A review of the features and applications of ZIF-8 and its derivatives for separating CO₂ and isomers of C₃⁻ and C₄⁻ hydrocarbons

Manel Bergaoui a,b, Mohamed Khalfaoui a,b, Ahmed Awadallah-F c,1, Shaheen Al-Muhtaseb c,*

* Research Group in Materials Science, Microelectronics and Nanotechnologies, Department of Technology, Higher Institute of Computer Sciences and Mathematics of Monastir, University of Monastir, Monastir, 5000, Tunisia
a Laboratory of Physical Chemistry of Materials, Department of Physics, Faculty of Sciences, University of Monastir, Monastir, 5000, Tunisia
b Department of Chemical Engineering, Qatar University, P.O. Box 2713, Doha, Qatar

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ABSTRACT

Metal organic framework (MOF) membranes have gained more attentions due to their abilities in various applications in gas and liquid separations. The majority of works are related to Zeolite imidazolate frameworks-8 (ZIF-8). This is often attributed to its high stability, easy synthesis, and good gas separation. They have gained a significant interest of scientists and have the aptitude to be utilized in other gas separations and applications. Indeed, the investigation of the literatures revealed that ZIF-8 and its derivatives have a substantial attention due to its high surface area, “gate opening” mechanism, etc., which makes it special in adsorption/membrane separations and other applications. The applications of ZIF-8 based materials for carbon dioxide (CO₂) gas adsorption and the C₃⁻ and C₄⁻ isomers’ (propane, propylene, n-butane and isobutane) gas separation also are discussed. Statistical physics approach was applied throughout this review as a perfect tool to discuss and understand properties of ZIF-8, especially the “gate opening pressure”. Subsequently, this review points to present highlights and applications of ZIF-8 and its derivatives for the purpose of carbon dioxide and hydrocarbon separations. Additionally, this study considers recent advancements of ZIF-8 synthesis and prospects for its use in gas separation. This study can help to better understand effective features of a sorbent and methods for gas separation process. As theoretical discussions are referred to as a crucial issue, this is the first study on Zeolitic Imidazolate Framework (ZIF) membrane application, which provides the use of statistical physics theoretical approach and considers the effect of nanogate opening pressures.

1. Introduction

In recent years, zeolitic imidazolate frameworks (ZIFs) have developed rapidly. Their structures are generated according to tetrahedral units where every metal ion (M) attaches to four organic imidazolate (Im) linkers (M–Im–M). Indeed, ZIFs are considered as a sub-family of MOFs, and their topology has been similar to that of zeolites (Song et al., 2012). ZIFs combine the advantages of both MOFs and zeolites since they have properties of these two materials such as crystallinity, porosity, and enthralling chemical and thermal stability (Sankar et al., 2019; Zou et al., 2018a). Moreover, ZIFs are considered as attractive candidates for several applications in gas separation by adsorption or in membranes, in sensing and in catalysis (Chen and Wang, 2020; Matsuoka et al., 2018; Samadi-Maybodi et al., 2015; Awadallah-F et al., 2019a). This advantage was ascribed to their excellent properties, including their high surface area, microporous structures, chemical and thermal stabilities (Park et al., 2006); and synthesis controllability due to their structural flexibility, which leads to a sensible design of both their pore sizes and surface functionality. Therefore, special properties and applications of the ZIF family are under heavy research, where zeolitic imidazolate framework-8 (ZIF-8) is the most popular and classic member of this family. An advantage of ZIF-8 nanoparticles is their excellent stability that enabled long term operation (Yuan et al., 2017).

Zeolitic imidazolate framework-8 (ZIF-8) (Zn(mIm)₂), where mIm is the 2-methylimidazolate) displays a solidate (SOD) topology (Fig. 1) that features a space group of interconnected six membered ring (propane, propylene, n-butane and isobutane) gas separation also are discussed. Statistical physics approach was applied throughout this review as a perfect tool to discuss and understand properties of ZIF-8, especially the “gate opening pressure”. Subsequently, this review points to present highlights and applications of ZIF-8 and its derivatives for the purpose of carbon dioxide and hydrocarbon separations. Additionally, this study considers recent advancements of ZIF-8 synthesis and prospects for its use in gas separation. This study can help to better understand effective features of a sorbent and methods for gas separation process. As theoretical discussions are referred to as a crucial issue, this is the first study on Zeolitic Imidazolate Framework (ZIF) membrane application, which provides the use of statistical physics theoretical approach and considers the effect of nanogate opening pressures.

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windows with an accessible diameter and pore width of 3.4 Å and 11.6 Å, respectively (Park et al., 2006; Banerjee et al., 2008; Sze Lai et al., 2014a). ZIF-8 contains 276 atoms in each unit cell. It crystallizes in cubic space group $\text{Pn3m}$ with a lattice constant of 16.992 Å (Awadallah-F et al., 2019a; Huang et al., 2006). ZIF8 and its derivatives have a highly stable structure and play an important role in promising membranes for gas separation processes. Due to its robustness and good separation ability, many researchers have conducted further studies on it. (Song et al., 2012; Awadallah-F et al., 2019a; Awadallah-F et al., 2019b; Awadallah-F et al., 2019c).

Recent advancements in the chemical and petrochemical industries led to the development of various methods and technologies for gas separation. Due to its widespread use, the global demand for high-purity gas is growing rapidly. Gas separation has a potential impact on the chemical processing industry. Therefore, many separation processes and techniques have been used for gas separation. Table 1 summarizes the most important methods and points out their advantages and disadvantages. The innovation of gas separation through adsorption technology is related to the discovery of new adsorbents, such as organometallic frameworks (MOFs), especially zeolite imidazole frameworks (ZIFs), which have excellent thermal and chemical stability, and have microporous voids, leading to the large-scale industrial application of ZIFs (Wang et al., 2016; Neelakanda et al., 2016; Melgar et al., 2015; Bernardo et al., 2009; Pullumbi et al., 2019; Wankat, 1991).

**Table 1**
Main technologies and methods of gas separation (Wang et al., 2016; Neelakanda et al., 2016; Melgar et al., 2015; Bernardo et al., 2009; Pullumbi et al., 2019; Wankat, 1991).

