermolecular building layer (SBL) pillaring strategy. Specifically, tbo-MOF-2 and its isoreticular, functionalized analogue, tbo-MOF-2-(CH₃O[Ph(CO₂H)₂])₂ (or tbo-MOF-3), which is characterized by pendant isophthalic acid moieties freely pointing into the cavities, were evaluated on the basis of potential use in methane storage and C₂+/CH₄ separation. The parent, tbo-MOF-2, showed high gravimetric and volumetric CH₄ uptake, close to the U.S. Department of Energy (DOE) target for methane storage at 35 bar and room temperature. Though the presence of the pendant isophthalic acid moiety in the analogous compound, tbo-MOF-3, led to a decrease in total CH₄ uptake, due mainly to the reduced size of the cavities, interestingly, it increased the affinity of the SBL-based tbo-MOF platform for propane, propene, ethane, and ethylene at low pressures compared with CH₄, due additionally to the enhanced interactions of the highly polarizable light hydrocarbons with the isophthalic acid moiety. Using Ideal Adsorption Solution Theory (IAST), the predicted mixture adsorption equilibria for the C₂H₆/CH₄, C₃H₈/CH₄, C₃H₆/CH₄, C₃H₆/CO₂ and C₃H₈/CO₂ systems showed high adsorption selectivity for C₂⁺ over methane for tbo-MOF-3 compared with tbo-MOF-2. The high working storage capacity of tbo-MOF-2 and the high affinity of tbo-MOF-3 for C₂⁺ over CH₄ and CO₂ make tbo-MOF an ideal platform for studies in gas storage and separation.

Introduction

The continuing rise in crude oil prices and the pressing responsibility to reduce emissions of greenhouse gases, as well as the need to fulfill growing demand for energy, have led to increased efforts to find substitute fuels and alternatives for gas separation.¹ In the short and medium term, methane (CH₄) is recognized as an attractive energy vector for use prior to any transition to an economy no longer based on fossil fuels, but this remains technologically challenging.² Natural gas (NG) represents the main source of CH₄; the processing of which involves removal of ethane (C₂H₆), propane (C₃H₈), and relatively heavier hydrocarbons (C₄+) from the raw gas, and is aimed at preventing condensation of volatile hydrocarbons in pipelines. Methane originating from NG must also meet strict specifications in terms of carbon dioxide (CO₂) content, which typically must not exceed 2%.³

For this reason, the development of novel separation agents with the ability to upgrade NG to high purity CH₄ before transportation, storage, and use in stationary (power plant) and mobile (vehicles) applications is essential. In this regard, suitable materials for processing the raw NG should exhibit good separation properties for CO₂ (compared with CH₄), but relatively lower affinity than C₂⁺ (or high C₂⁺/CO₂ selectivity) will be desirable to prevent weakening of the C₂⁺/CH₄ separation.⁴ When optimal methane purity for transportation in pipelines has been achieved, proper storage following the DOE standards (i.e., room temperature at a pressure not exceeding 35 bars) is then essential to allow use of the methane as fuel in vehicles.⁵

Metal–organic frameworks (MOFs) are a flourishing class of functional solid-state materials that are currently being explored for potential uses in catalysis, gas separation, storage of methane and hydrogen, and also carbon capture.⁶ To date, a
A vast amount of research on MOFs has focused on gas adsorption, storage, and separation, but little attention has been paid to the adsorption of light hydrocarbons. To our knowledge, no investigation has been reported yet on the “tuning” of MOF functionalities to target the selective removal of light hydrocarbons, such as C₃H₈ and C₂H₆, from CH₄-containing gases. Furthermore, there are very few systematic studies on the effect of MOF functionalization on CH₄ storage properties.

