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Selective Hysteretic Sorption of Light Hydrocarbons in a Flexible Metal–Organic Framework Material

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ABSTRACT: Porous MFM-202a (MFM = Manchester Framework Material, replacing the NOTT designation) shows an exceptionally high uptake of acetylene, 18.3 mmol g\(^{-1}\) (47.6 wt %) at 195 K and 1.0 bar, representing the highest value reported to date for a framework material. However, at 293 K and 10 bar \(\text{C}_2\text{H}_6\) uptake (9.13 mmol g\(^{-1}\)) is preferred. Dual-site Langmuir-Freundlich (DSL-F)- and Numerical Integration (NI)-based IAST methods have been used to analyze selectivities for \(\text{C}_1\) to \(\text{C}_3\) hydrocarbons. MFM-202a exhibits broadly hysteretic desorption of acetylene; such behavior is important for practical gas storage since it allows the gas to be adsorbed at high pressure but stored at relatively low pressure. Stepwise uptake and hysteretic release were also observed for adsorption of other unsaturated light hydrocarbons (ethene and propene) in MFM-202a but not for saturated hydrocarbons (methane, ethane, and propane). MFM-202a has been studied by in situ synchrotron X-ray powder diffraction to reveal the possible phase transition of the framework host as a function of gas loading. A comprehensive analysis for the selectivities between these light hydrocarbons has been conducted using both IAST calculation and dual-component mixed-gas adsorption experiments, and excellent agreement between theory and experiment was achieved.

INTRODUCTION

The large-scale separation of hydrocarbon mixtures for the production and purification of relevant energy resources and feedstocks is an extremely energy-consuming process. Natural gas, the largest reservoir for methane (\(\text{CH}_4\)), also contains ethane (\(\text{C}_2\text{H}_6\)), propane (\(\text{C}_3\text{H}_8\)), and other higher alkanes. The purification of \(\text{CH}_4\) has attracted much attention\(^{1,2}\) since it is an important target among hydrocarbon separations due to its wide ranging applications. Additionally, the purification of two very important industrial starting petrochemicals, ethene and propene (the former being the largest volume organic in the world), involves the removal of other light hydrocarbons (e.g., acetylene, ethene, and propene).\(^3\) The state-of-the-art separation method for light hydrocarbon mixtures is cryogenic distillation at high pressure based upon the small differences in vapor pressure for each component.\(^4\) This process is highly energy-intensive, and reductions in cost and energy consumption are required. To overcome these problems, selective adsorption by traditional porous materials (e.g., mesoporous silica, zeolites, and activated carbon) as adsorbents have been employed to separate hydrocarbon mixtures.\(^5-8\)

Compared with these traditional porous materials, metal–organic framework (MOFs) materials, as a newly emerged class of porous crystalline solids, show high adsorption capacities.\(^9-11\) Adsorbed gas molecules often form specific intermolecular interaction with open metal and other surface sites within MOFs, leading to the selective adsorption of certain gas species and substrates.\(^3,12-14\) Owing to their tailored porous structure and the availability of strong adsorption sites, there is great interest for the utilization of MOFs in hydrocarbon separations.\(^3,12,15\) The efficacy of MOFs to separate hydrocarbons is generally estimated by ideal adsorbed solution theory (IAST), which gives the selectivity value for multi-component mixed gases derived from the corresponding single component gas adsorption isotherms. For instance, the series of \(\text{M}_2(\text{dobdc})\) (\(\text{M} = \text{Mg, Mn, Fe, Co, Ni, Zn} \); \(\text{dobdc}^\pm = 2,5\)-dioxido-1,4-benzenedicarboxylate) has been analyzed for \(\text{C}_2\) and \(\text{C}_3\) hydrocarbon separations by IAST and confirms the potential of \(\text{M}_2(\text{dobdc})\) for the separation of ethene/ethane and propene/propane mixtures owing to the preferred binding of unsaturated hydrocarbons to the open metal sites.\(^15\) MFM-300(Al) \((\text{MFM} = \text{Manchester Framework Material, replacing the NOTT designation})\) shows an exceptionally high uptake of