<table>
<thead>
<tr>
<th>Separation method/technology</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption by Solvents</td>
<td>High recovery rate of separation</td>
<td>Degradation in the oxidizing environment</td>
</tr>
<tr>
<td>Membrane Separations</td>
<td>Many membranes are developed</td>
<td>High amount of energy required for regeneration</td>
</tr>
<tr>
<td>Cryogenic Separations</td>
<td>Direct production of liquid CO$_2$ for example</td>
<td>Cannot achieve a high degree of separation</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Easy regeneration</td>
<td>High energy consumption</td>
</tr>
</tbody>
</table>

Understanding how ZIF-8 interacts with alkanes is vital for its further development and commercialization in a wide range of applications. Applications of ZIF-8 materials are emerging due to their high porosity and stability, adjustable compositions and structural flexibility (Ma and Liu, 2019; Zou et al., 2018b). Both pristine ZIF-8 and its derivatives were developed as multifunctional materials making them attractive candidates for various applications such as environment protection (Pillai et al., 2019; Chen et al., 2019; Yoo et al., 2020), separations (Matsuoka et al., 2018); (Awadallah-F et al., 2019a; Awadallah-F et al., 2019b; Awadallah-F et al., 2019c), catalysis (Chen and Wang, 2020; Payra et al., 2020), sensing (Samadi-Maybodi et al., 2015), electronics (Abaral et al., 2020) and drug delivery (Chen et al., 2018). In this section, attention will be focused on the gas separation. Indeed, ZIF-8 materials have a high potential in gas separation due to their highly porous structure. Moreover, gas separation can be affected by several factors such as ZIF-8 nanoparticle characteristics; including pore sizes, chemical modification, loading percentage and structure and fabrication conditions (such as method, temperature, time, … etc.) (Gong et al., 2017).

In this review, we analyze and summarize the recent research developments of ZIF-8 materials and its derivatives as well as their applications, especially for CO$_2$ gas separation. This review consists of different aspects including synthesis procedures to generate ZIF-8 nanomaterials, common characterization techniques and a summary of their main applications in several significant areas. Finally, it gives the latest research on the hydrocarbon adsorption by ZIF-8 and doped ZIF-8, along with new correlations of their corresponding adsorption isotherms. The notion of gate-opening pressure ($P_g$) of ZIF-8 and its derivatives for the adsorption and separation of various gases was well discussed and evaluated basing on statistical physics approach. Indeed, the present review focuses not only on the experimental point of view of ZIF-8 and its derivatives as proved by other review works (Feng et al., 2021; Li et al., 2021; Chen et al., 2014; Sze Lai et al., 2014b), but it also highlights the theoretical approach applied to ZIFs. To the best of our knowledge, the statistical physics theoretical approach was applied for the first time on Zeolitic Imidazolate Framework (ZIF) membranes applications while attempting to consider the effect of nanogate opening pressures.

### 2. Synthesis

Great advances have been made in the synthesis methods of MOFs. Fig. 2 shows a timeline of the most popular synthetic methods qualified for the MOFs synthesis (Yaghi, 1997; Rubio-Martinez et al., 2017) that are applied until today (Lu et al., 2020; Fang et al., 2020). Nonetheless, the synthesis of MOFs is not restricted to these methods. Recently, Li et al. (2020) used an immersion deposition method for La@ZIF-8 synthesis. Likewise, ultrasound-assisted method was applied by Mahmoodi et al. (2019) for the synthesis of ZIF-8, CNT/Fe$_3$O$_4$/ZIF-8 and NH$_2$-CNT/Fe$_3$O$_4$/ZIF-8. Some synthetic methods described above such as microwave, solvothermal, sonochemical, solvent method, microfluidic, electrochemical and steam-assisted methods (Awadallah-F et al., 2019a; Cho et al., 2013; Fu et al., 2018; Shi et al., 2011; Biswal et al., 2013; Martinez-joaristi et al., 2012; Lucero et al., 2019; Xie et al., 2014) are summarized in Table 2. In fact, compared with the solvothermal method, the method of first synthesizing the zeolite imidazolate ester...

![Fig. 1. Three-dimensional structure of ZIF-8 in cubic unit cell at 111 plane, Zn (polyhedral), N (sphere), and C (line)) (Park et al., 2006; Banerjee et al., 2008; Sze Lai et al., 2014a).](image-url)
Table 2
State-of-the-art synthesis approaches and properties of ZIF-8 and its derivatives.

<table>
<thead>
<tr>
<th>Synthesis method</th>
<th>Zn(^{2+}) (mmol)</th>
<th>MeIMa (mmol)</th>
<th>Synthetic condition</th>
<th>Particle size ((\mu m))</th>
<th>(S_{BET}) (m(^2)/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIF-8 Microwave</td>
<td>4.45</td>
<td>39.5</td>
<td>Methanol, 60 °C, 24 h, 100 W</td>
<td>0.328</td>
<td>61.05</td>
<td>(Awadallah-F et al., 2019a)</td>
</tr>
<tr>
<td>Cu(_{x})/ZIF-8</td>
<td>(4.45 - (x))</td>
<td></td>
<td>Methanol, 120 °C, 3 h, 80 W</td>
<td>0.222</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZIF-8 Solvothermal</td>
<td>2</td>
<td>2</td>
<td>DMF, 140 °C, 24 h</td>
<td>150–200</td>
<td>1370</td>
<td>(Lee et al., 2015)</td>
</tr>
<tr>
<td>ZIF-8 Microwave</td>
<td>2</td>
<td>2</td>
<td>DMF, 120 °C, 3 h, 80 W</td>
<td>5–10</td>
<td>1250</td>
<td></td>
</tr>
<tr>
<td>ZIF-8 Sonocatalytic</td>
<td>10</td>
<td>10</td>
<td>TEA(^{+}) and NaOH(^{-})</td>
<td>0.7</td>
<td>1253</td>
<td>(Cho et al., 2013)</td>
</tr>
<tr>
<td>ZIF-8 Solvent method</td>
<td>1.5</td>
<td>3</td>
<td>Methanol, 1000 rpm, 60 °C</td>
<td>–</td>
<td>1410</td>
<td>(Fu et al., 2018)</td>
</tr>
<tr>
<td>ZIF-8 PVP(^{+}), ZIF-8/ CNTs</td>
<td>10</td>
<td>10</td>
<td>Methanol, 1000 rpm, 60 °C, 0.1 g (PVP),</td>
<td>0.47–1.9</td>
<td>945</td>
<td></td>
</tr>
<tr>
<td>ZIF-8 SDS(^{-}), ZIF-8/ CNTs</td>
<td>10</td>
<td>10</td>
<td>Methanol, 1000 rpm, 60 °C, 0.1 g (PVP),</td>
<td>0.13–0.42</td>
<td>976</td>
<td></td>
</tr>
<tr>
<td>ZIF-8 CTAB(^{+}), ZIF-8/ CNTs</td>
<td>10</td>
<td>10</td>
<td>Methanol, 1000 rpm, 60 °C, 0.1 g (PVP),</td>
<td>0.1–0.11</td>
<td>928</td>
<td></td>
</tr>
<tr>
<td>ZIF-8 Microfluidic (T- mixer)</td>
<td>2.25</td>
<td>157.5</td>
<td>H(_2)O, 10 min, 100 °C</td>
<td>0.3–0.9</td>
<td>1730 ±</td>
<td>Shi et al. (2011)</td>
</tr>
<tr>
<td>ZIF-8 GQD@ZIF-8(^{+})</td>
<td>0.3</td>
<td>2.43</td>
<td>Methanol, Under vacuum, 6 h</td>
<td>–</td>
<td>983</td>
<td>Biswal et al. (2013)</td>
</tr>
<tr>
<td>ZIF-8 Steam-assisted</td>
<td>0.5</td>
<td>5</td>
<td>H(_2)O, 120 °C, 24 h</td>
<td>0.036</td>
<td>983</td>
<td>Martinez Joaristi et al. (2012)</td>
</tr>
</tbody>
</table>

\(x\) was varied from 0 to 2.23 to alter the ratio of Cu(NO\(_3\))\(_2\)·2.5H\(_2\)O/Zn(NO\(_3\))\(_2\)·6H\(_2\)O into the solution.

