AN EXPERIMENTAL STUDY OF H₂ AND CO₂ ADSORPTION BEHAVIOR OF C-MOF-5 AND T-MOF-5: A COMPLEMENTARY STUDY

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Abstract - In this paper the cubic and tetragonal structure of MOF-5 were successfully synthesized and characterized by TGA and SEM analysis. Equilibrium adsorption isotherms of C-MOF-5 and T-MOF-5 for H₂ and CO₂ were measured up to 25 bar at 298 K using a volumetric method. The C-MOF-5 adsorbent synthesized in this study had a 0.107 and 79.9 wt% adsorption capacities at 298 K and 25 bar for H₂ and CO₂, respectively. T-MOF-5 had a H₂ adsorption capacity of 0.122 wt% and CO₂ adsorption capacity of 67.6 wt% at 298 K and 25 bar. This behavior was attributed to more ZnO units in the T-MOF-5 structure. The difference between H₂ and CO₂ adsorption capacity for the cubic and tetragonal structure of MOF-5, suggests that C-MOF-5 and T-MOF-5 are potential adsorbents for the separation of CO₂ and H₂ from gas mixtures, respectively. Langmuir, Freundlich and Sips isotherm models were used to correlate the adsorption isotherms. The results showed that, at 298 K, the fit of the Sips isotherm to the experimental data was better than Langmuir and Freundlich isotherms. According to TGA results, the thermal decomposition of C-MOF-5 requires a higher temperature than T-MOF-5.

Keywords: Adsorption; Hydrogen; Carbon dioxide; MOF-5; ZnO.

INTRODUCTION

In the last decades, there has been an increasing interest in developing gas storage systems for different applications such as H₂ storage or CO₂ capture (Marco-Lozar et al., 2012; Saha and Deng, 2009; Saha et al., 2009; Lou et al., 2014).

H₂ is important as a new source of energy for automotive applications. The main challenge in developing this technology is H₂ storage. The development of high H₂ storage capacity materials and safe transportation methods are recognized as requirements for the realization of a H₂ economy. Also, CO₂ emissions resulting from the burning of fossil fuels in ground transportation (cars, public/goods transport vehicles) are among the pressing global environmental problems (Lee et al., 2006).

Metal–organic frameworks (MOFs), also known as coordination polymers, are ideal crystalline substances for catalysis and gas separation and storage (Kurmoo et al., 2005; Zheng et al., 2006). In addition MOFs generally have high internal surface area and, due to the presence of organic linkers and metal ligands, it is possible to tune their pore size and volume (Mishra et al., 2012).

One of the most important MOFs is the Zn₄O₁₃C₂₄H₁₂ framework called MOF-5, which was first synthesized in 1999 (Li et al., 1999). This framework has potential applications for H₂ storage, CO₂ capture and catalysts (Eddaoudi et al., 2002). MOF-5 consists of Zn₄O as metal clusters connected by 1,4-benzenedicarboxylate (BDC) as a linkers to form a porous Zn₄O(BDC)₃ framework (Li et al., 1999). It has been recognized that MOF-5 occupies either
cubic (C-MOF-5) or tetragonal (T-MOF-5) structures (Li et al., 1999; Hafizovic et al., 2007; Kaye et al., 2007; Huang et al., 2003). Zhang and Hu (2011) showed that the composition of cubic and tetragonal MOF-5 calculated with the formulas of \( \text{Zn}_4.28\text{O}_{12.8}\text{C}_{24}\text{H}_{11.3} \) and \( \text{Zn}_4\text{O}_{13.2}\text{C}_{28}\text{H}_{12.6}(\text{ZnO})_{1.59}(\text{H}_2\text{O})_{1.74} \) respectively. They indicated that the formula of the C-MOF-5 sample was consistent with the stoichiometric formula of novel MOF-5 (\( \text{Zn}_4\text{O}_{13}\text{C}_{24}\text{H}_{12} \)) and the formula of the T-MOF-5 sample was very different from the stoichiometrical formula of novel MOF-5, owing to the presence of ZnO and \( \text{H}_2\text{O} \).