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and the NOTT designation) also shows great potential for the separation of C2 hydrocarbons because of its hydroxyl-decorated pore environment and suitable pore size. Direct comparison of the IAST method and experimental measurement of dual-component adsorption isotherms allows a better understanding of the selectivity for mixed gas adsorption. However, this experiment is usually very challenging in practice. Here, we report the adsorption of light hydrocarbons (both single component and binary mixtures) in an In(III)-tetraoxalyl system, MFM-202a, which has been reported as a flexible and defect material. This coordination complex exhibits the highest BET surface area (2220 m² g⁻¹) among all In(III)-MOFs, high CO₂ (19.7 mmol g⁻¹ at 195 K and 1 bar), and the highest SO₂ (13.6 mmol g⁻¹ at 268 K and 1 bar) uptake capacities with stepwise sorption and hysteretic desorption associated with a structural phase transition. MFM-202a exhibits type-I isotherms for C₁-C₃ hydrocarbons at 273–303 K. However, at 195 K, the adsorption of acetylene exhibits marked stepwise and an exceptionally high uptake coupled with significant hysteretic desorption. A similar adsorption—desorption hysteresis loop was also observed both for ethene but not for ethane. The uptakes of propane and propene are similar at 1 bar and 273–303 K but show differences both in terms of reversibility and capacities (12.1 mmol g⁻¹ at 201 K for propene and 9.0 mmol g⁻¹ at 195 K for propane) at low temperatures. The unsaturated hydrocarbon, propene, shows a hysteretic desorption isotherm, whereas propane exhibits fully reversible uptake. In situ synchrotron PXRD experiments revealed an absence of framework phase change as a function of gas loading, and thus the observed stepwise adsorption is attributed to structural pore filling. Selectivity data obtained from the IAST calculation and the analysis of adsorption isotherms for gas mixtures are in excellent agreement and suggest MFM-202a has potential for hydrocarbon separation, particularly for natural gas purification.

**EXPERIMENTAL SECTION**

**Materials and Methods.** All chemical reagents were used as received from commercial suppliers without further purification. MFM-202 was prepared from a previously reported method. The acetonitrile-exchanged sample of MFM-202 was activated at 323 K and 10⁻⁷ mbar for approximately 1 day to remove the free solvent in the pore, and hydrocarbon adsorption measurements were then carried out on an IGA-003 system (Hiden). The temperature was controlled by water bath (for the measurements at 273–303 K), acetonitrile—dry ice bath (for the 195 K measurements), and acetonitrile—dry ice bath (for the 201 K measurement) in separate experiments. All the hydrocarbons (CH₄, C₂H₆, C₃H₆, and C₄H₁₀) apart from CH₃H used for were ultrapure research grade (>99.99%) purchased from BOC or Air Liquide. C₂H₂ was purified by a dual-stage cold trap systems and an activated carbon filter to remove acetylene before use. The equimolar binary gases adsorption measurements were performed on the IGA system equipped with multiple identical mass flow controllers enabling mixing two different gas components to an equimolar mixture in this study.

**In Situ Synchrotron Powder X-ray Diffraction (PXRD).** The in situ PXRD experiments as a function of hydrocarbon loading were carried out at Beamline I11 Diamond Light Source (Oxford, UK) using high-resolution synchrotron diffraction (λ = 0.825774 Å). The sample was loaded into capillary gas cell, and the temperature was controlled by an Oxford open-flow Cryosystems. Desolvated MFM-202a was generated by heating the sample in situ under vacuum overnight. The C₂H₂ was loaded first, the resultant PXRD was measured at 0, 64, 209, 410, and 870 mbar loadings, and then the sample was degassed to 0 mbar. C₂H₆ and C₄H₁₀ were then loaded in sequence, and the corresponding PXRD were measured at 0, 100, 500, and 1000 mbar loadings. The PXRD data and Le Bail refinements were analyzed via the TOPAS software program.

**Calculation of Selectivity.** Myers and Prausnitz developed Ideal Adsorption Solution Theory (IAST) to estimate the amount adsorbed of each component from a mixture using the isotherms for the single components. The theory assumes that the adsorbed gases form an ideal solution, and therefore the method is applicable at relatively low pressures and surface coverages. It uses spreading pressure to characterize the adsorbed phase and assumes that the adsorbent structure is thermodynamically inert with its surface area being independent of the adsorbate. The pure component isotherms must be measured accurately at low surface coverage because the integration to obtain spreading pressure is sensitive to this part of the isotherm. This is particularly critical for components in low gas phase concentrations.

The IAST calculations for multicomponent mixtures can be carried out by the following methods. The isotherms of the pure components are fitted to appropriate equations to provide a mathematical description of the isotherm. Previous studies have used the Langmuir and/or dual site Langmuir Freundlich equations to describe the isotherms for the pure components. These equations are then integrated to obtain the spreading pressure as a function of amount adsorbed for each component. Alternatively, the spreading pressures can be obtained as a function of the amount adsorbed by direct numerical trapezoidal integration of the isotherm data for the pure components. The amounts adsorbed for mixtures and gas pressures are then calculated for specific spreading pressures with the estimation of selectivity data.

