Research Article
Enhanced CO₂ Adsorption and Selectivity of CO₂/N₂ on Amine@ZIF-8 Materials

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1. Introduction

Nowadays, the rising level of carbon dioxide in the atmosphere has become one of the biggest problems worldwide. As the main component of greenhouse gases, CO₂ contributes the most to global warming and climate change [1]. To date, the global CO₂ concentration has increased from 270 to 400 ppm with the industrial development and is anticipated to approach 950 ppm by 2100, which will bring about sincere environmental problems such as extreme weather, glacial melting, and ocean acidification [2, 3]. Therefore, reducing carbon dioxide emission has been proposed to be a scientific challenge of the highest order and thus has been explored by many researchers throughout the world utilizing different technologies [4–7]. Among these technologies, chemical absorption with aqueous organic amines like diethanolamine (DEA) has been widely used for CO₂ capture from industrial waste gases for some time, but they are still subject to volatilization or degradation of organic amines, instrument corrosion, and high energy consumption for solvent regeneration [8–10]. Therefore, adsorption technology using various kinds of solid porous adsorbents has been proposed for CO₂ capture and separation.

Different types of adsorbents have been investigated and developed for CO₂ adsorption, for example, carbon-based materials, zeolites, metal oxides, and mesoporous silica [7, 11–18]. Nevertheless, these conventional porous materials usually display limited performance toward CO₂ adsorption capacity as well as selectivity. Metal-Organic frameworks (MOFs) composed of metal ions and organic linkers, also known as porous coordination polymers, have developed rapidly and attracted significant attentions in the past two decades [19–26]. Owing to their diverse framework structure, high crystallinity, large surface area, and unlimited adjustability of pore structures and surface functionalities, MOFs exhibit great application prospects in the field of...
CO₂ capture [14, 15, 21, 23, 27–37]. Nevertheless, it still remains a challenge to design MOFs with quite high CO₂/N₂ selectivity as well as CO₂ adsorption capacity since the large surface area of MOFs usually leads to both increased CO₂ and N₂ adsorption capacities, resulting in limited CO₂/N₂ adsorption selectivity.

Many researches have tried to improve both the CO₂ adsorption capacity and selectivity of MOFs, for instance, ligand functionalization [38, 39], incorporation of open metal sites [29, 40, 41], construction of specific pores [17], and pre-/postmodification for amine grafting/impregnation [36, 42–48]. Zhu et al. [42] reported that the polyethyleneimine-modified UiO-66-NH₂ (Zr) exhibited a considerable enhancement toward CO₂/N₂ selectivity (48 vs. 25) and moderate desorption energy (68 kJ/mol CO₂). Additionally, Justin et al. [49] described that the tris (2-aminoethyl) amine- (TAEA-) appended-Zn₄O (NH₂-BDC)₁.₂(BrAcNH-BDC)₁.₈ displayed a dramatically increased CO₂/N₂ (15/85) selectivity (143) at 313 K and a zero-coverage Qₑ of CO₂ adsorption of 62.5 kJ/mol. However, the high heat of adsorption owing to the strong interaction usually signifies high energy for adsorbent regeneration process. Thus, the development of adsorbents with high CO₂ adsorption capacity, CO₂/N₂ selectivity, moderate energy consumption, and good stability still remains a challenge for real application.

In the current work, in order to improve its CO₂ adsorption capacity and CO₂/N₂ selectivity, the ZIF-8 will be post-synthetically modified by using methylamine (MA), ethylenediamine (ED), and N,N’-dimethyl ethylenediamine (MMEN) to obtain a series of novel amine@ZIF-8 materials. Then, the pore structure, PXRD, surface chemistry, and thermogravimetric stability of the prepared amine@ZIF-8 materials would be characterized. The pure-component CO₂ and N₂ isotherms on the amine@ZIF-8 would be measured separately at ambient temperatures. In

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**Scheme 1**: Preparation of amine-functionalized ZIF-8 using three different amines.