\(^{a}\) Copper.

\(^{b}\) Dimethylformamide.

\(^{c}\) Trimethylamine.

\(^{d}\) Sodium hydroxide.

\(^{e}\) Polyvinylpyrrolidone.

\(^{f}\) Carbon nanotubes.

\(^{g}\) Sodium dodecyl sulfate.

\(^{h}\) Cetyltrimethylammonium bromide.

\(^{i}\) Graphene quantum dots.

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Fig. 3. XRD patterns of (A) Z-(AMeOH) and Z-B(DMF) samples (Dz et al., 2019), (B) ZIF-8 samples synthesized at (a) 80 °C; (b) 100 °C; (c) 120 °C and (d) 140 °C within 0.5 h under microwave irradiation (Lai et al., 2016) and (C) ZIF-8, Cu\(_{10}\%)/ZIF-8 and Cu\(_{30}\%)/ZIF-8 samples (Awadallah-F et al., 2019a).
framework (ZIF) requires complicated and long steps (Park et al., 2006). Generally speaking, smaller and uniform crystals with a thinner size distribution have been discovered by microwave-assisted methods, which are very desirable for some useful applications (Lucero et al., 2019). Bao et al. (2013) shows that the samples produced by the hydrothermal method have irregular shapes and variable particle sizes. However, a homogeneous sample having a hexagonal shape and an average particle diameter of about 0.350 μm was obtained by the microwave radiation synthesis method. On the other hand, the average particle size is affected by other synthesis conditions, such as Zn:2Melmolar ratio, solvent, reaction temperature, irradiation time, precursor concentration, pressure, and mixed metal content (Fu et al., 2018; Munoz-Gil and Figueiredo, 2019; Dumme et al., 2015).

3. Common characterization techniques

Various techniques were used to characterize the synthesized ZIF8 material in the goal to study the structure, morphology, physico-chemical properties and thermal stability of the material.

3.1. Crystal structure prediction

The crystal structure and purity of ZIF8 can be demonstrated by characterization experiments using single crystal X-ray diffraction (XRD) methods. The high crystallinity of the produced ZIF8 material originates from the (001) very sharp peak at 2θ = 7.36° (Samadi-Maybodi et al., 2015; Li et al., 2019; Duan et al., 2020). Moreover, from the XRD pattern, the particle size distribution could be estimated based on Scherrer Equation (Lai et al., 2016). Fig. 3 (A) shows an X-ray diffraction analysis of ZIF-8 that was synthesized with methanol and dimethylformamide solvents as denoted, respectively, by Z-A(MeOH) and Z-B (DMF) (Du et al., 2019). Indeed, high crystallinity of both samples was deduced from the diffraction peak (011) at 2θ = 7.36°. However, Z-B (DMF) has higher symmetric planes since its diffraction peaks intensity is higher compared to those of Z-A(MeOH), which indicates the effect of solvent in ZIF-8 synthesis. On the other hand, Lai et al. (2016) have studied the temperature effect from 80 °C to 140 °C, where XRD characterization leads to detecting the higher crystallinity of ZIF-8 synthesized at 120 °C and 140 °C (Fig. 3 (B)). Indeed, to generate a supersaturation condition for the formation of ZIF-8 during a small period time (0.5 h), a lower temperature of 100 °C is insufficient, which led to the absence of its characteristic peak.

In addition, some studies have reported the synthesis of mixed metal/ligand ZIF (Chen et al., 2018; Kaur et al., 2016; Botas et al., 2010; Caskey et al., 2008; Zhang et al., 2019; Liu et al., 2019). Awadallah et al. (Awadallah-F et al., 2019a) have showed that similar XRD patterns were detected for both ZIF-8 and Cu/ZIF-8 (Fig. 3 (C)). This indicates that the crystal structure in the I43m space group is retained after ZIF8 doping.

3.2. Size and morphology-controlled nanocrystals

Scanning electron microscope SEM imaging was used to study the morphology and crystal size distribution as a function of synthesis conditions. Indeed, as shown in Fig. 4, the development of ZIF-8 crystals was established by time progressing from cubes displaying 6 (100) faces to rhombic dodecahedra displaying 12 (110) faces. Probably, the latter is being the most stable ZIF-8 equilibrium morphology (Schejn et al., 2014; Jing et al., 2020).

Jian et al. (2015a) investigated the development of ZIF-8 crystals depending on synthesis time (Fig. 5 (A)). Bumpy spherical particle surfaces are detected at 5 min. The period that presents the metastable phase for ZIF-8 growth was achieved when time increasing to 20–60 min. Thereafter, crystals with heterogeneous hexagonal facets begin to display. Homogeneous surfaces with little defects were established for ZIF-8 crystals at 4 h. By increasing time up to 8 h, the formation of various little ZIF-8 crystallites was attained, whereas the quantity turned into trivial at 16 h. The mechanism of Ostwald ripening (Challa et al., 2011) allows to describe this phenomenon. The well-known typical morphology of ZIF-8 given by rhombic dodecahedron shape with 12 {111} surfaces was attended at 24 h. After 3 days, this equilibrium shape is preserved.

Jing et al. (2020) showed that the morphology and the average particle size changed with molar ratio of Ag/AgCl co-doped ZIF-8 as shown in Fig. 5 (B). Indeed, an average size of 600 ± 24 nm was found after 24 h of reaction time for ZIF-8 nanoparticles with a rhombic dodecahedron shape (Fig. 5a (B)). A reduction of the ZIF-8 particle size to 550 nm was detected by the addition of 5 mmol of AgNO3 with a well-defined truncated rhombic dodecahedral crystals (Fig. 5b (B)). When 10 mmol of AgNO3 is added, ZIF-8 average particle size decreased to 400 ± 18 nm. Thereafter, little Ag/AgCl nanoparticles are created in ZIF-8 nanomaterials (Fig. 5c (B)). For a 15 mmol of AgNO3, the average size decreased to 300 ± 22 nm with a well-defined shrunken cubic crystals (Fig. 5d (B)). Finally, when adding 20 mmol of AgNO3, ZIF-8 particle size decreased to 200 ± 20 nm (Fig. 5e (B)). This same decrease of particle size has been also detected by Awadallah et al. (Awadallah-F et al., 2019a) in the case of Cu/ZIF-8, where the obtained nanocrystal size decreases following the increase of Cu2+ percentage (Fig. 5 (C)).