We have calculated the binary mixed gases isotherms by two methods using a dual-site Langmuir—Freundlich (DSLF) method and a Numerical Integration (NI) method combined with IAST. DSLF is a frequently used model to fit the isotherms, which adopts the least-squares errors to estimate the overall error and finally gives six parameters that determine the sorption profile with the minimum residual sum of squares. The equation for DSLF is given as

\[ N = P_1 \times \frac{P_{x_1}^{3} Q_1}{1 + P_{x_1}^{3} Q_1} + P_2 \times \frac{P_{x_2}^{3} Q_2}{1 + P_{x_2}^{3} Q_2} \]

Here, \( x \) is the pressure of the pure gas at equilibrium with the adsorbed phase (kPa), \( N \) is the gas amount adsorbed per gram of adsorbent (mmol g⁻¹), \( P_1 \) and \( Q_1 \) are the saturated saturation capacities of sites \( P \) and \( Q \) (mmol g⁻¹), and \( P_{x_1}^{3} \) and \( P_{x_2}^{3} \) represent deviations from an ideal homogeneous surface. The fitted parameters were then used to predict multicomponent adsorption using IAST. The equation for the calculation of selectivity (\( S \)) between gas 1 and gas 2 is shown as

\[ S = \frac{x_1/y_1}{x_2/y_2} \]

where \( x_1 \) and \( y_1 \) are the mole fractions of component \( i \) in the adsorbed and gas phase, respectively, and \( i \) equals 1 or 2. In this work, selectivities for equimolar binary gases of C₂H₂/CH₄, C₂H₆/CH₄, C₃H₆/CH₄, C₄H₁₀/CH₄, C₂H₂/CH₃, C₂H₆/CH₃, C₃H₆/CH₃, C₄H₁₀/CH₃, C₂H₂/C₄H₁₀, and C₂H₆/C₄H₁₀ have been calculated for MFM-202a at ambient conditions (i.e., 293 K and up to 1 bar). The other method used in this work, NI, is adopted as a means to simulate the uptake of binary gases. The application of an NI method to the prediction of isotherm or selectivity data precludes the uncertainty originating from the use of a certain type of adsorption model (e.g., the Langmuir model). The predicted isotherm was obtained by using the numerical trapezoidal integration of the appropriate graph for each pure gas adsorption isotherm. The limits for the calculation of the spreading pressures are set by the limits for the pure component experimental isotherms and the gas phase concentrations in the mixture. In this paper, IAST calculations within the range covered by the experimental isotherms are given as solid lines, whereas extrapolations beyond this range using equations to describe the isotherm with the lowest spreading pressure outside the range of the
experimental isotherm data are shown by dashed lines in all figures. However, it is worth mentioning that the IAST method becomes less accurate when a) the host material surfaces contain strong binding sites and/or b) the two gases show significantly different sorption capacities.

The errors of predicted selectivity values based upon DSLF-IAST and NI-IAST methods are calculated by the equation:

\[ y = \left( \frac{x_1 - x_2}{x_2} \right) \times 100\% \]  

where \( y \) is the error, and \( x_1 \) and \( x_2 \) are the uptake amounts for the experimental measurement and IAST prediction (mmol g\(^{-1}\)), respectively, at specific pressure and temperature.

RESULTS AND DISCUSSION

Crystal Structure. MFM-202 was synthesized from \( S',S''\)-bis(4-carboxyphenyl)-[1,1':3',1''-quaterphenyl]-4,4''-di-carboxylic acid (H\(_4\)L, Figure 1a) and In(NO\(_3\))\(_3\) using the reported method.\(^{24}\) The material has a 4,4-diamondoid framework structure with each ligand coordinating to four In(III) centers through the deprotonated carboxylates and vice versa to give an interpenetrated open structure (Figure 1b). The desolvated sample MFM-202a shows a different (more porous) structure due to the phase change (pore rearrangement) on removal of free solvent molecules from the pore. Desolvated MFM-202a has a pore size of \( 9 \times 9 \) Å, a BET surface area of 2220 m\(^2\) g\(^{-1}\), and a large pore void comprising \( \sim 70\% \) of the cell volume as estimated by PLATON/SOLV.\(^{27}\)

Adsorption Properties. The uptake of CH\(_4\) in MFM-202a at 195 K and 1 bar is 6.21 mmol g\(^{-1}\) (Figure 2), corresponding to a storage density of 104.5 kg m\(^{-3}\) (Figure 2), reaching 25% of the density of liquid methane at its boiling point (422.4 kg m\(^{-3}\) at 111.7 K). The uptake reaches saturation at 195 K and 16 bar (13.1 mmol g\(^{-1}\), Figure S1). At higher temperature and 20 bar, CH\(_4\) adsorption in MFM-202a shows moderate uptake (6.7–}
4.7 mmol g$^{-1}$ from 273 to 303 K) compared with other MOFs with similar pore volume. For example, MOF-5 exhibits a CH$_4$ storage capacity of ca. 6.9 mmol g$^{-1}$, and HKUST-1 shows ca. 9.4 mmol g$^{-1}$ at 298 K 20 bar. The moderate uptake of methane in MFM-202a at ambient conditions is consistent with the pore size and lack of open metal sites.