**Figure 1**: PXRD patterns of ZIF-8 and amine-modified ZIF-8 samples.

**Figure 2**: N₂ adsorption-desorption isotherms of modified ZIF-8 samples at 77 K.
addition, the equimolar CO₂/N₂ selectivity is estimated by using an ideal adsorbed solution theory (IAST) model. Moreover, the Qₘₚ of CO₂ adsorption on the amine@ZIF-8 was calculated. Finally, the reusability of amine@ZIF-8 toward CO₂ adsorption was also investigated. The multiple gravimetric adsorption-desorption performance is expected to provide an application basis for industrial CO₂ capture.

2. Materials and Methods

2.1. Materials. Zn (NO₃)₂·6H₂O (Alfa Aesar, 99.99% purity), was purchased from Alfa Aesar Chemical; 2-methylimidazole (98% purity), N,N′-dimethylformamide (99.9%), anhydrous methanol (99.8%), ammonia (analytical pure), methylamine (analytical pure), and N,N′-dimethylethylenediamine (97%) were bought from J&K Chemical; chloroform (analytical pure) was obtained from Guangzhou Chemical Reagent Factory; and ethylenediamine (≥ 99.5%) was purchased from Aladdin.

2.2. Synthesis and Modification. Preparation and amine modification of ZIF-8 were carried out according to the reported procedures with a few modifications [50, 51]. The concentration gradients of methylamine (MA), ethylenediamine (ED), and N,N′-dimethylethylenediamine (MMEN) used are listed in Table S1. In this work, the MA-modified ZIF-8 with different concentrations were named as MA1-ZIF-8, MA2-ZIF-8, etc. The name of ED-modified ZIF-8 and MMEN-modified ZIF-8 was in the same manner.

2.3. Characterization. The PXRD patterns were obtained by an X-ray diffractometer (D8 advance, Bruker) using Cu Kα line focused radiation (wavelength λ = 0.15406 nm). The chemical bonds and surface organic groups were observed using a FTIR spectrophotometer (Bruker TENSOR II Apparatus, Bruker Optics Inc., Germany). The thermal stability was characterized by using a thermogravimetric analyzer (TA-550 apparatus, TA Instruments, USA). The porous structures were analysed using a Quantachrome Autosorb IQ2 instrument. All the tested samples were degassed at 473 K under vacuum overnight.

2.4. CO₂ and N₂ Adsorption Isotherms at Ambient Temperature. The specific adsorbed amounts of pure CO₂ and N₂ were measured using a static volumetric method on the Quantachrome Autosorb IQ2 instrument at three temperatures (273 K, 288 K, and 298 K, respectively). The initial activation of amine@ZIF-8 materials was performed at 523 K for 8 h under vacuum. Helium (ultrahigh purity) was the purge gas; CO₂ and N₂ were both of 99.999% purities.

2.5. Reusability Assessment. The regeneration performance was studied to evaluate the recyclability of the amine@ZIF-8. In this study, both volumetric and gravimetric adsorption-desorption cycles were carried out. For the volumetric experiments, multiple CO₂ adsorption-desorption cycles on amine@ZIF-8 were operated by the Quantachrome Autosorb IQ2 instrument at 298 K. During each cycle, the maximum adsorption pressure was set at 1 bar; while the minimum...
The desorption pressure was 1 mbar. The whole desorption process was under vacuum at 473 K for 8 h. For the gravimetric method, the six adsorption-desorption cycles were determined on a TA550 system under different regeneration temperatures (125°C and 150°C, respectively) [52, 53]. Before the recycle experiment, 5 mg of modified ZIF-8 sample was put in a platinum pan and heated to 150°C with a speed of 10°C/min and under high-purity N₂ (99.999%, 60 mL/min) to desorb any preadsorbed gases on the surfaces of the sample. Then, the sample was retained under N₂ atmosphere until a constant weight was reached at 25°C. After that, the gas was switched to a CO₂/N₂ mixture stream (60 mL/min of total flow, 90% CO₂, balance N₂) and kept for 30 min.