Adsorption technology may be applied to the processing of NG using diverse categories of industrially proven families of adsorbents, such as alumino-silica gels, activated carbons, metal oxides, and molecular sieve adsorbents. Similarly, a range of different approaches for the separation of CH₄ from C₂, and/or CO₂ may be envisaged, including techniques based on equilibrium, kinetics, and molecular sieving.

In this work, the power of designing and targeting a unique MOF platform is explored. Specifically, our supermolecular building layer (SBL) approach to the tbo platform (a unique blueprint network for the design and synthesis of porous, functional 3-periodic MOFs) offers potential for materials with appreciable gas storage, as well as facile functionalization, which can be used to target equilibrium-based gas separation of hydrocarbons. Though ligand expansion and metal substitution have provided a few analogues of HKUST-1, a prototypical MOF having tbo topology (which we dubbed tbo-MOF-1), decoration of the cavities via ligand functionalization has remained elusive. On the contrary, our unique SBL approach has allowed for the development and simple modification of an analogous layer-based tbo-MOF platform (see Video illustrating the SBL approach for the expansion and/or decoration of the tbo-MOF platform, ESI†). Our deconstruction of tbo-MOF-1 into potential 2-periodic building units (i.e., SBLs) led to our top-down design and bottom-up synthesis of the first (parent) SBL-based tbo-MOF, tbo-MOF-2. The successful development of tbo-MOF-2 indicated the potential for rational design and synthesis of iso-reticular structures, functionalized and/or expanded, which possess extra-large, nanocapsule-like cages, have high porosity, and are potentially promising for use in gas separation and storage.

The overall framework of tbo-MOF-2 (the parent MOF in this study) is neutral and consists of three different types of open cages (Fig. 1 and S1, ESI†), nearly the same size as in tbo-MOF-1. The largest, a truncated cuboctahedron of 17.787 × 18.349 Å diameters (14.387 Å sphere including van der Waals (vdW) radii), is surrounded by six truncated cubes and eight truncated tetrahedra. The truncated cubes have diameters of 15.424 Å (height) and 16.102 Å (width) (12.024 Å vdw sphere), and each is surrounded by six truncated cuboctahedra and eight truncated tetrahedra. The truncated tetrahedra have diameters of 12.521 Å (height) and 10.220 Å (width) (6.820 Å vdw sphere), and are surrounded by four truncated tetrahedra and four truncated cubes.

As a first example of its tunability, tbo-MOF-2 was modified, pre-synthesis, by functionalization of the quadrangular organic ligand with two extra, pendant isophthalic acid arms. As in tbo-MOF-2, the necessary tetra-isophthalic acid moieties coordinate to Cu²⁺, forming paddlewheels, while the two extra isophthalic acid moieties remain not coordinated (i.e., free) and point into the larger polyhedral cavities, resulting in tbo-MOF-3 (Fig. 1). Thus, this strategy permits access to made-to-order MOFs and exploitation of their consequential functionalized nanocages; in fact, the potential impact on enhancement of CO₂ energetics was explored. In light of the slight enhancement in CO₂ adsorption and selectivity upon functionalization with multiple carboxylic acids (Fig. S5, ESI†), we found it compelling to extend the study and further explore the effect on hydrocarbon adsorption and separation. Here, we report on the effect of pendant isophthalic acid moieties in tbo-MOF-3 on the adsorption properties of CH₄, C₂H₆, C₃H₈, C₃H₆, and C₂H₆, as compared with the corresponding properties of the parent, tbo-MOF-2. Particular attention is paid to the C₃H₈/CH₄ and C₂H₆/CH₄–CO₂ separation systems, as well as to storage of CH₄.

Experimental section

Methods for the synthesis and activation of tbo-MOF-2 and tbo-MOF-[CH₂O[Ph(CO₂H)₂]] (tbo-MOF-3) have been reported elsewhere by our group. High pressure single gas adsorption studies were carried out using a Rubotherm magnetic suspension balance (for more details, see ESI†). The low pressure sorption properties were determined using a Quantachrome AS-1 instrument.