To determine the maximum uptake of C$_2$ and C$_3$ hydrocarbons and evaluate the potential of hydrocarbon storage in MFM-202a, we carried out isotherm measurements at low temperature. Adsorption of C$_2$H$_2$, C$_2$H$_4$, and C$_2$H$_6$ in MFM-202a shows exceptionally high uptakes of 18.3, 14.8, and 11.9 mmol g$^{-1}$, respectively at 195 K and 1 bar, corresponding to 500.0 kg m$^{-3}$, (the density of adsorbed C$_2$H$_2$ is 69% of the solid acetylene density at 192 K, 729 kg m$^{-3}$), 435.6 kg m$^{-3}$ (the density of adsorbed C$_2$H$_4$ is 77% of liquid ethane density at 169 K, 568 kg m$^{-3}$), and 375.5 kg m$^{-3}$ (the density of adsorbed C$_2$H$_6$ is 69% of liquid ethane density at 185 K, 544 kg m$^{-3}$).

Interestingly, the unsaturated hydrocarbons, C$_2$H$_2$ and C$_2$H$_6$, both exhibit stepwise adsorption and hysteretic desorption isotherms, whereas the saturated C$_3$H$_8$ retains the highly reversible type-I isotherm. C$_2$H$_2$ adsorption shows a step at 27 mbar with an initial uptake of 5.3 mmol g$^{-1}$; an additional 11.4 mmol g$^{-1}$ adsorption of C$_2$H$_2$ was gained at 450 mbar where it reaches saturation. The desorption shows unprecedented hysteretic release of adsorbed C$_2$H$_2$ molecules with 75% adsorbed molecules retained at 100 mbar, 37% retained at 10 mbar, and 24% retained at 2 mbar, indicating a strong interaction between adsorbed C$_2$H$_2$ molecules and the host at 195 K. 100% of adsorbed C$_2$H$_2$ molecules were released upon applying vacuum to the sample. Similar observation has been observed for CO$_2$ uptakes at low temperature. Like CO$_2$, C$_2$H$_2$ has a significant quadrupole moment, which may induce specific host–guest interactions together with other soft binding interactions resulting in the stepwise adsorption and the desorption hysteresis. Such broad hysteretic sorption behavior is rarely observed for C$_2$H$_2$ adsorption in the desorption hysteresis. Such broad hysteretic sorption binding interactions resulting in the stepwise adsorption and hysteretic release of adsorbed C$_2$H$_4$ molecules with 13% retained at 2 mbar, indicating the interaction between adsorbed C$_2$H$_4$ molecules and the host is weaker than that of C$_2$H$_2$. This represents a very rare example of marked stepwise and broadly hysteretic adsorption of ethene in a porous MOF material. In comparison, C$_2$H$_6$ shows fully reversible type-I adsorption without steps. Given the similar molecular structures and volatilities of these three C$_2$ hydrocarbons (Table 1), this result indicates that the π electrons in C$_2$H$_2$ and C$_2$H$_4$ induce stronger interactions with the MOF host than C$_2$H$_6$ leading to the presence of adsorption steps and hysteresis. C$_2$H$_2$ has more π electron density than C$_2$H$_4$ resulting in a more significant step and broader hysteresis loop in the isotherm data.

Similarly, the unsaturated hydrocarbon propene, C$_3$H$_6$, also shows a narrow adsorption step with hysteretic desorption process (12.1 mmol g$^{-1}$ at 201 K and 200 mbar, Figure 2), while propane, C$_3$H$_8$, exhibits fully reversible uptakes (9.0 mmol g$^{-1}$ at 195 K and 125 mbar). This result is consistent with the different behaviors of saturated and unsaturated C$_2$ hydrocarbon adsorption in MFM-202a, representing the first example of π electron-dependent hysteretic gas adsorption in MOFs. At more ambient temperatures (273–303 K), both C$_3$H$_4$ and C$_3$H$_6$ isotherms show reversible type-I profile with very sharp uptakes at low pressure (Figure 4a), indicating the presence of strong affinity between the MOF host and C$_3$ hydrocarbons. At 293 K and 1 bar, adsorption capacity of C$_3$H$_6$ and C$_3$H$_8$ in MFM-202a are measured as 7.18 and 6.76 mmol g$^{-1}$, respectively, comparable to the best-behaving MOFs reported to date.