Arjmandi and Pakizeh (2013) showed that T-MOF-5 had lower surface area, lower porosity, smaller and more uniform pore size, and more ZnO units compared with C-MOF-5. Sarmiento-Perez et al. (2012) used the Grand Canonical Monte Carlo (GCMC) simulation of CO\(_2\) adsorption on MOF-5 and found the surprising role of the BDC organic ligand in this process. They reported that the organic ligands (BDC) have an important role in CO\(_2\) adsorption on MOF-5.

Skoulidas and Sholl (2005) applied the equilibrium molecular dynamics (EMD) and GCMC to calculate the diffusion and adsorption of CH\(_4\), CO\(_2\), N\(_2\), and H\(_2\) in C-MOF-5. They reported that at low pressure (1-2 bar), a significant increase in CH\(_4\), CO\(_2\), N\(_2\), and H\(_2\) adsorption was not observed and at high pressure (6-7 bar), only CO\(_2\) adsorption was increased.

Spencer et al. (2005) used neutron powder diffraction to determine the H\(_2\) adsorption sites in the MOF-5 structure. They reported that the ZnO cluster was primarily responsible for H\(_2\) adsorption while the organic ligand (BDC) played only a secondary role.

Arjmandi and Pakizeh (2014) synthesized and characterized (by XRD, FTIR, \( \text{N}_2 \) adsorption technique at 77 K and particle size analysis) C-MOF-5 and incorporated it in polyetherimide (PEI) as filler to make C-MOF-5/PEI MMMs and study the effect of C-MOF-5 on CH\(_4\), CO\(_2\), N\(_2\), and H\(_2\) gas permeation through the MMMs. The results showed that C-MOF-5 nanocrystals have the potential (as filler in MMMs) to enhance H\(_2\) separation from CO\(_2\), CH\(_4\), and N\(_2\).

Table 1 summarizes the pore textural property of C-MOF-5 and T-MOF-5 according to our previous studies.

In the present work, to estimate the amount of ZnO in T-MOF-5 compared to C-MOF-5, thermogravimetric analysis (TGA) was performed. To study the effect of more ZnO in the structure of T-MOF-5, the excess adsorption measurements (by the volumetric method) of H\(_2\) and CO\(_2\) on C-MOF-5 and T-MOF-5 were studied at 298 K up to 25 bar. The two samples were characterized for their topology by scanning electron microscopy (SEM) imaging.

**EXPERIMENTAL**

**Synthesis of Adsorbents**

The cubic and tetragonal forms of MOF-5 were synthesized based on previously reported procedures (Kaye et al., 2007; Huang et al., 2003). All chemicals used in this study were obtained from Sigma-Aldrich.

For the synthesis of C-MOF-5, 0.45 g of \( \text{Zn(NO}_3\text{)}_2·6\text{H}_2\text{O} \) (>98%) and 0.083 g of \( \text{H}_2\text{BDC} \) (>99%) were dissolved in 100 mL of DMF (99.8%) and 1 mL of \( \text{H}_2\text{O} \). After heating the solution at 70 °C under vigorous stirring, it was placed in an oven at 100 °C for 15 h. The reaction flask was then cooled down to 25 °C. After removing the solvent, the white powder was washed six times with 60 mL of anhydrous DMF and six times with 60 mL of anhydrous CH\(_2\)Cl\(_2\) (>99.8%) (each time 10 h), respectively. Finally, the C-MOF-5 crystals were dried at 125 °C for 24 h under vacuum.