In addition, it has been observed that by changing the molar ratio of 2-methylimidazole (Hmim)/zinc nitrate hexahydrate (Zn), the morphology and average size can also be changed (Jian et al., 2015a; Kida et al., 2013; Tanaka et al., 2012). Zhang et al. (2018) shows that ZIF-8 synthesized with a Hmim/Zn molar ratio of 1 has a cubic shape with particles sizes of 0.4 μm and 0.8 μm. When the Hmim/Zn molar ratios are greater than unity, the morphology of all samples changes to truncated rhombic dodecahedron or rhombic dodecahedron shapes. Furthermore, a decrease of average particle size from 1.0 μm to 0.1 μm was detected by increasing the Hmim/Zn molar ratio from 4 to 16, respectively (Zhang et al., 2018).

3.3. Chemical characterizations

Functional groups: The presence of an imidazole group and a Zn–N interaction was confirmed by Fourier-transform infrared (FT-IR) spectra of ZIF-8, which confirms that the synthesis of ZIF-8 crystals was succeeded (Samadi-Maybodi et al., 2015; Du et al., 2019; Binaeian et al., 2019). Indeed, for pure ZIF-8, peaks at 2920–3180 cm–1 show the stretching of aliphatic and aromatic C–H of imidazole ring, respectively. The peaks for out-of-plane and in-plane bending of imidazole ring are below 800 cm–1 and in the region of 900–1350 cm–1, respectively. The peak around 1600 cm–1 is due to the C=N stretch mode, while the sharp peaks at around 1300–1500 cm–1 were attributed to the stretching of the entire ring. Finally, the peak at 420 cm–1 shows the stretching of Zn–N bond when the zinc atoms in ZIF-8 connect to the nitrogen atoms of 2-methylimidazole linker during ZIF-8 synthesis (Samadi-Maybodi et al., 2019).
Fig. 6 (i) shows an example of ZIF-8 and Cu/ZIF-8 FTIR spectra (Awadallah-F et al., 2019a), where some peaks were shifted compared to 2-methylimidazole molecule. This finding leads to conclude that the final products of ZIF-8, Cu\textsubscript{10\%}/ZIF-8 and Cu\textsubscript{30\%}/ZIF-8 were created without leaving any remains of unreacted 2-methylimidazole (Awadallah-F et al., 2019a).

Raman spectra: Raman spectra give structural fingerprint of molecules. The standard Raman peaks for ZIF-8 and doped ZIF-8 materials are regrouped in Table 3 (Awadallah-F et al., 2019a; Pillai et al., 2019; Radhakrishnan and Narayana, 2016; Tanaka et al., 2015; Tsotsalas et al., 2016).

Surface Composition: Elemental composition and binding energy of ZIF-8 materials was analyzed by X-Ray photoelectron spectroscopy (XPS) analysis technique (Awadallah-F et al., 2019a; Liu et al., 2016; Chin et al., 2018). Fig. 6(iii) illustrates an example of whole XPS spectra of ZIF-8, Cu\textsubscript{10\%}/ZIF-8 and Cu\textsubscript{30\%}/ZIF-8 samples. Indeed, the results showed the presence of not only ZIF-8 framework elements (such as Zn, C, N and O) in ZIF-8 nanomaterials, but also Cu in the Cu\textsubscript{10\%}/ZIF-8, and Cu\textsubscript{30\%}/ZIF-8 samples. The binding energies of Cu\textsubscript{10\%}/ZIF-8 and Cu\textsubscript{30\%}/ZIF-8 samples was affected by the admission of Cu\textsuperscript{2+} into matrix where a shift to lower energy values was attained compared to ZIF-8 sample (Awadallah-F et al., 2019a).

3.4. Thermal stability analysis

The decomposition of samples with temperature was monitored using thermogravimetric analysis (TGA) that was carried out using a PerkinElmer Pyris6 TGA analyzer under a N\textsubscript{2} gas in the range of 150 °C–1000 °C with heating rate 10 °C/min. This technique is frequently used to identify the limits of materials’ thermal stability (Howarth et al., 2016). For instance, Awadallah et al. (Awadallah-F et al., 2019a) showed that the thermal stability of ZIF-8 decreases with the presence of Cu\textsuperscript{2+} (Fig. 7). Moreover, no weight loss was detected at 150 °C, for ZIF-8 and Cu\textsubscript{10\%}/ZIF-8, whereas Cu\textsubscript{30\%}/ZIF-8 presents a weight loss of 1.49%. The weight loss at 514 °C for ZIF-8 is 4.88%; whereas for Cu\textsubscript{10\%}/ZIF-8 and Cu\textsubscript{30\%}/ZIF-8, this value becomes 5.48%. At 1000 °C, the weight loss of ZIF-8 is 74.75%; whereas for Cu\textsubscript{10\%}/ZIF-8 and Cu\textsubscript{30\%}/ZIF-8, the weight losses are 82.35%, and 66.53%, respectively (Awadallah-F et al., 2019a).

On the other hand, Schejn et al. (2015) also showed a similar trend where no weight loss was detected until 350 °C for adsorbents Cu\textsubscript{1\%}/ZIF-8, Cu\textsubscript{5\%}/ZIF-8, Cu\textsubscript{10\%}/ZIF-8, Cu\textsubscript{25\%}/ZIF-8; indicating good thermal stabilities for all samples. Thereafter, the order of thermal stability in the range of 350 °C–400 °C is Cu\textsubscript{1\%}/ZIF-8 > Cu\textsubscript{5\%}/ZIF-8 > Cu\textsubscript{10\%}/ZIF-8 > Cu\textsubscript{25\%}/ZIF-8. A sharp weight loss of 63–64% was detected when the temperature was raised from 400 to 500 °C; with the corresponding order: Cu\textsubscript{5\%}/ZIF-8 > Cu\textsubscript{10\%}/ZIF-8 > Cu\textsubscript{25\%}/ZIF-8 > Cu\textsubscript{1\%}/ZIF-8. Indeed, the difference in the ranges of temperature...
corresponding to thermal stability of adsorbents studied by Awadallah et al. (Awadallah-F et al., 2019a) and Schejn et al. (2015) could be attributed to the differences in experimental conditions such as the respective synthesis methods. Moreover, the stability of ZIF-8 was improved by iron adding as Fe-ZIF-8(1:9) up to 250 °C and Fe-ZIF-8(2:8) up to 289 °C (Thanh et al., 2018). This phenomenon was also exhibited for TiO₂/ZIF-8 (Chandra et al., 2016).

3.5. Physical properties through gas adsorption

Using surface area and porosimetry analyzers that involve N₂ adsorption-desorption isotherm measurement at 77 K, along with possibly built-in density functional theory (DFT) calculations, is an effective characterization method that can provide details on the physical properties of ZIF-8 such as its surface area, micropore volume, total pore volume, and pore size distributions. The nitrogen adsorption-desorption isotherms of ZIF-8 show, generally, a type I isotherm as reported in several studies (Lai et al., 2016; Du et al., 2019; Zhang et al., 2019; Pan et al., 2011), representing a microporous structure. Fig. 8(a) shows an example that represents this last behavior. Indeed, a microporous structure was confirmed by a rise in the adsorbed volume at very small relative pressures (Jian et al., 2015a).