<table>
<thead>
<tr>
<th>gas</th>
<th>kinetic diameter (Å)</th>
<th>critical temp (°C)</th>
<th>dipole moment (x 10$^{-20}$ C m)</th>
<th>quadrupole moment (x 10$^{-20}$ C$^2$ m$^2$)</th>
<th>polarizability (x 10$^{-20}$ cm)</th>
<th>molecular radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>3.758</td>
<td>~82.60</td>
<td>0</td>
<td>0</td>
<td>25.93</td>
<td>2.276</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>3.3</td>
<td>35.75</td>
<td>0</td>
<td>5.00</td>
<td>42.52</td>
<td>33.3–39.3</td>
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<tr>
<td>C$_2$H$_4$</td>
<td>4.163</td>
<td>9.2</td>
<td>0</td>
<td>2.17</td>
<td>4.43–44.7</td>
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<td>32.17</td>
<td>0</td>
<td>62.6</td>
<td>62.6</td>
<td>2.946</td>
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<tr>
<td>C$_3$H$_6$</td>
<td>4.678</td>
<td>91.06</td>
<td>1.22</td>
<td>63.7</td>
<td>63.9–63.7</td>
<td>2.276</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>4.3–5.118</td>
<td>96.7</td>
<td>0.28</td>
<td>39.3</td>
<td>39.5</td>
<td>2.276</td>
</tr>
</tbody>
</table>

Table 1. Summary of Physical Parameters of Light Hydrocarbons$^{15,33}$

The PXRD patterns of C$_3$H$_6$ and C$_3$H$_8$ in MFM-202a are measured as 7.18 and 6.76 mmol g$^{-1}$, respectively, comparable to the best-behaving MOFs reported to date.

Investigation of the Mechanism of Hysteretic Adsorption. To investigate the binding interaction between adsorbed C$_2$ hydrocarbons and the framework host and the possible framework phase transition, we carried out in situ synchrotron X-ray powder diffraction of MFM-202a on separate loadings of C$_2$H$_2$, C$_2$H$_4$, and C$_2$H$_6$ at 195 K. The PXRD of MFM-202a shows shifts in peaks slightly to a higher value of 2θ as the pressure of C$_2$H$_4$ increases from 0 to 1000 mbar indicating a contraction of the unit cell parameters (Figures 2, S7 and S10) with a slight broadening of peak widths, possibly due to the breakdown of MOF particles and presence of guest–host disorder upon C$_2$H$_2$ adsorption. In contrast, the in situ PXRD patterns of C$_2$H$_2$ and C$_2$H$_4$-loaded MFM-202a show small shifts to lower values 2θ as the pressure increases. The unit cell volumes consequently increase on loading of C$_2$H$_4$ and C$_2$H$_6$ (Figures S11 and S12). Upon desorption of C$_2$H$_2$, C$_2$H$_4$, and C$_2$H$_6$, the PXRD patterns of MFM-202a return to that of the desolvated bare MOF confirming the overall stability of the framework structure. This study confirms the absence of framework phase change albeit with the presence of adsorption steps and hysteretic desorption for C$_2$H$_2$ and C$_2$H$_4$. This observation is similar to that of CO$_2$-loaded MFM-202a but contrasts to that observed...
for SO₂-loaded MFM-202a.\textsuperscript{24,25} Given the large pore size of 9 × 9 Å, no noticeable confinement effect of adsorbed gas molecules in the pore of MFM-202a was seen upon desorption. Therefore, the observed adsorption step and hysteresis are most likely due to the pore filling effect in this defect MOF material.\textsuperscript{32–37} Owing to the complexity of the crystal structure

Table 2. Comparison of Hydrocarbons Uptakes and Isosteric Enthalpies of Adsorption ($Q_s$) for a Series of MOFs