For the synthesis of T-MOF-5, 1.19 g of \( \text{Zn(NO}_3\text{)}_2·6\text{H}_2\text{O} \) (>98%) and 0.34 g of \( \text{H}_2\text{BDC} \) (>99%) were dissolved in 40 mL of DMF (99.8%) at room temperature. After adding three drops of aqueous \( \text{H}_2\text{O}_2 \) solution, 2.3 mL of triethylamine (TEA, >99.5%) was added dropwise to the reaction flask under strong agitation at 70 °C for 2 h. After heating the solution at 70 °C under vigorous stirring, it was placed in an oven at 100 °C for 15 h. The reaction flask was then cooled down to 25 °C. After removing the solvent, the white powder was washed six times with 60 mL of anhydrous DMF and six times with 60 mL of anhydrous CH\(_2\)Cl\(_2\) (>99.8%) (each time 10 h), respectively. Finally, the C-MOF-5 crystals were dried at 125 °C for 24 h under vacuum. A schematic representation of the synthesis of C-MOF-5 is summarized in Figure 1.

For the synthesis of T-MOF-5, 1.19 g of \( \text{Zn(NO}_3\text{)}_2·6\text{H}_2\text{O} \) (>98%) and 0.34 g of \( \text{H}_2\text{BDC} \) (>99%) were dissolved in 40 mL of DMF (99.8%) at room temperature. After adding three drops of aqueous \( \text{H}_2\text{O}_2 \) solution, 2.3 mL of triethylamine (TEA, >99.5%) was added dropwise to the reaction flask under strong agitation at 70 °C for 2 h. After placing the flask in an oven at 100 °C for 15 h, it was removed from the oven and cooled down to 25 °C. The white solid obtained was filtered and washed with DMF three times. Finally, the T-MOF-5 was dried at 125 °C for 24 h under vacuum. A schematic representation of the synthesis of T-MOF-5 is summarized in Figure 2.
Table 1: Pore textural properties of C-MOF-5 and T-MOF-5 samples.

<table>
<thead>
<tr>
<th>Species</th>
<th>BET specific surface area (m²/g)</th>
<th>Pore diameter (Å)</th>
<th>Pore volume (cm³/g)</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>C-MOF-5</td>
<td>2387</td>
<td>8.67</td>
<td>0.99</td>
<td>Arjmandi and Pakizhe (2014)</td>
</tr>
<tr>
<td>T-MOF-5</td>
<td>1280</td>
<td>6.30</td>
<td>0.58</td>
<td>Arjmandi et al. (2014)</td>
</tr>
</tbody>
</table>

Figure 1: Synthesis of C-MOF-5; (1) Zn(NO₃)₂·6H₂O, (2) H₂BDC, (3) DMF + H₂O, (4) Magnetic stir bar, (5) Magnetic hotplate, (6) Oven, (7) Reaction flask at 25 °C (with powder + solution), (8) Petri dish, (9) DMF, (10) CH₂CL₂, (11) Vacuum oven, (12) C-MOF-5 powder in a Petri dish with a porous lid.


Characterization of Adsorbents

As mentioned above, the XRD, FTIR, N₂ adsorption, surface area measurement and pore textural properties of MOF-5 samples/forms were presented in our previous studies (Arjmandi and Pakizhe, 2014; Arjmandi et al., 2014). In this article, thermogravimetric analysis (TGA-50 Shimadzu) in a N₂ atmosphere was used to evaluate the amount of ZnO units in T-MOF-5. Scanning electron microscopy (SEM) images of C-MOF-5 and T-MOF-5 were taken using a Cam Scan SEM model KYKYEM3200 microscope.

Gas Sorption Measurements

The H₂ and CO₂ adsorption capacities of C-MOF-5 and T-MOF-5 were determined in the apparatus based on the volumetric method shown in Figure 3.

Figure 3: Schematic diagram of the volumetric adsorption apparatus: (1) H₂ gas cylinder, (2) CO₂ gas cylinder, (3) and (4) needle valve, (5) regulator, (6)-(8) needle valve, (9) gas charge cell, (10) adsorption cell, (11) needle valve, (12) regulator, (13) needle valve, (14) vacuum pump, (15) pressure transducer, (16) pressure digital indicator, (17) computer.
The apparatus consisted of two high-pressure stainless steel vessels including the gas charge and adsorption cells (built in-house). The gas charge vessels were connected to a regulator and needle valve (Swagelok, 6DB series) to control the pressure of the gas entering the gas charge cell. Before the sorption process, C-MOF-5 and T-MOF-5 were degassed at 100 °C for about 24 h and the system was evacuated by a vacuum pump (Welch, DuoSeal 1376). Two high precision pressure transducers (Danfoss, MBS 3000 – 2611 – 1 AB04) measured the changes in pressure of the gas and adsorption cell in H2 and CO2 adsorption experiments. The H2 and CO2 adsorption experiments were conducted at pressures ranging from 0 to 25 bar at ambient temperature.