3. Results and Discussion

3.1. Characterization of Amine@ZIF-8 Materials. The postsynthetic modification route is demonstrated in Scheme 1. The amount of amine grafted on the ZIF-8 material is the key factor that may greatly affect its porous structure. Figure 1 shows the PXRD patterns of amine@ZIF-8 materials. Clearly, the modified ZIF-8 materials all show diffraction peaks at 7.29°, 10.32°, 12.65°, 16.50°, and 18.01°. These peaks are the same as the characteristics of the diffraction spectrum of the original ZIF-8. The peak positions are also consistent as compared to the simulated ZIF-8, implying that amine@ZIF-8 materials still maintain a complete crystal structure without structural collapse [30].

Figure 2 depicts the N₂ adsorption-desorption isotherms at 273 K, 288 K, and 298 K. (a) ZIF-8; (b) MA-ZIF-8; (c) ED-ZIF-8; (d) MMEN-ZIF-8. The CO₂ adsorption isotherms on the amine@ZIF-8 materials at 273 K, 288 K, and 298 K. The amount of amine grafted on the ZIF-8 material is the key factor that may greatly affect its porous structure. Figure 1 shows the PXRD patterns of amine@ZIF-8 materials. Clearly, the modified ZIF-8 materials all show diffraction peaks at 7.29°, 10.32°, 12.65°, 16.50°, and 18.01°. These peaks are the same as the characteristics of the diffraction spectrum of the original ZIF-8. The peak positions are also consistent as compared to the simulated ZIF-8, implying that amine@ZIF-8 materials still maintain a complete crystal structure without structural collapse [30].

Figure 2 depicts the N₂ adsorption-desorption isotherms at 273 K, 288 K, and 298 K. (a) ZIF-8; (b) MA-ZIF-8; (c) ED-ZIF-8; (d) MMEN-ZIF-8.
Table 1 lists the parameters of porous structures for amine@ZIF-8. It can be seen that with the increase of MA, ED, and MMEN, the BET specific surface areas all showed a trend of first increasing and then decreasing. In addition, the total pore volume also presented the same trend as well as the micropore volume. Compared with the original ZIF-8, the BET specific surface areas of MA2-ZIF-8, MMEN2-ZIF-8, and ED1-ZIF-8 increased by 118.2%, 92.0%, and 29.8%, respectively. Furthermore, their total pore volume increased separately by 130.8%, 100%, and 48.7%. Moreover, the micropore volumes of MA2-ZIF-8, MMEN2-ZIF-8, and ED1-ZIF-8 raised separately by 110.8%, 75.7%, and 18.9%. Thereafter, the MA2-ZIF-8, ED1-ZIF-8, and MMEN2-ZIF-8 can be recognized as the three best samples among the amine@ZIF-8 materials, and they would be marked as MA-ZIF-8, ED-ZIF-8, and MMEN-ZIF-8, respectively, in the following adsorption experiments. However, it should be pointed out that the BET surface area of the as-made ZIF-8 was lower than that synthesized by Park et al. [54], but still in the range of the reported ZIF-8 (see Table S2). This, possibly, indicated that the prepared ZIF-8 in this work still contained some residual species in the cavities (e.g., CHCl₃, DMF, or unreacted Hmim) which could not desorbed during the activated step. In addition, the different results between these three amine@ZIF-8 samples were probably owing to the different reactivities of amines. Therefore, the reason of the increases of the BET surface area and pore volume might be that, after the postsynthetic modification, some occlusive pores of the ZIF-8 were reopened, and more new pores were formed at meanwhile [45]. Nevertheless, when the loading amount of MA, ED, and MMEN added further, the surface areas and pore volumes begun to decrease because of hindrance effect of the introduced amines [55, 56].

![Figure 6: The N₂ adsorption isotherms on the amine@ZIF-8 materials at 273 K, 288 K, and 298 K. (a) ZIF-8; (b) MA-ZIF-8; (c) ED-ZIF-8; (d) MMEN-ZIF-8.](image-url)
Figure S1 exhibits the DFT pore size distributions of ZIF-8 and amine@ZIF-8 materials. Apparently, for each MA-ZIF-8, MMEN-ZIF-8, and ED-ZIF-8 material, the main pore size was lower than that of the as-made ZIF-8. Figure 3 demonstrates the DFT pore size distributions for the best amine@ZIF-8 materials. It can be noticed that the main pore size of the original ZIF-8 is distributed at 10.87 Å, while those of the MA-ZIF-8, ED-ZIF-8, and MMEN-ZIF-8 are distributed at around 9.26 Å, suggesting that the introduction of an amine group would result in reduced pore size [47]. This might be due to the new formed pores with the introduction of MA, ED, and MMEN, respectively. The reduced pore size also indicated that there were mainly micropores in the amine@ZIF-8 frameworks.