<table>
<thead>
<tr>
<th>compounds</th>
<th>CH$_4$</th>
<th>C$_2$H$_2$</th>
<th>C$_2$H$_4$</th>
<th>C$_2$H$_6$</th>
<th>C$_3$H$_6$</th>
<th>C$_3$H$_8$</th>
<th>$Q_s$ (kJ mol$^{-1}$) at low coverage</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFM-202a$^a$</td>
<td>0.45</td>
<td>3.44</td>
<td>2.90</td>
<td>4.21</td>
<td>7.18</td>
<td>6.76</td>
<td>14 23 18 18 33 27</td>
<td>this work</td>
</tr>
<tr>
<td>Fe$_2$(dobdc)$^b$</td>
<td>0.77</td>
<td>6.89</td>
<td>6.02</td>
<td>5.00</td>
<td>6.66</td>
<td>5.67</td>
<td>20 47 45 25 44 33</td>
<td>3</td>
</tr>
<tr>
<td>Cu-TDPAT$^c$</td>
<td>1.26</td>
<td>7.93</td>
<td>7.34</td>
<td>6.89</td>
<td></td>
<td></td>
<td>21 43 50 30</td>
<td>13</td>
</tr>
<tr>
<td>PAF-40$^d$</td>
<td>0.54</td>
<td>1.80</td>
<td>1.95</td>
<td>2.39</td>
<td></td>
<td></td>
<td>18 25 36</td>
<td>42</td>
</tr>
<tr>
<td>PAF-40-Fe$^d$</td>
<td>0.62</td>
<td>2.31</td>
<td>1.85</td>
<td>2.58</td>
<td></td>
<td></td>
<td>23 30 48</td>
<td>42</td>
</tr>
<tr>
<td>PAF-40-Mn$^d$</td>
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<td>2.18</td>
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<td></td>
<td></td>
<td>16 25 35</td>
<td>42</td>
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<tr>
<td>MFM-300$^d$</td>
<td>0.29</td>
<td>6.34</td>
<td>4.28</td>
<td>0.85</td>
<td></td>
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<td>n.a. 32 16 11</td>
<td>16</td>
</tr>
<tr>
<td>UTXA-35a$^e$</td>
<td>0.43</td>
<td>2.90</td>
<td>2.16</td>
<td>2.43</td>
<td>3.29</td>
<td>2.97</td>
<td>~18 ~29 ~28 ~30 ~33 ~42</td>
<td>14</td>
</tr>
<tr>
<td>M’MOF-3a$^f$</td>
<td>~1.9</td>
<td>~0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>27 27</td>
<td>16, 30</td>
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<tr>
<td>PAF-1-SO$_3$Ag$^g$</td>
<td>4.06</td>
<td>2.23</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>106 27</td>
<td>16, 30</td>
</tr>
</tbody>
</table>

$^a$Data was measured and processed at 293 K and 1 bar. $^b$Data was measured and processed at 318 K and 1 bar. $^c$Data was measured and processed at 298 K and 1 bar. $^d$Data was measured and processed at 298 K and 1.1 bar. $^e$Data was measured and processed at 296 K and 1 atm. $^f$Data was measured and processed at 295 K and 1 bar. $^g$Data was measured and processed at 296 K and 1 bar.

Table 3. Comparison of Uptake Ratios and Absolute Differences for a Series of MOFs

<table>
<thead>
<tr>
<th>compounds</th>
<th>C$_2$H$_2$ /CH$_4$</th>
<th>C$_2$H$_4$ /CH$_4$</th>
<th>C$_2$H$_6$ /CH$_4$</th>
<th>C$_3$H$_6$ /CH$_4$</th>
<th>C$_3$H$_8$ /CH$_4$</th>
<th>C$_2$H$_2$ - CH$_4$</th>
<th>C$_2$H$_4$ - CH$_4$</th>
<th>C$_2$H$_6$ - CH$_4$</th>
<th>C$_3$H$_6$ - CH$_4$</th>
<th>C$_3$H$_8$ - CH$_4$</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFM-202a$^a$</td>
<td>7.64</td>
<td>6.44</td>
<td>9.36</td>
<td>15.96</td>
<td>15.02</td>
<td>2.99</td>
<td>2.45</td>
<td>3.76</td>
<td>6.73</td>
<td>6.31</td>
<td>this work</td>
</tr>
<tr>
<td>Fe$_2$(dobdc)$^b$</td>
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<td>7.82</td>
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<td>8.65</td>
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<td>3.61</td>
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<td>3.73</td>
<td>2.98</td>
<td>4.16</td>
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<tr>
<td>PAF-40-Fe$^d$</td>
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<td>4.18</td>
<td>4.18</td>
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<td>3.73</td>
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<td>UTXA-35a$^e$</td>
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</table>

$^a$Data was measured and processed at 293 K and 1 bar. $^b$Data was measured and processed at 318 K and 1 bar. $^c$Data was measured and processed at 298 K and 1 bar. $^d$Data was measured and processed at 298 K and 1.1 bar. $^e$Data was measured and processed at 296 K and 1 atm.

Figure 3. Variation of the thermodynamic parameters $Q_s$ and $\Delta S$ with error bars for MFM-202a as a function of hydrocarbon uptake.
of MFM-202a, satisfactory Rietveld refinements to extract the location of adsorbed gas molecules could not be obtained. Analysis of the lattice parameters via Le Bail refinements are shown in the SI.

