Synthesis of Amino-Impregnated ZIF-8 for CO2 Adsorption

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Abstract. Zeolitic imidazolate framework-8 (ZIF-8) is well known for its high thermal stability, high surface area and remarkable water stability as compared to the other adsorbents. However, ZIF-8 shows relatively low CO2 capture ability. In this work, ZIF-8 is modified with amino-groups via wetness impregnation method and the performance of the resultant adsorbents in CO2 capture is investigated. Two different types of amino-groups including tetraethylenepentamino (TEPA) and pentaethylenehexamino (PEHA) were used. The concentrations of TEPA and PEHA were prepared at 30, 50 and 70 volume% in chloroform solution, respectively, prior to impregnation over ZIF-8. The Fourier transform infrared (FTIR) results showed that, successful incorporation of amino groups into ZIF-8 was achieved. Meanwhile, based on SEM images, severe agglomeration of particles was observed for 50% and 70% TEPA and PEHA-impregnated ZIF-8. Subsequently, it was found that ZIF-8 impregnated with 30% TEPA showed the highest CO2 adsorption capacity of 1.9983 mmol g⁻¹ as compared the other adsorbents prepared in this work. This has signified the improvement of CO2 adsorption capacity by using amino-impregnated ZIF-8, which was up to 199.6% compared to the parent ZIF-8. Overall, the adsorbents developed in the present work are potential to be used in the industrial CO2 adsorption processes.

1. Introduction

Since the past decades, adsorbent with high CO2 uptake capacity is mandatory due to the presence of low concentration of CO2 especially in the flue gas mixture [1]. To date, it remains challenging for the researchers to find a highly efficient adsorbent for CO2 capture. The typical solid sorbents reported for CO2 capture include porous carbons [1], metal oxide [2], zeolites [3-5], metal organic frameworks (MOFs) [6-8] and porous polymer [9]. These materials are selected based on their primary advantages with highly developed porosity and ability to adsorb large capacity of CO2.

Nevertheless, these adsorbents have exhibited limitation in CO2 absorption under the condition of flue gas with the decreased interaction between adsorbent and CO2. Therefore, in order to improve the CO2 capture capacity, solid-supported amino sorbents have been developed. In these composite sorbents, the strong interaction between amino and CO2 molecules has resulted in high CO2 uptake at the low pressures of CO2 [10]. It is reported that amino functionalized solid adsorbents are promising materials for the CO2 capture attributed to their tenability and lower heat capacity as compared to liquid amino solutions [11]. Thus far, many researches have been conducted in modifying the current existing sorbents with amino groups [10-18].

Zeolitic imidazole framework-8 (ZIF-8) is one of the most studied type of MOFs material attributed to its remarkable properties, such as high thermal stability, high surface area and hydrophobicity [19].
However, it exhibits relatively low CO\textsubscript{2} capture ability as compared to the other MOF adsorbents such as HKUST-1, MOF-505 and MIL-47 [20]. Therefore, in order to increase the CO\textsubscript{2} adsorption capacity, modification of ZIF-8 by incorporating amino functional group via impregnation method was reported by Martínez et al (2016) [17]. However, their study is still at the preliminary stage. In addition, the effect of the other amino groups on the performance of the resultant impregnated-ZIF-8 adsorbents in CO\textsubscript{2} adsorption is yet to be reported.

Herein, this work presents the incorporation of two different types of amino functional groups, tetraethylenepentamino (TEPA) and pentaethylenehexamino (PEHA), into ZIF-8 by using wetness impregnation method. Then, the morphology and structural property of the resultant adsorbents were characterized using scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FTIR). Subsequently, the performance of the resultant adsorbents in CO\textsubscript{2} adsorption were evaluated.

2. Experimental

2.1. Synthesis of ZIF-8
ZIF-8 particles were prepared based on the procedures reported in our previous work [21]. Firstly, zinc nitrate hexahydrate and 2-methylimidazole were prepared and dissolved in 200 mL of methanol, respectively. Then, the solutions were mixed rapidly and stirred for an hour at room temperature. Subsequently, the cloudy solution was centrifuged at 4000 rpm for 10 minutes to separate the nano-crystals from the solution. The nano-crystals was then washed with fresh methanol for 3 times and dried overnight in an oven at 85 °C.

2.2. Wetness Impregnation of ZIF-8
ZIF-8 was activated under vacuum condition (10\textsuperscript{-3} bar) at 150°C for 5 hours prior to impregnation. Tetraethylenepentamino (TEPA) solution was prepared by varying the volume % of TEPA in chloroform as follows: 30%, 50% and 75%. For wetness impregnation method, TEPA solution was added drop-wise over ZIF-8 adsorbent [17]. In order to remove the excess chloroform, the impregnated ZIF-8 was dried at 70°C under vacuum condition. Same procedures were repeated by using pentaethylenehexamino (PEHA) as amino group. Table 1 shows the samples prepared in the present work.

| Samples     | Volume % in chloroform |
|-------------|------------------------|
|             | TEPA | PEHA |
| ZIF-8-30%TEPA | 30   | 0    |
| ZIF-8-50%TEPA | 50   | 0    |
| ZIF-8-70%TEPA | 70   | 0    |
| ZIF-8-30%PEHA | 0    | 30   |
| ZIF-8-50%PEHA | 0    | 50   |
| ZIF-8-70%PEHA | 0    | 70   |

2.3. Characterization

2.3.1. Scanning Electron Microscope (SEM)
The surface morphology of the resultant samples were observed using SEM (Hitachi TM3030) at magnification of 5000.