According to the material balance, the total amount of gas initially available in the gas charge and sorption cells should be equal to the amount of gas in these cells at the steady state plus the amount of gas adsorbed, based on the following equation:

\[
\frac{P V}{ZRT} v_1 + \frac{P V}{ZRT} v_2 = \frac{P V}{ZRT} v_p + P V + N_{ads} \tag{1}
\]

where subscripts 1, 2, c and a denote the initial state, final equilibrium state, gas charge cell and adsorption cell, respectively. Also \( V, P, T, R \) and \( N_{ads} \) represent volume, pressure, temperature, the universal gas constant and amount of gas adsorbed by the adsorbent, respectively. As is evident from Eq. (1), compressibility factors (\( Z \)) are required for proper data analysis of the pure gases. The compressibility factors of H2 and CO2 were calculated from the Peng-Robinson (PR) equation of state.

RESULTS AND DISCUSSION

Physical Properties of MOF-5s

The results of thermogravimetric analysis (TGA) are shown in Figure 4 for both tetragonal and cubic MOF-5 nanocrystals. For T-MOF-5, a 15% weight loss occurred in the range of 30–300 °C and then a 43% weight loss, beginning at about 350 °C. For C-MOF-5, 1.5 and 51.5 wt% weight losses were also observed in the same temperature range of T-MOF-5 weight losses. According to Zhang’s experimental results (Zhang and Hu, 2011) it can be said that, for both samples, the first weight loss in TGA corresponds to desorption of water and the second one is associated with the decomposition of MOF-5 to release CO2 and benzene (Zhang and Hu, 2011). As reported by Zhang and Hu (2011) based on calculation from the chemical formula of novel MOF-5 (Zn4O13C24H12), the weight percent of ZnO units is around 42 wt%. The solid products from the decomposition of both MOF-5s consist of carbon and ZnO (Zhang and Hu, 2011). As shown in Figure 4, the final residual weights of T-MOF-5 and C-MOF-5 were 57 and 48.5 wt%, respectively (regardless of water). For the same amount of carbon in MOF-5s (Zhang and Hu, 2011), the decomposition products of T-MOF-5 contain 8.5 wt% more ZnO than those of C-MOF-5. In addition, C-MOF-5 is more stable than T-MOF-5 because the decomposition temperature of C-MOF-5 is higher than that of T-MOF-5.

Figure 5 shows the scanning electron microscopic images of C-MOF-5 and T-MOF-5 nanocrystals synthesized in this work. The range of particle size of both the C-MOF-5 and T-MOF-5 nanocrystals was 100-150 nm, with no defined morphology. Similar SEM pictures were obtained in literature (Huang et al., 2003; Perez et al., 2009), with aggregates similar in size (70–100 nm) to the nanocrystals synthesized in this study that showed no defined crystal morphology.

![Figure 4: Thermogravimetric curves of (a) C-MOF-5 and (b) T-MOF-5 samples.](image)

Adsorption Equilibrium

The adsorption isotherms of CO2 and H2 on both MOF-5s at 298 K and pressures in the range 0–25 bar are plotted in Figures 6 and 7, respectively.

