

Polyethyleneimine entwine thermally-treated Zn/Co zeolitic imidazolate frameworks to enhance CO₂ adsorption

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Abstract—In order to solve the problems of deficient CO₂ adsorption sites on Zn/Co zeolitic imidazolate frameworks(ZIFs), Zn/Co ZIFs were thermally treated to promote physical adsorption sites on Zn-N and Co-N bonds and then impregnated with polyethyleneimine (PEI) to promote -NH- and -NH₂- chemical adsorption sites. The CO₂ adsorption capacity detected on Micromeritics ASAP 2020C increased by 53% to 1.07mmol/g at 298K and 1bar, when Zn/Co ZIF was treated at optimal temperature of 450 °C to obtain the maximum Me-N₂ unsaturated adsorption sites. This was because of a partial cleavage of coordination bonds between Zn-N, Co-N, C=N and C-N along with dissociation of rationally free methyl groups in the framework ligands, which was supported on density functional theory (DFT) calculation. The Zn/Co ZIF treated at 450 °C and then impregnated with 40wt% PEI exhibited the highest CO₂ adsorption capacity of 1.82 mmol/g under the condition of at 298K and 1bar, which was 2.6 times higher than that of raw Zn/Co ZIF. In addition, this adsorbent is proved to be regenerable and stable during 9 cycle CO₂ adsorption-desorption tests, therefore, PEI- thermally treated Zn/Co ZIF exhibits a very promising application in CO₂ capture from flue gas and natural gas.

Keywords—CO₂ capture, adsorption, ZIF, PEI

I. INTRODUCTION

The rapid development of global industrialization has resulted in growing concentrations of carbon dioxide(CO₂) in the atmosphere, which has become a major environment problem[1] CO₂ is traditionally removed in gas purification application by using alkanolamines, such as monoethanolamine(MEA)[2], diethanolamine(DEA)[3], and methyldiethanolamine(MDEA)[4, 5].However, this chemical absorption technology suffers from high regenerative energy consumption, solvent loss, and corrosion, which hinders extensive application[6].

Thus, it is crucial to develop innovative sorbent materials achieving efficient separation of CO₂.

Recently, a new class of microporous solid materials known as metal organic framework (MOFs) have emerged as potential adsorbents for effective separation and purification of gas mixtures[7-9].Despite the high number of novel MOFs synthesized, only a very limited number of them display satisfactory CO₂ capture performance at low pressure or ambient temperature because of the weak interaction between CO₂ and framework structure[10, 11]

Post-synthetic amine functionalization has been shown to be effective in improving the CO₂ adsorption capacity of MOFs by exploiting the high affinity between CO₂ and the amine groups[12-14]. Functionalization of magnesium-based MOFs with diamines has been widely reported to improve the CO₂ working capacity of the solids while increasing their CO₂/N₂ selective factor compared with their unmodified counterpart[15, 16]. Zeolitic imidazolate frameworks(ZIFs), a MOF sub-family containing a sodalite-type cage similar to zeolites and imidazole bridging with the metallic node(e.g., Zn and Co)[7], have high thermal dynamic stability, chemical and moisture stability. Dual metal Zn/Co ZIFs is a sub-family in ZIFs that is constructed by an easy and straightforward room temperature technique using both Zn(NO₃)₂ and Co(NO₃)₂ as the metal precursors and 2-methylimidazole as the linker [7]. Besides, the preparation of ZIFs is more convenient for large-scale industrial CO₂ removal applications[18]. The only drawback of ZIFs is the lower CO₂ working capacity compared to the top-performing MOFs. Hence, it is important to enhance the CO₂ adsorption capacity of ZIFs via amine functionalization. To the best of our knowledge, the literature on this approach is scarce in last decade. Xian et al. synthesized novel PEI-impregnated ZIF-8 (PEI@ZIF-8) composites for CO₂/N₂ separation[19]. In addition to post-synthetic amine modification of MOFs, the CO₂ adsorption capacity of MOFs can be also increased by some simple methods. In 2014, Srinivas Gadipelli et al.

modified the structure of ZIF-8 by conducting a thermal treatment in a nitrogen atmosphere. This treatment resulted in the CO₂ adsorption capacity of ZIF-8 increasing from 0.7 mmol/g to 1.79 mmol/g (1bar, 298K) [21].