Table 3

<table>
<thead>
<tr>
<th>Raman shift (cm⁻¹)</th>
<th>Peak assignment</th>
</tr>
</thead>
</table>

In the Raman spectra of ZIF-8 and Cu/ZIF-8 (Fig. 6(ii)), standard peaks for ZIF-8 material were observed (Awadallah-F et al., 2019a). Indeed, the shift of some peaks compared to the 2-methylimidazole molecule confirms the formation of the final product.

Fig. 6. (i) FTIR spectra, (ii) Raman spectra and (iii) XPS analysis of (a) ZIF-8, (b) Cu₁₀/ZIF-8 and (c) Cu₃₀/ZIF-8 adsorbents (Awadallah-F et al., 2019a).

Fig. 7. TGA thermograms of ZIF-8, Cu₁₀/ZIF-8 and Cu₃₀/ZIF-8 samples in the range of 150 °C–1000 °C with heating rate 10 °C/min (Awadallah-F et al., 2019a).

3.5. Physical properties through gas adsorption

Using surface area and porosimetry analyzers that involve N₂ adsorption-desorption isotherm measurement at 77 K, along with possibly built-in density functional theory (DFT) calculations, is an effective characterization method that can provide details on the physical properties of ZIF-8 such as its surface area, micropore volume, total pore volume, and pore size distributions. The nitrogen adsorption-desorption isotherms of ZIF-8 show, generally, a type I isotherm as reported in several studies (Lai et al., 2016; Du et al., 2019; Zhang et al., 2019; Pan et al., 2011), representing a microporous structure. Fig. 8(a) shows an example that represents this last behavior. Indeed, a microporous structure was confirmed by a rise in the adsorbed volume at very small relative pressures (Jian et al., 2015a).

Typical type-I isotherms were also obtained for samples ZIF-8, Zn/Co-ZIF-8, and Cu/ZIF-8 (Fig. 8(b)), which indicates the presence of almost full microporosity (Awadallah-F et al., 2019d). However, behavior variation of isotherms to type-IV was achieved for P/P₀ values above 0.95. This could be attributed to the intra-aggregate voids that cause the presence of some large pores (Awadallah-F et al., 2019d).

The physical properties were affected by the synthesis conditions. For example, the specific surface areas presented in Table 1 changed with synthetic methods. Indeed, Jian et al. (2015a) have shown that the
Fig. 8. (a) N₂ adsorption-desorption isotherms on ZIF-8 (Jian et al., 2015b), (b) N₂ adsorption-desorption onto ZIF-8, Zn/Co-ZIF-8, and Cu/ZIF-8 (Awadallah-F et al., 2019d).

reduction of the Hmim/Zn molar ratio from 70 to 10 leads to decreasing the BET surface area and the total pore volume of particles from 1126 m²g⁻¹ to 0.57 cm³g⁻¹ to 31.9 m²g⁻¹ and 0.15 cm³g⁻¹, respectively. This decrease was caused by the greater particle size distributions at little Hmim/Zn molar ratio. Khan et al. (2018) have confirmed that smaller particles have larger BET surface areas, higher micropore volumes, and larger external surface areas.

On the other hand, the effect of synthesis of ZIFs with pure or mixed metal and/or pure or mixed ligand on the physical properties has been reported in several studies (Awadallah-F et al., 2019b; Chen et al., 2018; Kaur et al., 2016; Botas et al., 2010; Gaskey et al., 2008; Zhang et al., 2019; Liao et al., 2015). Synthesis of Cu²⁺/ZIF-8 nanomaterials with various doping percentages (1%, 5%, 10% and 25%) was studied by Schejn et al. (2015). Indeed, the physical properties of pure ZIF-8 \( (S_{\text{BET}} = 1700 \text{ m}^2\text{g}^{-1}, V_{\text{micr}} = 0.662 \text{cm}^3\text{g}^{-1}) \) are shown to decrease only at a high doping percentage (25% of Cu²⁺); whereas the pore size distribution is centered around 1.2 nm for all doping percentages of Cu, which agrees with that of the ZIF-8 (Jian et al., 2015a; Challa et al., 2011; Kida et al., 2013; Tanaka et al., 2012; Zhang et al., 2018; Binaeian et al., 2019; Xu et al., 2019; Schejn et al., 2015). Moreover, the decrease of both the specific surface area and pore volume when ZIF-8 is loaded with Ag/AgCl nanoparticles is probably associated to diverse catalytic extents of ZIF-8 as explained by Jing et al. (2020). Similarly, the ZIF-8 pore size did not change by Ag/AgCl loading since these nanoparticles were just inlaid in the body of ZIF-8 (Jing et al., 2020).

The temperature also has an effect onto the physical properties of ZIF-8 as described by Lai et al. (2016) for temperatures ranging from 80 °C to 140 °C. A successful synthesis of highly crystalline ZIF-8 was achieved at 120 °C with BET surface areas of up to 690.75 m²g⁻¹ and micropore volumes of up to 0.32 cm³g⁻¹.

4. Potential applications of ZIF-8 materials and its derivatives

4.1. Separation of carbon dioxide (CO₂) gas

Effective CO₂ separation from other gases by adsorption or membranes is one of ZIF-8 advantages (Gong et al., 2017). Chi et al. (2015) investigated the CO₂/CH₄ separation using mixed matrix membranes (MMMs) generated from poly(styrene-block-ethylene-ranbutylene-bloc k-styrene) (SEBS) with different particle sizes of ZIF-8 and a fixed loading of 30 wt%. This is the ideal ZIF-8 concentration that leads to a good gas separation performance as reported in the literature (Chi et al., 2015; Zornoza et al., 2011). Indeed, the selectivity of CO₂/CH₄ separation is nearly independent of ZIF-8 particle sizes since the surface areas of particles remain constant; whereas the selectivity can be enhanced from 4.3 to 5.4 when adding ZIF-8 to the membrane (SEBS/ZIF-8 MMMS) compared to the neat polymer membrane (SEBS) (Chi et al., 2015). However, in a previous work (Zornoza et al., 2011) it is reported that ZIF-8 particle sizes could affect CO₂/CH₄ selectivity since ZIF-8 adsorbents have different surface areas with different sizes. Furthermore, a theoretical investigation of H₂ separation from CO₂ was presented by Bayati et al. (2019) using a ZIF-8 materials. The ZIF-8 nanomaterials exhibited a high tendency for CO₂ adsorption, while the diffusion coefficient of H₂ was much higher than that of CO₂. From a theoretical point of view, the obtained results prove that ZIF-8 has a H₂/CO₂ permeselectivity greater than 30 at relatively low pressures (below 300 kPa), and it decreases at higher pressures. This result was interpreted by the progressive decrease of CO₂ adsorption contribution at lower pressures.