Figure 4 illustrates the infrared spectra of amine@ZIF-8 materials. First of all, the infrared spectra of amine@ZIF-8 materials were basically similar to those of ZIF-8. Secondly, the peak intensities of MA-ZIF-8 and ED-ZIF-8 material at around 3136 cm⁻¹ were significantly enhanced, and at 2960 cm⁻¹ and 2930 cm⁻¹, the intensities of the antisymmetric stretching vibration peaks of -CH₃ and -CH₂ increased, too. Thirdly, after the modification, a new N-H stretching vibration peak appeared at about 3136 cm⁻¹, signifying the successful introduction of N-H bond into MMEN-ZIF-8, MA-ZIF-8, and ED-ZIF-8 materials. Fourthly, the antisymmetric stretching vibration peaks of -CH₃ and -CH₂ increased at around 2960 cm⁻¹ and 2930 cm⁻¹ after the modification, indicating that two groups -CH₃ and -CH₂ were introduced after modification. In summary, after ZIF-8 materials are modified with different organic amine groups, N-H bonds have been successfully introduced. The thermal stability of amine@ZIF-8 was evaluated by TGA experiment under N₂ flow from 30°C to 800°C (see FIGURE S2). It can
3.2. CO₂ and N₂ Adsorption on Amine@ZIF-8 at Ambient Temperature

3.2.1. CO₂ Adsorption Isotherms on Amine@ZIF-8 Materials. Figure 5 exhibits the CO₂ adsorption isotherms of amine@ZIF-8 materials at different temperatures (298 K, 288 K, and 273 K). Clearly, the CO₂ adsorption capacities of amine@ZIF-8 materials increased dramatically at each temperature. At 298 K, their CO₂ amounts adsorbed were in the following way: MA-ZIF-8 > MMEN-ZIF-8 > ED-ZIF-8 > ZIF-8. Moreover, by comparison with the original ZIF-8, the CO₂ adsorption capacities on MA-ZIF-8, MMEN-ZIF-8, and ED-ZIF-8 increased by 118.2%, 90.2%, and 29.8%, respectively. This may be caused by the obvious increase in the BET surface area and micropore pore volume of amine@ZIF-8 materials [52]. In addition, the N-H group introduced would also promote their adsorption performance toward CO₂.

3.2.2. N₂ Adsorption Isotherms on Amine@ZIF-8 Materials. Figure 6 displays the N₂ adsorption isotherms on amine@ZIF-8 materials at different temperatures (298 K, 288 K, and 273 K). It can be observed that the N₂ adsorption capacities of amine@ZIF-8 materials significantly increased. And, the order of their adsorption capacity for N₂ is as follows: MA-ZIF-8 > MMEN-ZIF-8 > ED-ZIF-8 > ZIF-8. Moreover, compared with the original ZIF-8 material, the adsorption capacity of MA-ZIF-8, MMEN-ZIF-8, and ED-ZIF-8 for N₂ increased by 42.2%, 33.3%, and 15.0%, respectively. The increase might be due to the increased specific surface area and total pore volume after amine modification.

3.3. Adsorption Selectivity of CO₂ vs. N₂ on Amine@ZIF-8 at Ambient Temperature. The ideal adsorbed solution theory (IAST) developed by Myers and Praunitz was proved to be an efficient method to evaluate the adsorption equilibrium of gas mixtures and selectivity using single-component isotherms [45]. Before carrying out the IAST simulation, the single-component adsorption isotherms of CO₂ and N₂ were separately fitted by the dual-site Langmuir-Freundlich (DSLF) equation (see equation S1).