The formula of the C-MOF-5 sample (Zn428O128C24H13) is consistent with the stoichiometric formula of novel MOF-5 (Zn4O13C24H12). The comparison of the results for CO2 and H2 adsorption on C-MOF-5 in this study with those for CO2 and H2 adsorption on novel MOF-5 in the literature (Marcolozar et al., 2012), indicates the accuracy of the experimental system shown in Figure 3.
According to Figure 6, the adsorption capacity of CO₂ on C-MOF-5 at 298 K and 25 bar is 79.9 wt%, which is about 18% higher than the adsorption capacity of CO₂ on T-MOF-5 at 298 K. In contrast, as shown in Figure 7, T-MOF-5 showed an adsorption capacity of 0.122 wt% for H₂, which is about 12.3% higher than the adsorption capacity of C-MOF-5 for H₂.

For physisorptive materials (such as MOFs) and some gases (such as CH₄), the adsorption capacity has a strong correlation with the surface area and pore volume. For these gases the structure and chemical composition of the adsorbent are not important for the adsorption capacity (Coates, 2000; Zhou, 2010; Anbia et al., 2012). In contrast, for H₂ and CO₂ the structure and chemical composition of the adsorbent are important to increase the adsorption capacity.

As noted in the previous sections, the T-MOF-5 nanocrystals have lower surface area, lower porosity and smaller and more uniform pore size than C-MOF-5 nanocrystals.

Also as mentioned earlier, T-MOF-5 contains less CO₂ and organic ligand molecule and more inorganic clusters (containing ZnO units) than C-MOF-5. The difference between the amount of ZnO units in the cubic and tetragonal structures of MOF-5 brings about the difference of H₂ and CO₂ adsorption capacities. Considering that the organic ligand and inorganic clusters in the MOF-5 structure are the major sites of adsorption of CO₂ and H₂, respectively, it can be expected that CO₂ adsorption on T-MOF-5 should be less than that on C-MOF-5. As well, H₂ adsorption on T-MOF-5 is more than that on C-MOF-5.

Accordingly, the higher CO₂ adsorption capacity of C-MOF-5 was attributed to the organic ligand and the higher H₂ adsorption capacity of T-MOF-5 was attributed to the inorganic clusters.

The adsorption selectivities for H₂ and CO₂ were calculated from their adsorption isotherms. The adsorption selectivity of a gas A over gas B was calculated by using Eq. (2) (Lee et al., 2009):

\[
\alpha_{A/B} = \frac{V_A}{V_B} \left|_{P,T} \right.
\]

where \( V_A \) and \( V_B \) are the volumes of gases A and B, respectively, adsorbed at any given pressure P and temperature T. The orders of adsorption selectivity for CO₂ and H₂ showed that CO₂/H₂ in T-MOF-5 (553.77) was lower than CO₂/H₂ in C-MOF-5 (746.73). This occurred because there were more adsorption sites for CO₂ (organic ligand) in C-MOF-5 than in T-MOF-5 and more H₂ adsorption sites (inorganic clusters) in T-MOF-5 than in C-MOF-5.

Results reported so far in the literature on CO₂ and H₂ adsorption are summarized in Table 2.

Figure 5: SEM images of (a) C-MOF-5 and (b) T-MOF-5 samples.

Figure 6: CO₂ adsorption capacity at 298 K and 25 bar of C-MOF-5 and T-MOF-5.

Figure 7: H₂ adsorption capacity at 298 K and 25 bar of C-MOF-5 and T-MOF-5.
Table 2: High-pressure CO$_2$ and H$_2$ excess adsorption data at 298 K for selected porous MOFs.