4.2. Separation of C₃ and C₄ hydrocarbons

ZIF-8 materials also exhibit excellent separation performances for hydrocarbons (Awadallah-F et al., 2019a; Yuan et al., 2017; Awadallah-F et al., 2019c; Pan et al., 2012). The high quality of ZIF-8 nanoparticles, functionalized by 5,6-dimethylbenzimidazole (DMBIM) through shell-ligand-exchange (SLE) reaction and integrated into polydimethylsiloxane (PDMS), prepared by Yuan et al. (2017) showed a significantly enhanced C₃H₆/N₂ separation performance in comparison with the pure PDMS membrane. Indeed, a C₃H₆ permeability over 2.10 × 10⁴ Barrer and C₂H₆/N₂ selectivity of 99.5 were achieved. Another mixed matrix membrane fabricated by Zhang et al. (2012) via 6FDA-DAM polyimide and a ZIF-8 also showed a significantly enhanced propylene/propane (C₃H₆/C₃H₄) separation performance in comparison with the pure 6FDA-DAM membrane. The permeability and the ideal selectivity of C₃H₆ and C₂H₆/C₃H₆ of 56.2 Barrer and 31.0, respectively, were established when using ZIF-8 (48.0 wt%)/6FDA-DAM mixed matrix membrane. These values are, respectively, 258% and 150% greater than those obtained by the pure 6FDA-DAM membrane.

A novel approach was developed recently for the gas separation of isomers that are typically challenging to separate (e.g., propylene vs. propylene and n-butane vs. isobutane) based on the concept of their distinguished threshold of nanogate-opening pressure (P₀). After this pressure threshold, long-chained molecules (e.g., C₅ and C₆ hydrocarbons) start to adsorb onto ZIFs as studied by Awadallah et al. (Awadallah-F et al., 2019a; Awadallah-F et al., 2019c). Indeed, ZIF-8 (Awadallah-F et al., 2019a; Awadallah-F et al., 2019c) and Cu/ZIF-8 (Awadallah-F et al., 2019a) and Co/ZIF-8 (Awadallah-F et al., 2019c) samples seem to widen the opening of their nanogates (meaning six-membered rings) at different threshold pressures during adsorption of diverse long-chain gases (such as propane, propylene, isobutane and n-butane) to a point that enables each of these molecules to be adsorbed (Awadallah-F et al., 2019a). Adsorption of such hydrocarbons will not occur at any pressures below this threshold. Consequently, P₀ has an important role in gas separation phenomenon on ZIFs where its value differs for each gas on the same ZIF. As a result, the separation of isomers
using ZIF-8 materials can be highly facilitated at intermediate pressure values between the $P_0$ values for the corresponding component. At such intermediate pressure ($P$), the component that has a $P_0$ value lower than $P$ will be adsorbed, while that with a $P_0$ value higher than $P$ will remain in the gas phase.

The values of $P_0$ were evaluated for each ZIF versus each gas by Awadallah et al. (Awadallah-F et al., 2019a) through fitting equilibrium adsorption data toward an empirical adsorption isotherm model that was modified from the Langmuir adsorption isotherm model to account for the adsorption process at such threshold pressures. On this basis, we seek in the next section to evaluate the $P_0$ value, with an understanding of framework responses and adsorption energetics against other theoretical adsorption isotherm models founded on a statistical physics approach, while respecting the author’s permission (Awadallah-F et al., 2019a). Indeed, to the best of our knowledge, statistical physics theoretical approach was applied here for the first time on Zeolitic Imidazolate Framework (ZIF) membranes applications while attempting to consider the effect of nanogate opening pressures.

5. Correlation of adsorption data on ZIFs with nanogate opening pressures

An important number of investigations on ZIF-8 focused extensively on understanding how to correlate their experimental adsorption properties to theoretical methods such as molecular simulations (Krokidas et al., 2018), conventional molecular dynamics (Krokidas et al., 2017), DFT simulations (Hobday et al., 2018; Zheng et al., 2017), theoretical modeling (Awadallah-F et al., 2019a; Awadallah-F et al., 2019b; Awadallah-F et al., 2019c; Autie-Castro et al., 2017) etc. The modeling of adsorption isotherms in gas or liquid phase adsorption is a powerful method for surface characterization (Al-Ghouti and Da’ana, 2020). Therefore, the fitting of experimental data by either theoretical or empirical models is necessary to investigate adsorption systems. Here, as an illustration, we present a combined experimental and computational approach to study the adsorption of small-to-medium sized molecules, especially of natural hydrocarbon gases by ZIF-8 (Awadallah-F et al., 2019a).

Table 4 shows theoretical models developed by our research group to account for the nanogate opening pressures for the adsorption of long-chained molecules on ZIFs. These models include the Modified Langmuir Model (MLM), Modified Ideal Monolayer Model (MIMM) and the Modified Real Monolayer Model (MRMM) presented in Equations (1)–(3), respectively. The last two models (MIMM and MRMM) are based on a statistical physics approach. Indeed, the statistical physics approach gives a physical meaning to the model’s parameters and allows to describe phenomena outside the realm of traditional physics (Khalafoui et al., 2003, 2015). The main advantage of the MRMM with respect to the MIMM is that it takes into account lateral interactions between adsorbed molecules (Khalafoui et al., 2019a; Awadallah-F et al., 2019c). This parameter is hypothetically introduced to represent the pressure threshold at which the ZIF crystal can adsorb the corresponding gas molecule where it is understood to widen its nanogate opening. According to this hypothesis, the same principle was applied to our two theoretical models (Equations (2) and (3)) by introducing the new parameter $P_0$.

The determination of the models’ parameters is performed by nonlinear regression based on minimising the sum of squared errors, which corresponds to the least sum of squared errors (LSSE), between