Results and discussion

CH₄ storage

In order to investigate the potential of the tbo-MOF compounds for CH₄ storage, adsorption of CH₄ was carried out at 25 °C and up to 50 bars. The excess and absolute gravimetric adsorption uptakes of CH₄ on tbo-MOF-2 (parent) and tbo-MOF-3 are shown in Fig. 2. As can be seen in Fig. 2, the tbo-MOF-2, parent, material exhibits one of the highest CH₄ gravimetric uptakes (ca. 225 cm³ g⁻¹) for MOFs at the standard conditions (298 K and 35 bar), albeit with low CH₄ adsorbed phase density.
Analysis of data at 50 bars for tbo-MOF-2 showed that the volumetric working storage capacity, assuming desorption at 5 bars and 298 K, is close to the value observed for tbo-MOF-1 (ca. 152 vs. ca. 175 cm$^3$(STP) per cm$^3$); however, the adsorbed phase density in the case of tbo-MOF-2 is still much lower (ca. 0.14 g cm$^{-3}$) than in tbo-MOF-1 (ca. 0.182), even at 50 bar (Fig. S3, ESI†). In light of these results, it is expected that higher working capacity will be obtained for tbo-MOF-2 at higher pressures, consistent with the higher porosity for tbo-MOF-2. In addition, considering its tunability as compared to tbo-MOF-1, it is expected that there is plenty of potential for improvement toward CH$_4$ storage on the tbo-MOF-2 platform.

As anticipated, on the basis of the much lower pore volume, functionalization of tbo-MOF-2 with the isophthalic acid moieties led to a significant decrease in the gravimetric uptake and adsorbed phase density at 35 bar and 298 K. The volumetric uptake for the corresponding tbo-MOF-3, as calculated using the theoretical density of 1.005 g cm$^{-3}$, was much lower than that of the parent tbo-MOF-2 (Fig. S3, ESI†). The lower uptake of CH$_4$ for tbo-MOF-3 than for the parent tbo-MOF-2 is explained by its lower surface area and pore volume (1386 m$^2$ g$^{-1}$ and 0.41 cm$^3$ g$^{-1}$ for tbo-MOF-3 compared with 2932 m$^2$ g$^{-1}$ and 1.02 cm$^3$ g$^{-1}$ for tbo-MOF-2, Fig. S2, ESI†), as determined using Ar adsorption at 87 K. Thus, in terms of gas storage, the parent tbo-MOF-2 shows better promise for CH$_4$ at 298 K, as well as for H$_2$ storage at 77 K (Fig. S4, ESI†), while functionalization with isophthalic acid moieties led to a logically lower porosity and, consequently, low uptake of CH$_4$ at high pressure (35 bar).

CH$_4$ separation from C$_2$H$_6$, C$_3$H$_8$, C$_2$H$_4$, C$_3$H$_6$: NG upgrading and treatment of refinery off-gases (ROG)

The performance of tbo-MOF-2 and tbo-MOF-3 was also evaluated as equilibrium-based adsorbents for NG upgrading and treatment of ROG. In particular, the separation of CH$_4$ from gas mixtures containing CO$_2$, C$_2$H$_6$, C$_2$H$_4$, C$_3$H$_6$, and C$_3$H$_8$ was investigated. Fig. 3 shows the adsorption isotherms of CH$_4$, CO$_2$, C$_2$H$_6$, C$_2$H$_4$, C$_3$H$_6$, and C$_3$H$_8$, carried out at 298 K on tbo-MOF-2 and tbo-MOF-3, respectively (Fig. 3). Overall, the parent tbo-MOF-2 showed relatively higher gas uptake than the tbo-MOF-3 and the sequence was similar for the two compounds, particularly at low pressures, but with steeper isotherms for tbo-MOF-3, specifically for CO$_2$, C$_2$H$_6$, C$_2$H$_4$, C$_3$H$_6$, and C$_3$H$_8$. The higher interaction of these probe molecules with tbo-MOF-3 relative to tbo-MOF-2 is apparent from the relatively high Toth adsorption coefficient, $K$, as determined from fitting the single adsorption isotherms to the Toth equation (Table S3, ESI†).