Figure 7 presents the single-component isotherms and the DSLF fitted ones. Obviously, the DSLF model can be applied favourably to fit the single-component adsorption data. From the fitting parameters listed in Table 2, it can be observed that the correlation coefficients R² are all up to 0.9999, implying the well fitted single-component isotherms using the DSLF model. Figure 8 exhibits predicted selectivities of amine@ZIF-8 materials as a function of total bulk pressure for equimolar CO₂ and N₂ mixtures at 298 K. Clearly, the CO₂/N₂ selectivity of amine@ZIF-8 materials decreased with the increase of pressure. Moreover, the adsorption selectivities of CO₂/N₂ on amine@ZIF-8 materials are always higher than those of ZIF-8, particularly in the low-pressure region. Furthermore, the CO₂/N₂ selectivity on MA-ZIF-8 is the highest in the pressure range. And, the CO₂/N₂ adsorption selectivities on the amine@ZIF-8 were in the order of MA – ZIF – 8 > ED – ZIF – 8 > MMEN – ZIF – 8 > ZIF – 8. Especially, at 0.01, 0.5, and 1.0 bar, the CO₂/N₂ selectivities of MA-ZIF-8 were up to 31, 16, and 14, respectively, which is almost three times of those of the original ZIF-8.

3.4. Isosteric Heat of Adsorption. The isosteric heat of adsorption (Qₜₛ) determines the regeneration temperature of adsorbents used during a PSA or TSA process. The enthalpies of CO₂ adsorption (at 273 K, 288 K, and 298 K) on ZIF-8, MA-ZIF-8, ED-ZIF-8, and MMEN-ZIF-8 materials were calculated with the virial method [57, 58]. Figure 9(a) shows the Qₜₛ of CO₂ on the amine@ZIF-8 materials. Obviously, at the very beginning of adsorption, the Qₜₛ values were in the following order: MA – ZIF – 8 > MMEN – ZIF – 8 > ED – ZIF – 8 > ZIF – 8, suggesting a much stronger interaction between CO₂ and amine@ZIF-8 frameworks. Besides, the Qₜₛ of CO₂ evidently decreased with the increase of CO₂ amounts adsorbed on the amine@ZIF-8. This phenomenon can be attributed to the surface heterogeneity of the amine@ZIF-8 samples. Figure 9(b) shows that Qₜₛ of N₂ adsorption on the amine@ZIF-8. As compared to Figure 9(a), it is visible that the Qₜₛ of N₂ on each of the material was lower than that of CO₂, confirming the favorable selectivity of the modified ZIF-8 materials for CO₂/N₂. Moreover, the Qₜₛ of N₂ on the amine@ZIF-8 are all almost independent of the N₂ uptake, indicating the weak interaction between N₂ and the modified ZIF-8 material. In addition, the Qₜₛ of CO₂ on ED-ZIF-8, MMEN-ZIF-8, and MA-ZIF-8, respectively, all gets higher, and the Qₜₛ of N₂ turns lower than that of original ZIF-8 at meantime. As a consequence of that, the CO₂/N₂ selectivities of the amine@ZIF-8 all become higher in comparison with those of ZIF-8.
3.5. Cyclic Adsorption-Desorption Performances of CO$_2$ on MA-ZIF-8 Material. In order to assess the reusability of CO$_2$ on the modified ZIF-8, we further performed the CO$_2$ adsorption-desorption cycle test on MA-ZIF-8 material. Figure 10 presents the variation curves of CO$_2$ uptake on MA-ZIF-8 material during four continuous cycles of CO$_2$ volumetric adsorption and desorption experiments at 298 K. It can be seen that after four adsorption-desorption cycles, the CO$_2$ desorption efficiency was higher than 99%, and only about 0.01 wt% CO$_2$ remains on the adsorbent. This indicated that the adsorption of CO$_2$ on the MA-ZIF-8 sample was reversible, and the MA-ZIF-8 sample had good regeneration performance. In addition, the shapes of the four adsorption-desorption cycle curves were analogous, denoting that MA-ZIF-8 was very stable and suitable for CO$_2$ adsorption.