<table>
<thead>
<tr>
<th>Theoretical models</th>
<th>Equations</th>
<th>Parameters</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified Langmuir Model (MLM)</td>
<td>$Q_e(P) = \begin{cases} 0 &amp; P \leq P_0 \ \frac{m_p b_0 (P - P_0)}{1 + b_0 (P - P_0)} &amp; P \geq P_0 \end{cases}$</td>
<td>$Q_e$(mole/kg) is the adsorbed amount, $P$ (MPa) is the exposure pressure, $m_p$ is the monolayer adsorption capacity, $b_0$ is the adsorption affinity, $P_0$(MPa) is the gate-opening pressure,</td>
<td>(Awadallah-F et al., 2019a)</td>
</tr>
<tr>
<td>Modified Ideal Monolayer Model (MIMM)</td>
<td>$Q_e(P) = \begin{cases} 0 &amp; P \leq P_0 \ n \times N_a \times a \times \frac{1}{P - P_0} &amp; P \geq P_0 \end{cases}$</td>
<td>$n$ is the number of adsorbed molecule(s) per site, $N_a$ is the receptor sites density/mol(kg), $a$ is defined as: $a = a_1 - a_2 = p_0$, where $a_1$ (MPa) is the half-saturation pressure,</td>
<td>Khalafoui et al. (2003)</td>
</tr>
<tr>
<td>Modified Real Monolayer Model (MRMM)</td>
<td>$Q_e(P) = \begin{cases} 0 &amp; P \leq P_0 \ \frac{n N_a}{1 + \frac{1 - b_0 (P - P_0)}{(P - P_0)}} &amp; P \geq P_0 \end{cases}$</td>
<td>$b$ (MPa$^{-1}$) represents the covolume of the adsorbate molecule, $a J$/MPa is the corresponding molecular pressure cohesion, $\beta$ is expressed as (1/$k_B T$), where $k_B$ is the Boltzmann’s constant and $T$ the experimental temperature, $w$ is the characteristic concentration which was related to the energetic parameter as: $w = Z_{0z} e^{-\Delta \epsilon / RT}$ where $p_{sat}$ is the saturated vapor pressure, $R$ (J/K/mol) is the ideal gas constant, $\Delta \epsilon$ (J/mol) is the adsorption energy and $Z_{0z}$ is the translational partition function of an ideal gas molecule per volume unit,</td>
<td>Khalafoui et al. (2015)</td>
</tr>
</tbody>
</table>
the experimental and correlated data using the Solver add-in of Microsoft Excel (Microsoft Corporation, 2016). The LSSE is defined by

\[
\text{LSSE} = \text{Minimum} \left[ \sum_{i=1}^{j} (Q_{\text{calc}} - Q_{\text{meas}})^2 \right]
\]  

(5)

where \(Q_{\text{calc}}\) is the correlated adsorbed amount (theoretical isotherm), \(Q_{\text{meas}}\) is the measured adsorbed amount, \(i\) is the data point number and \(j\) is the total number of data points. The corresponding errors were calculated based on the absolute relative error (ARE) (Kapoor and Yang, 1989):

\[
\text{ARE} \ (\%) = \frac{100}{j} \sum_{i=1}^{j} \left| \frac{Q_{\text{calc}} - Q_{\text{meas}}}{Q_{\text{meas}}} \right|
\]  

(6)

5.1. Experimental adsorption isotherms

Experimental adsorption isotherm data of \(n\)-butane, isobutane, propane, and propylene onto pure and Cu/ZIF-8 nanomaterials at 25 °C are presented in Fig. 9 (Awadallah-F et al., 2019a). It is observed from this figure that all gases exhibit no adsorption where the pressure increases up to an intermediate value that is specific for each gas on each adsorbent, which is defined by \(P_0\). Indeed, when \(P\) is less than \(P_0\), the opening nanogate of the ZIF crystal is considered to be insufficient for the free passage of molecules which hinders their adsorption, and thus the adsorbed quantity is zero. After this intermediate pressure, the behaviour of the adsorption isotherms exhibit a type-I behaviour according to the IUPAC classification (Awadallah-F et al., 2019a; Sing, 1985) where a plateau was reached. This behaviour was attributed to a surface saturation condition, which indicates that mesopores are filled as proved by Boudjema et al. (2020). The different aspects detected for \(n\)-butane, isobutane, propane, and propylene adsorption were attributed to the stereochemistry of each gas (Awadallah-F et al., 2019a).

It can be noticed from Fig. 9a that the sequential order in terms of equilibrium adsorption capacity onto ZIF-8 is \(n\)-butane > propane > isobutane \(\approx\) propylene. For Cu\(_{10}\%)/ZIF-8 adsorbent (Fig. 9b), this order becomes as \(n\)-butane > isobutane > propane > propylene. However, for Cu\(_{30}\%)/ZIF-8 adsorbent (Fig. 9c), the order becomes propane > \(n\)-butane \(\approx\) propylene > isobutane. Moreover, an increase of the adsorption rate of different gases was observed by Awadallah et al. (Awadallah-F et al., 2019a) following the increases of the concentration of Cu/ZIF-8 nanomaterials.

The values of nanogate opening pressures (\(P_0\)) for each gas is distinct on each adsorbent. Differences between \(P_0\) values become more obvious for the Cu/ZIF-8, especially on Cu\(_{30}\%)/ZIF-8. Consequently, coper-doped zeolitic imidazolate framework-8 showed an interesting tool for gas separation (Awadallah-F et al., 2019a; Goyal et al., 2018) based on the differences between the \(P_0\) values of different components on the same adsorbent. For instance, if the operation pressure is set between the \(P_0\) values of two components, the component with the lower \(P_0\) value will be adsorbed whereas that with a higher \(P_0\) value will not be adsorbed.

5.2. Theoretical fitting

All fitting parameters retrievable by MLM, MIMM and MRMM models are illustrated in Table 5. They are analyzed to investigate the adsorption systems more deeply. Hence, the best fitting model assessment was based firstly on minimizing SSE error function and then evaluated based on the magnitude of the ARE values. The lowest ARE values were obtained using the MRMM model (Table 5), leading to select it as the best fitting model.

Fig. 10 shows an example of experimental adsorption isotherm correlation of propylene onto Cu\(_{10}\%)/ZIF-8 using the three adsorption isotherm models (Equations (1)-(3)). The best correlation between experimental isotherm and theoretical one is observed from MRMM. The better presentation of the MRMM model for experimental adsorption
data exhibiting nanogate opening pressures can also be evidenced by its lower ARE values. Furthermore, the superiority of the MRMM model can be attributed to its ability to describe an intermediate adsorption process among the neighboring adsorbed molecules. Indeed, adsorbed molecules can establish attraction or repulsion force with the neighboring molecules, subsequently, adsorbate-adsorbate interactions cannot be neglected (Khalfioui et al., 2015). Hence, the adsorbent surface chemistry plays an important role in the interactions kind involved in the adsorption process (Lin et al., 2015; Nakhlí et al., 2020). As a result, in the next paragraph, we try to interpret some parameters related to the MRMM fitting of the studied systems.

Fig. 11 shows the evolutions of w and b parameters with P0 of n-butane, isobutane, propane and propylene gases onto ZIF-8 and Cu/ZIF-8. Indeed, w is the characteristic concentration that varies inversely with the energetic parameter as presented by Equation (4) (Table 4), and b represents the covolume of the adsorbate molecule. It can be noticed that the same evolution behavior has been detected for both w and b parameters with P0. Moreover, the same evolution was also detected following the values of w and molecular pressure cohesion (a) parameters with P0 (Table 5). Consequently, it can be concluded that the higher covolume of adsorbate molecule and the higher molecular pressure cohesion led to the lower adsorption energy. Indeed, the change of parameters with a could be attributed to the stereochemistry of each gas (Awadallah-F et al., 2019a) that affect the adsorption energy.

The adsorption energy is an important parameter that leads to a better understanding of the results obtained by Awadallah et al.