**Room Temperature Adsorption.** The adsorption of C₂ hydrocarbons in MFM-202a shows near-linear reversible type-I isotherms at 273−303 K and 1 bar (Figures S2−S4). C₂H₆ exhibits the highest uptake capacity of 6.69 mmol g⁻¹ at 273 K and 1 bar with the observed capacity following the order C₂H₆ > C₂H₂ > C₂H₄. However, this sequence for uptake capacity differs at 195 K in the order C₂H₂ > C₂H₄ > C₂H₆. This result reveals that at low temperature the interaction between π electrons and the host plays an important role in gas adsorption in addition to van der Waals force. Furthermore, MFM-202a shows an impressive C₂H₆ uptake capacity at 293 K and 10 bar of 9.13 mmol g⁻¹ (saturation uptake). The ethane uptake is comparable to the best-behaving MOFs reported to date (Tables 2 and 3), such as UTSA-35a (2.43 mmol g⁻¹ at 296 K and 1 atm near saturated uptake), Cu-TDPAT (6.89 mmol g⁻¹ at 298 K and 1 bar near saturated uptake), and Fe₂(dobdc) (5.00 mmol g⁻¹ at 318 K and 1 bar near saturated uptake). Interestingly, the C₃ hydrocarbon uptake exhibits an intersection at 293 K between 0.25 and 0.3 bar, at which the adsorption capacity of C₃H₆ overtakes that of C₃H₈. Compared with CH₄, C₂H₂, C₂H₄, C₃H₆, and C₃H₈, the steep isotherm of C₃H₈ below 0.25 bar indicates that C₃H₈ has the highest affinity to the framework, consistent with the polarizability of this molecule (Table 1). Under the same conditions, MFM-202a shows relatively low uptake of CH₄ compared with C₂ and C₃ hydrocarbons, indicating the potential of this system for the purification of natural gas.

**Analysis of Thermodynamics.** The isosteric enthalpies of adsorption (Qst) and entropy (ΔS) were calculated using the Clausius−Clapeyron equation as a function of gas loadings from the singe adsorption isotherms at 273−303 K (Figure 3). The Clausius−Clapeyron plots showed good linearity even when structural dynamics and specific interactions were apparent. The values of Qst for CH₄ uptake increase steadily from 14 to 19 kJ mol⁻¹ upon increasing CH₄ loading (Table 2). Similar observations were also found for uptake of C₂H₄ (18−20 kJ mol⁻¹) and C₂H₆ (18−21 kJ mol⁻¹). In comparison, the values of Qst for C₂H₂ (22 to 23 kJ mol⁻¹) were almost unchanged with C₂H₂ uptake up to 3 mmol g⁻¹. C₃ hydrocarbons have higher enthalpies of adsorption (C₃H₆, 27−42 kJ mol⁻¹; C₃H₈, 27−39 kJ mol⁻¹) than CH₄ and C₂ hydrocarbons, and both exhibit a gradual increase with increasing gas uptakes. At low surface coverage, where the adsorbate−adsorbent interaction plays a major role, the sequence of Qst values for saturated hydrocarbon is C₃H₈ > C₂H₆ > CH₄. This observation is consistent with the increased polarizability of gas molecules (Table 1) that contributes to the molecular interaction with the framework. For the unsaturated hydrocarbons, the sequence of the interaction strength is C₃H₆ > C₂H₂ > C₂H₄. It is noticeable that the uptake of C₃H₆ overtakes C₂H₄ at ~5.7 mmol g⁻¹, where the Qst value of the former shows a dramatic increase but the latter reaches a near plateau region. The entropies for the hydrocarbons all follow a trend of gradual decrease corresponding to the continuous ordering of the system except...
that the C₃H₈ shows a fluctuation below the uptake amount of 2 mmol g⁻¹ and thereafter decreases gradually. Overall, the enthalpies of adsorption for MFM-202a are generally lower than the reported MOFs with open metal sites [e.g., ∼30 kJ mol⁻¹ for C₂ hydrocarbon adsorption in UTSA-35a,¹³ Cu-TDPAT,¹³ and Fe₂(dobdc)³,] indicating a possible reduced energy consumption for the regeneration of MFM-202a as solid absorbents.

Selectivity Studies. Both DSLF- and NI-based IAST methods used here can predict the equimolar binary gas adsorption isotherm and the contribution of each gas in the total uptake for the mixture adsorption at a given pressure as shown in Figure 4. By comparison of predicted and experimental adsorption isotherm data for gas mixtures, we can validate the calculated IAST selectivity. The comparison of two IAST approaches gives insight into the errors and uncertainties generated by the adoption of an isotherm model to describe the experimental data. The calculated C₂H₆/C₂H₄ binary gases uptake by the NI-IAST prediction has encountered lower divergence than that by the DSLF-IAST method within the experimental spreading pressure range, which is probably due to the inherent drawback of DSLF-IAST based on near-linear uptake isotherms as shown in Figure 4b. In contrast, DSLF-IAST and NI-IAST are consistent with each other in the calculation of C₂H₆/C₂H₄ and C₃H₆/C₃H₈ mixed gases uptake, and both show good agreement with the experimental data. Apart from the binary gases uptake prediction, we have further calculated the contribution of each gas to the total uptakes as shown in Figures 4 and 5. The gas with high uptake shows high contribution to the total uptake, indicating the retention of the competitive interaction with the framework even in the mixed gas system.