Figure 11 presents the six gravimetric CO$_2$ adsorption-desorption cycles for MA-ZIF-8, where the desorption processes were evaluated at 125°C and 150°C, respectively. As it was noted, after each desorption process, an obvious decrease can be observed. Furthermore, when the desorption temperature increased from 125°C to 150°C, there was only a slight variation in the weight of MA-ZIF-8. For MMEN-ZIF-8 and ED-ZIF-8, similar phenomenon can be observed (see Figures S3 and S4). Therefore, the desorption temperature has little effect on the CO$_2$ capture during cycles. It also can be concluded that 125°C is enough for the regeneration of amine@ZIF-8 materials.
4. Conclusions

The as-synthesized ZIF-8 material was successfully modified with methylamine, ethylenediamine, and N, N’-dimethylethylenediamine by using a postsynthetic method to enhance its adsorption capacity and selectivity toward CO\textsubscript{2}. The BET surface areas of MA-ZIF-8, ED-ZIF-8, and MMEN-ZIF-8 increased by 118.2%, 29.8%, and 90.2%, respectively, in comparison with ZIF-8. Moreover, the N-H groups were grafted into the surfaces of the amine-modified samples. In addition, the three amine@ZIF-8 materials (MA-ZIF-8, ED-ZIF-8, and MMEN-ZIF-8) all had higher CO\textsubscript{2} adsorption capacities in contrast to ZIF-8 samples, increasing by 110.5%, 49.4%, and 64.8%, respectively. This enhancement was mainly because of their larger surface areas and stronger interaction between CO\textsubscript{2} and the Lewis basic amine groups. The IAST theory was employed to predict the adsorption equilibrium and selectivity from the single-component isotherms. The amine@ZIF-8 materials all showed larger CO\textsubscript{2}/N\textsubscript{2} selectivity than that of ZIF-8, particularly in the low-pressure region. Moreover, at 0.01, 0.5, and 1.0 bar, the selectivities of CO\textsubscript{2}/N\textsubscript{2} on the MA-ZIF-8 were separately up to 31, 16, and 14, which is almost three times of that of ZIF-8. The Q\textsubscript{st} of CO\textsubscript{2} adsorption on the
MA-ZIF-8, MMEN-ZIF-8, and ED-ZIF-8 all become higher, while the $Q_a$ of N$_2$ on these samples was slightly lower as contrast to that on ZIF-8. Furthermore, six gravimetric CO$_2$ adsorption-desorption recycle runs on MA-ZIF-8, MMEN-ZIF-8, and ED-ZIF-8 indicated the good repeatability and feasibility of the modified ZIF-8 for CO$_2$ capture, highlighting the possibility of using MA-ZIF-8 for industrial CO$_2$ adsorption and separation.

**Data Availability**

The data used to support the findings of this study are included within the article.

**Conflicts of Interest**

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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**Supplementary Materials**

Concentrations of MA, ED, and MMEN used in the postsynthetic modification processes, DFT pore size distributions, thermal gravimetric analysis, and six gravimetric CO$_2$ adsorption-desorption cycles of the modified ZIF-8 materials are shown in the Supplemental Material. Figure S1: DFT pore size distributions for ZIF-8 and amine-modified ZIF-8 materials. (a) MA@ZIF-8; (b) ED@ZIF-8; (c) MMEN@ZIF-8. Figure S2: thermogravimetric (TG) profiles of ZIF-8 and modified ZIF-8. (a) ZIF-8 and MA samples; (b) ZIF-8 and ED samples. Figure S3: six gravimetric CO$_2$ adsorption-desorption cycles on the MMEN-ZIF-8 at 298 K and desorption at 125°C and 150°C, respectively. (a) 125°C; (b) 150°C. Figure S4: six gravimetric CO$_2$ adsorption-desorption cycles on the ED-ZIF-8 at 298 K and desorption at 125°C and 150°C, respectively. (a) 125°C; (b) 150°C. Table S1: concentration gradients of MA, ED, and MMEN used in the ZIF-8 postmodification process. Table S2: textural properties of the ZIF-8 samples prepared using different synthesis and purification conditions. (Supplementary Materials)

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