### Table 5
Fitting parameters of MLM, MIMM and MRMM models for the adsorption at 25 °C.

#### ZIF-8

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Formula</th>
<th>a (1/mpa)</th>
<th>w (mpa)</th>
<th>b (1/mpa)</th>
<th>P0 (mpa)</th>
<th>LSSE ARE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Butane</td>
<td>5.485</td>
<td>90.395</td>
<td>0.125</td>
<td>0.089</td>
<td>30.288</td>
<td>0.061 2.8%</td>
</tr>
<tr>
<td>Isobutane</td>
<td>3.621</td>
<td>31.278</td>
<td>0.120</td>
<td>0.018</td>
<td>0.034</td>
<td>0.002 2.6%</td>
</tr>
<tr>
<td>Propane</td>
<td>4.373</td>
<td>29.955</td>
<td>0.123</td>
<td>0.148</td>
<td>0.121</td>
<td>0.012 1.2%</td>
</tr>
<tr>
<td>Propylene</td>
<td>3.610</td>
<td>38.769</td>
<td>0.141</td>
<td>0.024</td>
<td>1.576</td>
<td>0.110 0.5%</td>
</tr>
</tbody>
</table>

#### Cu/ZIF-8

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Formula</th>
<th>a (1/mpa)</th>
<th>w (mpa)</th>
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<th>P0 (mpa)</th>
<th>LSSE ARE (%)</th>
</tr>
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<tbody>
<tr>
<td>n-Butane</td>
<td>5.108</td>
<td>0.122</td>
<td>0.117</td>
<td>0.100</td>
<td>0.278</td>
<td>0.047 3.9%</td>
</tr>
<tr>
<td>Isobutane</td>
<td>3.316</td>
<td>0.114</td>
<td>0.090</td>
<td>0.049</td>
<td>0.034</td>
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<td>0.090</td>
<td>0.049</td>
<td>0.034</td>
<td>0.002 2.3%</td>
</tr>
<tr>
<td>Propylene</td>
<td>3.444</td>
<td>0.130</td>
<td>0.050</td>
<td>0.047</td>
<td>0.034</td>
<td>0.002 2.3%</td>
</tr>
</tbody>
</table>

#### Cu/ZIF-8

<table>
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<tr>
<th>Parameter</th>
<th>Formula</th>
<th>a (1/mpa)</th>
<th>w (mpa)</th>
<th>b (1/mpa)</th>
<th>P0 (mpa)</th>
<th>LSSE ARE (%)</th>
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</tr>
</tbody>
</table>
These authors have shown the importance of $P_0$ parameter in relation with gas separation performances. Indeed, $P_0$ values were found to be the same for both n-butane and isobutane couple in the case of ZIF-8 adsorbent since they have the same chemical formula (C$_4$H$_{10}$), and hence the stereochemistry of each gas can explain the difference in adsorption capacity (Awadallah-F et al., 2019a). Indeed, n-butane molecule can easy penetrate the nanogate with less difficulty compared to the branched isobutane molecule (Awadallah-F et al., 2019a) and this is due to the linearity of the first one. Then, there is a difficulty to separate these molecules on ZIF-8 due to the approaching values of $P_0$. The same reflection was observed for propane and propylene in the case of ZIF-8 adsorbent (Awadallah-F et al., 2019a). Thereafter, the $P_0$ values were changed for each couple following the increases of Cu/ZIF-8 percentage. Therefore, it was concluded that Cu$_{30\%}$/ZIF-8 adsorbent is more adequate than Cu$_{10\%}$/ZIF-8 and ZIF-8 adsorbents for gases separation on the basis of differences between their $P_0$ values (Awadallah-F et al., 2019a). As a result, the conclusion about adsorption energy parameter deduced from $w$ supports well these results. Indeed, as presented in Table 6, the variations of adsorption energy (estimated from $\Delta w$) and of $P_0$ increase follow the increase of Cu/ZIF-8 percentage for each couple of n-butane/isobutene and propane/propylene. Then, it can be deduced that the increase of copper percentage doped in ZIF-8 affects as well the adsorption energy, and then the variation of $P_0$ values for each pair of isomers. Consequently, the importance of $P_0$ parameter in relation with gas separation performances detected by Awadallah et al. (Awadallah-F et al., 2019a) could be related to the importance of the adsorption energy for each gas following the increase of copper percentage doped into ZIF-8. On the other hand, the difference in adsorption capacity from one gas to another by changing the copper percentage doped in ZIF-8 does not follow the same order. This point was attributed to several factors, as the stereochemistry and the polarity of each gas.

### 6. Conclusions

This review focuses on the latest synthesis methods of ZIF-8 and its derivatives; in addition to their common characterization techniques and their corresponding applications. Light was shed on the potential application of ZIF-8 in gas separation and the theoretical modeling of their adsorption isotherms was discussed. A statistical physics approach was applied in this review to correlate the experimental adsorption isotherms of some gases by ZIF-8 and its derivatives. As a state of the art, we treated the case of n-butane, isobutane, propane and propylene gases separations using ZIF-8 and Cu/ZIF-8 nanomaterials (Awadallah-F et al., 2019a). Some specific properties such as “gate opening” mechanism, is systematically described and discussed based on the statistical physics approach.
As main conclusions, by increasing the Cu/ZIF-8 percentage, the values of the gate opening pressure ($P_0$) were changed for each isomer pair of n-butane/isobutane and propane/propane, which enhances the performances of gas separation at pressures between their corresponding $P_0$ values. Consequently, Cu$_{30w}$/ZIF-8 adsorbent is more suitable than Cu$_{15w}$/ZIF-8 and ZIF-8 adsorbents for gas separations thanks to the exhibited differences in $P_0$ values. This point was confirmed by the adsorption energy parameter derived from statistical physics approach. Indeed, the importance of gate opening pressure could be related to the importance of the adhesion energy for each gas following the increases of Cu/ZIF-8 percentage. From this, we can infer that the specific characteristics of ZIF-8 and its derivatives will allow for various important applications ranging from sensing and electronic devices to drug delivery, and thereby offers a promising field to be explored. In view of the great interest of several research groups, new concepts and techniques for the synthesis of ZIF are being adopted. In addition, the rapid growth of new applications and new opportunities for further exploration of ZIF materials will continue to emerge in the future. In fact, due to the lack of functional groups in natural ZIF8 particles, they are not suitable for many applications. For this, functional groups were necessary through the use of, e.g., amino reactive imidazole derivatives and doped ZIFs materials. Moreover, computational methods are important nowadays to complement experimental measurements.

**Availability of data and material**

All data generated or analyzed during this study are included in this article.

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**Author contributions**

Manel Bergaoui: Conceptualization, Investigation, Work Execution, Methodology, Software, Writing- original draft. Ahmed Awadallah-F: Conceptualization, Investigation, Work Execution, Methodology, Software, Writing- original draft. Mohamed Khalfaoui: Conceptualization, Investigation, Methodology, Supervision, Validation, Writing - reviewing and editing. Shaheen A. Al-Muhtaseb: Conceptualization, Investigation, Methodology, Supervision, Validation, Writing - reviewing and editing.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**References**