2.3.2. Fourier Transform Infrared Spectroscopy (FTIR)
The functional groups presented in the resultant samples were investigated using FTIR (Perkin Elmer Spectrum One). The FTIR spectra were obtained at wavenumber ranged from 450 to 4000 cm\textsuperscript{-1}.
2.4. CO₂ adsorption capacity
CO₂ adsorption capacities of the resultant adsorbents were measured through CO₂ physisorption analyzer (BELSORP Mini II) at temperature of 298.2 K. The adsorption measurement was performed using pure CO₂ gas at pressure ranging from 0 to 1 bar.

3. Results and discussion

3.1. Characterization

3.1.1. Scanning Electron Microscope (SEM)

Figure 1 shows the SEM images of ZIF-8 and amino-impregnated ZIF-8 adsorbents. Referring to Figure 1, amino-impregnated ZIF-8 samples displayed changes on the surface morphology as shown in Figures 1 (b) to (g). At loading of 30% of TEPA, the particles started to aggregate and when the percentage of TEPA increased to 50% and 70%, the agglomeration become significant. On the other hand, for 30%, 50% and 70% PEHA-impregnated ZIF-8, severe particle agglomeration is observed, in which all small particles have lumped together. This could be due to the presence of excess amino molecules, which have spilled over the external surface of the ZIF-8 particles.

Figure 1. SEM images of (a) ZIF-8 and ZIF-8 impregnated with (b) 30% TEPA, (c) 50% TEPA, (d) 70% TEPA, (e) 30% PEHA, (f) 50% PEHA and (g) 70% PEHA.
3.1.2. Fourier Transform Infrared Spectroscopy (FTIR)

Figure 2 shows the FTIR spectra for ZIF-8, TEPA- and PEHA-impregnated ZIF-8. Referring to Figure 2, ZIF-8 synthesized in the present work exhibits significant IR bands that represented the vibration of imidazole units and the origin of the bonds. The results are comparable to the IR absorption table [22] and literature reported data [23]. The bands at 2930 cm\(^{-1}\) is mainly caused by the C–H stretch of the imidazole, while the peak at 1445 cm\(^{-1}\) is attributed to the entire ring stretching. On the other hand, a clear shift was observed in the band at about 3400 cm\(^{-1}\) for all the amino-impregnated ZIF-8 samples. This has indicated the presence of amino groups with the N-H stretch. Besides, N-H bending was also found in all the amino-impregnated ZIF-8 as shown in the band at about 1655 cm\(^{-1}\). These results revealed the successful impregnation of amino–groups into the ZIF-8 adsorbents.

![Figure 2. FTIR Spectra.](image)

3.2. CO\(_2\) adsorption capacity

Table 2 shows the CO\(_2\) adsorption capacities of the adsorbents prepared in this work. As shown in Table 2, modification of ZIF-8 via wetness impregnation using two different types of amino-containing molecule has exhibited an improvement in CO\(_2\) adsorption. The CO\(_2\) adsorption capacity obtained for ZIF-8 is 0.6670 mmol g\(^{-1}\). Meanwhile, ZIF-8 impregnated with 30 % of TEPA shows the highest CO\(_2\) adsorption capacity of 1.9983 mmol g\(^{-1}\), followed by ZIF-8 impregnated with 30% PEHA (1.4979 mmol g\(^{-1}\)), 50% TEPA (1.3231 mmol g\(^{-1}\)), 70% TEPA (1.1609 mmol g\(^{-1}\)) and 50% PEHA (0.5006 mmol g\(^{-1}\)). All impregnated adsorbents have exhibited enhancement in CO\(_2\) adsorption, which is mainly contributed by the strong interaction between amino groups and CO\(_2\) gas molecules [17].

However, it can be observed from Table 2 that CO\(_2\) adsorption capacity of the ZIF-8 decreases with the increase in the percentage of amino groups. This might be due to partial blockage of the ZIF-8 microporous framework by the excess amino molecules. Hence, the CO\(_2\) adsorption capabilities of the ZIF-8 were affected. Meanwhile, in the case of TEPA-impregnated ZIF-8, the decrease in CO\(_2\) adsorption was less accentuated than PEHA-impregnated ZIF-8. Besides, 50% and 70% PEHA impregnated ZIF-8 exhibited comparatively lower CO\(_2\) adsorption uptake than ZIF-8. This can be explained by the severe agglomeration of the particles as shown in SEM images. As a result, the CO\(_2\) adsorption capacity of the sample decreased significantly.
4. Conclusion

Modifications of ZIF-8 via wetness impregnation using TEPA and PEHA and the performance of the resultant adsorbents in CO\(_2\) adsorption have been demonstrated in this work. The successful incorporation of amino groups into ZIF-8 were verified by FTIR peaks. SEM results showed that, for 50\% and 70\% TEPA and PEHA-impregnated ZIF-8, severe agglomerations of particles were occurred. In this work, 30\% of TEPA impregnated ZIF-8 showed the highest CO\(_2\) adsorption capacity of 1.9883 mmol g\(^{-1}\) as compared to the parent ZIF-8, which showed CO\(_2\) adsorption of 0.6673 mmol g\(^{-1}\). Overall, enhancement in CO\(_2\) adsorption using 30\% TEPA-impregnated ZIF-8 has been demonstrated.

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\begin{array}{|c|c|}
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\text{Adsorbents} & \text{CO}_2\text{ Adsorption Capacity (mmol g}^{-1}\text{)} \\
\hline
\text{ZIF-8} & 0.6673 \\
\text{ZIF-8-30\% TEPA} & 1.9883 \\
\text{ZIF-8-50\% TEPA} & 1.3231 \\
\text{ZIF-8-70\% TEPA} & 1.1609 \\
\text{ZIF-8-30\% PEHA} & 1.4979 \\
\text{ZIF-8-50\% PEHA} & 0.5006 \\
\text{ZIF-8-70\% PEHA} & 0.0000 \\
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