As mentioned above, we have previously shown that, upon isophthalic acid functionalization, the energetics of CO$_2$ with the tbo-MOF-3 was enhanced, which, as a result, leads to an increase in CO$_2$/CH$_4$ and CO$_2$/N$_2$ selectivities (Fig. S5 and S6†) as compared to tbo-MOF-2. In order to evaluate the effect of isophthalic acid functionalization of tbo-MOF-2 on other gas separation properties (e.g., C$_2$H$_4$/CH$_4$), ideal adsorption solution theory (IAST) analysis was applied to the single gas adsorption data of C$_2$H$_6$, C$_3$H$_8$, C$_2$H$_4$, C$_3$H$_6$, CH$_4$, and CO$_2$, making use of the Toth model for best fitting. The use of IAST is justified for
tbo-MOFs, as the platform is a highly ideal system due to chemical and structural homogeneity. Interestingly, compared with the parent material, a significant enhancement was observed in C3H8/CH4, C2H6/CH4, C3H6/CH4, and C2H4/CH4 selectivities for the tbo-MOF-3 ([Fig. 4, S7 and S8, ESI† respectively]). This finding indicates that the isophthalic acid moieties increase the interaction of the C2+ with the tbo-MOF-3 framework, as a result of their relatively high polarizability (Table S2, ESI†) and lower boiling points.

Comparison of IAST analysis of C2H4/CH4 and C3H6/CH4 gas mixture adsorption on tbo-MOF-2 and its functionalized analogue revealed the same enhancement in selectivity toward C3H6 and C2H4 (Fig. S7 and S8†). The high selectivity toward olefins in the presence of H2 is a highly desirable feature for the treatment of ROG.

NG and ROG also contain an appreciable amount of CO2, and a high affinity of any separation agent for CO2 may negatively affect the separation of C2+/CH4, this being the case for zeolites such as 5A. A suitable separation agent for C2+/CH4 must also have a high affinity for C2+, when functioning in CO2-containing mixtures. Fig. S9 (ESI†) shows that the C3H6/CO2 selectivity is also high for both compounds (18 to 10 at 1 bar and 298 K for tbo-MOF-2 and tbo-MOF-3, respectively). Overall, the results here show that, in terms of the separation factor, use of the isophthalic acid functionalized tbo-MOF-2 analogue (tbo-MOF-3) will be more effective for the removal of C2+, from CH4 in CO2-containing streams, indicating the importance of the ability to design and functionalize structures.

Conclusions
In this work, it has been demonstrated that the parent SBL-based tbo-MOF, tbo-MOF-2, which is analogous to the prototypical tbo-MOF-1, displayed a particularly high working uptake for CH4, suitable for storage. The CH4 gravimetric uptake on the parent tbo-MOF-2 was one of the highest reported for MOFs, while its functionalization with isophthalic acid moieties, expectedly, resulted in lower CH4 uptake. As compared to tbo-MOF-1, tbo-MOF-2 exhibited much lower adsorbed phase density at the same given pressures. This indicates that the CH4 storage working capacity for tbo-MOF-2 would be much higher than tbo-MOF-1 at higher pressures, potentially suitable for CH4 storage for stationary applications.
Upon functionalization with carboxylic acid, the separation performance of CH₄ from C₂H₆, C₂H₄, C₃H₆, C₃H₈, and CO₂-containing gas streams was greatly enhanced, this being a vitally important feature for the upgrading of natural gas and treatment of refinery off-gases. Further research is in progress to investigate various types of functionalities within our tbo-MOF platform in order to target similar or other applications in gas storage and separation.

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Notes and references