Figure 5. Comparison between experimental equimolar binary hydrocarbons uptakes and IAST prediction from the pure components. Solid symbols: experimental gas uptake; dashed cyan lines: extrapolation of the DSLF-IAST predicted equimolar binary gases uptake beyond the isotherm experimental range; dashed gray/orange lines: extrapolations of the calculated contribution of pure gas in the predicted binary gases uptakes beyond the isotherm experimental range.
predictions for gas mixture to higher uptakes subject to larger uncertainty. In this study, the NI-IAST method cannot be applied to calculate the uptake for C2 or C3 hydrocarbons in equimolar mixtures with CH4 over a considerable pressure range where the uptakes of C2 and C3 hydrocarbons are much higher (approximately 6–16 times) than that of CH4. Thus, we adopted the DSLF-IAST method for prediction of C2 and C3 hydrocarbons over CH4 as shown in Figure 5. In the DSLF-IAST calculations for C2/CH4 mixtures, the results for C2 gases over CH4 are consistent with the experimental measurements at 293 K, with extrapolation errors of −1.7% for C2H4/CH4, 3.3% for C2H6, and 2.5% for C2H2/CH4 at 1 bar. The error increases with pressure; for example, the DSLF-IAST result for C2H6/CH4 overestimates the experimental data by 9.4% at 10 bar and 293 K. For adsorption of C3/CH4 mixtures, the DSLF-IAST predictions also fit very well with the experimental data within the experimental spreading pressure range, with extrapolation errors of 2.1% for C3H6/CH4 and −0.4% for C3H8/CH4 at 293 K and 1 bar. This again validates that DSLF-IAST is reliable within the experimental spreading pressure range, but it shows noticeable errors when significant extrapolation of isotherm data is applied. It is worth noting that although IAST has been widely used to estimate the selectivity of competitive adsorption in MOFs, the comprehensive analysis of the associated errors is reported here for the first time.

The selectivity data for MFM-202a were calculated by the DSLF-IAST method based upon the single component isotherms at 293 K. The C2H2/CH4 selectivity is estimated as 105 at 0.01 bar and gradually drops to 87 at 1 bar (Figure 6). The C3H8/CH4 selectivity lies in the range of 63 and 75 at 0.01 bar and 1 bar, respectively. This result indicates that MFM-202a has stronger binding to the saturated hydrocarbons at ambient conditions and may have potential for the selective removal of saturated hydrocarbons (propane, ethane).

Direct comparison of the uptake ratios and difference between two hydrocarbon adsorption isotherms also gives insights to the selectivity. Interestingly, the ratios of the adsorption uptakes for C2H6/CH4 (9.36), C3H8/CH4 (15.96), and C3H6/CH4 (15.02) at 1 bar and 293 K are to the best of our knowledge among the highest values in comparison with other MOFs (Table 3). For example, the PAF-40 series (PAF-40, PAF-40-Fe, and PAF-40-Mn) shows ca. three to five times higher uptake for C3H8, C2H6, and C2H4 over CH4 at 273–298 K and 1 bar. This analysis indicates the potential application of MFM-202a in the purification of natural gas by the selective removal of higher saturated hydrocarbons.

**CONCLUSIONS**

The adsorption of light hydrocarbons in a flexible porous MOF material, MFM-202a, has been comprehensively investigated at various temperatures. MFM-202a shows reversible isotherms for hydrocarbon adsorption at 273–303 K. However, the unsaturated hydrocarbons, acetylene, ethene, and propene, exhibit marked stepwise adsorption isotherms at low temperatures due to the pore filling effect in the flexible framework material with structural defects, as confirmed by in situ synchrotron X-ray powder diffraction experiments. MFM-202a shows very high acetylene uptake of 18.3 mmol g⁻¹ at 195 K and 1 bar. A comprehensive analysis of the selectivity using both the NI- and DSLF-based IAST methods and measurement of mixed gas adsorption isotherms indicates that MFM-202a has great potential for purification of CH4 (natural gas). The extrapolation errors for the widely used DSLF-IAST method for the estimation of selectivity data from single component uptake isotherms and the validity of the selectivity via IAST calculations have been quantified and discussed.

**ASSOCIATED CONTENT**

▲ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b00443.

Substrate sorption isotherms, in situ PXRD, unit cell parameters analyses, lists of DSLF parameters, dual-site Langmuir fitting model pure hydrocarbon sorption isotherms and comparison of substrate selectivities (PDF)
(20) Tan, Y.; He, Y.; Zhang, J. High and selective sorption of $C_2$ hydrocarbons in heterometal-organic frameworks built from tetraedral units. RSC Adv. 2015, 5, 7794–7797.