<table>
<thead>
<tr>
<th>MOFs</th>
<th>BET surface area (m$^2$/g)</th>
<th>Pressure (bar)</th>
<th>H$_2$ uptake (wt%)</th>
<th>H$_2$ uptake (mol/m$^3$)</th>
<th>CO$_2$ uptake (wt%)</th>
<th>CO$_2$ uptake (mol/m$^3$)</th>
<th>Ref.</th>
</tr>
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<td>MIL-53-Al$^a$</td>
<td>-</td>
<td>25</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>44.04</td>
<td>10122.52</td>
</tr>
<tr>
<td>MIL-53-Cr$^a$</td>
<td>-</td>
<td>25</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>44.04</td>
<td>10122.52</td>
</tr>
<tr>
<td>MIL-100$^b$</td>
<td>1900</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>79.27</td>
<td>12596.92</td>
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<tr>
<td>MIL-101$^b$</td>
<td>4230</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>176.16</td>
<td>17545.71</td>
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<td>MIL-47$^a$</td>
<td>-</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>484.84</td>
<td>11247.25</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>95.57</td>
<td>13046.81</td>
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<td>IRMOF-6</td>
<td>2804</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>87.20</td>
<td>12866.85</td>
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<td>MOF-177</td>
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<td>14396.48</td>
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<td>MIL-100</td>
<td>-</td>
<td>90</td>
<td>0.15</td>
<td>515.91</td>
<td>-</td>
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<td>80</td>
<td>0.43</td>
<td>912.76</td>
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<tr>
<td>PCN-10$^a$</td>
<td>1407</td>
<td>45</td>
<td>4.2</td>
<td>15973.17</td>
<td>-</td>
<td>-</td>
<td>Wang et al. (2008)</td>
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<tr>
<td>PCN-11$^a$</td>
<td>1931</td>
<td>45</td>
<td>5.04</td>
<td>18751.12</td>
<td>-</td>
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<tr>
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<td>-</td>
<td>50</td>
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<td>-</td>
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<td>HKUST-1</td>
<td>1154</td>
<td>65</td>
<td>0.35</td>
<td>-</td>
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<tr>
<td>IRMOF-8</td>
<td>-</td>
<td>30</td>
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<td>3800</td>
<td>100$^c$</td>
<td>0.57$^e$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Kaye et al. (2007)</td>
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<tr>
<td>IRMOF-5$^a$</td>
<td>3800</td>
<td>100$^c$</td>
<td>7.60</td>
<td>20884.18</td>
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<td>Kaye et al. (2007)</td>
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<td>MOF-5 + Pt/AC</td>
<td>-</td>
<td>100</td>
<td>4.0</td>
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<td>-</td>
<td>Li and Yang (2006)</td>
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<tr>
<td>MOF-5c</td>
<td>-</td>
<td>100$^d$</td>
<td>7.60</td>
<td>20884.18</td>
<td>-</td>
<td>-</td>
<td>Li and Yang (2006)</td>
</tr>
<tr>
<td>C-MOF-5</td>
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<td>25</td>
<td>0.107</td>
<td>296.71</td>
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<td>T-MOF-5</td>
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<td>0.122</td>
<td>347.38</td>
<td>67.56</td>
<td>8811.51</td>
<td>This study</td>
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$^a$ Measured at 302 K
$^b$ Measured at 304 K
$^c$ Measured at 77 K
$^d$ Absolute pressure
$^e$ Absolute adsorption

The equilibrium adsorption isotherm is the basis for describing the interaction between adsorbent and adsorbate. In this study, the Langmuir (1916), Freundlich (1906) and Sips (1948) models were used to correlate the adsorption isotherms.

The Langmuir isotherm is written as:

$$q_e = \frac{a_m p}{1 + b p}$$  \hspace{1cm} (3)$$

where $q_e$ is the H$_2$ and CO$_2$ adsorbed amount on MOF-5, $p$ is the gas pressure, $a_m$ and $b$ are the Langmuir isotherm equation parameters.

The Freundlich isotherm is given by:

$$q_e = k_F p^{1/n}$$  \hspace{1cm} (4)$$

where $k_F$ and $n$ are the Freundlich isotherm equation parameters that can be determined from the experimental H$_2$ and CO$_2$ adsorption isotherms.

The Sips isotherm is a combined form of the Langmuir and Freundlich equations deduced for heterogeneous adsorption systems circumventing the limitation of the increasing adsorbate concentration associated with the Freundlich isotherm model. At low adsorbate concentrations, the Sips isotherm reduces to the Freundlich isotherm; while at high concentrations, it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm. The Sips isotherm is given by:

$$q_e = \frac{k_s p^\beta}{1 + \alpha_s p^\beta}$$  \hspace{1cm} (5)$$

where $k_s$, $\alpha_s$ and $\beta$ are the Sips isotherm constants. These three isotherms were fitted to each of the adsorption data. The adsorption isotherm equation parameters for the Langmuir, Freundlich and Sips equations are listed in Table 3.

Figure 8(a),(b) compares the experimental H$_2$ and CO$_2$ adsorption isotherm on the cubic and tetragonal structures of MOF-5 through the Langmuir, Freundlich and Sips isotherms.

It can be seen from these figures that all three isotherm models can reasonably describe the H$_2$ and CO$_2$ adsorption isotherms on the two MOF-5 adsorbents, but none of them is accurate enough to predict all isotherms without any error.

The criteria associated with the selection of the best isotherm model were essentially based on the correlation coefficient and R$^2$. The correlation coefficient shows the fit between experimental data and the isotherm model, while the value of R$^2$ quantifies the goodness of fit between the experimental data.
and calculated data used for plotting the isotherm curves. The results presented in Table 3 show that the Sips isotherm fits better than the Langmuir and Freundlich isotherms at 298 K (especially for CO2 adsorption on both MOF-5s).

![Image of correlation between isotherms]

Figure 8: (a) Correlation of CO2 adsorption isotherm on C-MOF-5 and T-MOF-5 and (b) Correlation of H2 adsorption isotherm on C-MOF-5 and T-MOF-5 with Langmuir, Freundlich and Sips isotherm models.

Table 3: Summary of adsorption isotherm model parameters for H2 and CO2 in C-MOF-5 and T-MOF-5.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Gas</th>
<th>Isotherm model parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Langmuir</td>
</tr>
<tr>
<td>C-MOF-5</td>
<td>H2</td>
<td>a_b = 0.2242 b_0 = 0.0356 R² = 0.9981</td>
</tr>
<tr>
<td></td>
<td>CO2</td>
<td>a_b = 712.9 b_0 = 0.0055 R² = 0.9870</td>
</tr>
<tr>
<td>T-MOF-5</td>
<td>H2</td>
<td>a_b = 0.2441 b_0 = 0.0396 R² = 0.9981</td>
</tr>
<tr>
<td></td>
<td>CO2</td>
<td>a_b = 2352 b_0 = 0.0013 R² = 0.9870</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

There are two structures of MOF-5: one with the cubic structure (C-MOF-5) and the other tetragonal (T-MOF-5). T-MOF-5 had a lower surface area, lower porosity, smaller and more uniform pore size, and more ZnO units than C-MOF-5. Both the cubic and tetragonal structures of MOF-5 were synthesized and characterized by TGA and SEM and used as adsorbents for H2 and CO2 adsorption studies. We found that the CO2 adsorption capacity of C-MOF-5 at 298 K and 25 bar is greater than that of T-MOF-5, with capacities of 79.9 and 67.5 wt%, respectively. Also we found that the H2 adsorption capacity of C-MOF-5 at 298 K and 25 bar is less than that of T-MOF-5, with capacities of 0.107 and 0.122 wt%, respectively. This behaviour was attributed to more ZnO units in T-MOF-5 than C-MOF-5. The difference between the H2 and CO2 adsorption capacities of T-MOF-5 and C-MOF-5 shows that T-MOF-5 is a better adsorbent for H2 storage and C-MOF-5 is a better adsorbent for CO2 capture. The Sips isotherm fit better to the experimental data than the Langmuir and Freundlich isotherms.

Thermal decomposition of T-MOF-5 and C-MOF-5 produced the same products: benzene, CO2, carbon and ZnO. However, the thermal decomposition of C-MOF-5 required a higher temperature than that of T-MOF-5, indicating that C-MOF-5 is more stable than T-MOF-5.

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**REFERENCES**


Arjmandi, M., Pakizeh, M., Mixed matrix membranes incorporated with cubic-MOF-5 for improved Polyetherimide gas separation membranes: Theory and experiment. Journal of


Freundlich, H. M. F., Over the adsorption in solution. Journal of the American Chemical Society, 38, 2221-2295 (1916).