In this study, a novel PEI-thermally treated Zn/Co ZIF adsorbent was synthesized by impregnation of PEI (MW=600g/mol) on Zn/Co ZIF adsorbents thermally treated at specific temperatures. The effect of the treatment temperature on the CO₂ working capacity of Zn/Co ZIF was revealed by XPS, FTIR, XRD and SEM analysis. Subsequently, PEI was impregnated on the samples in varying amounts and the CO₂ adsorption isotherms were obtained.

II. Figures and Tables

Fig. 1 shows the N₂ adsorption-desorption isotherms and the BJH pore size distributions of the Zn/Co ZIF samples treated at various temperatures. The BET surface areas of the Zn/Co ZIF samples treated at 400, 450, 500 °C were 1257, 1063, and 158 m²/g, respectively, while the mean pore size were 2.23, 2.72 and 9.77nm, respectively. The SEM images of the raw Zn/Co ZIF, Zn/Co ZIF treated at various temperatures and PEI impregnate treated Zn/Co ZIF sample are given in Fig.2. The Zn/Co ZIF particles were regular dodecahedron and the particle diameter ranged from 100 to 120nm. SEM images confirm that PEI was successfully loading on the Zn/Co ZIF particles.

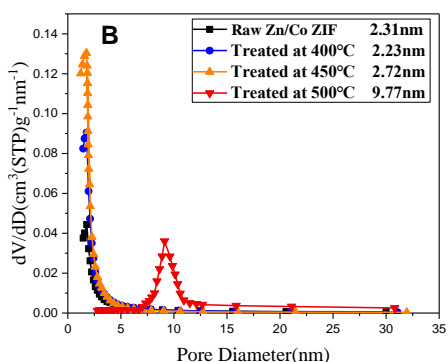
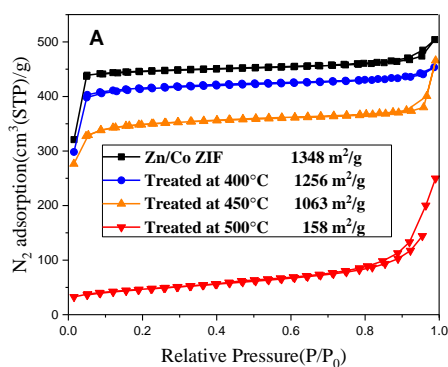
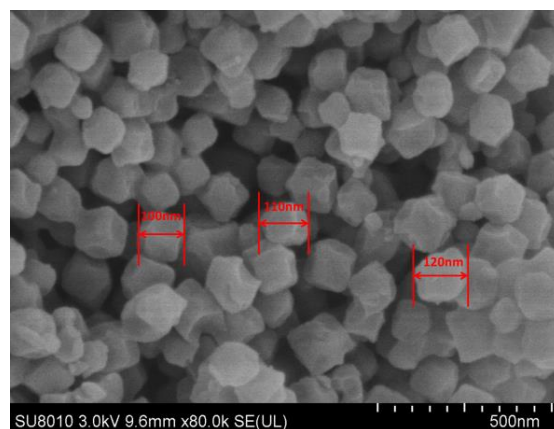
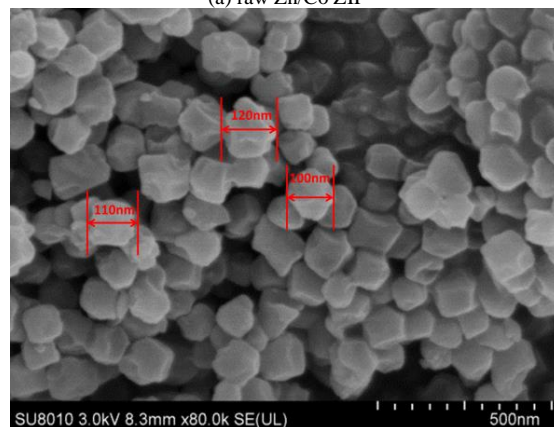


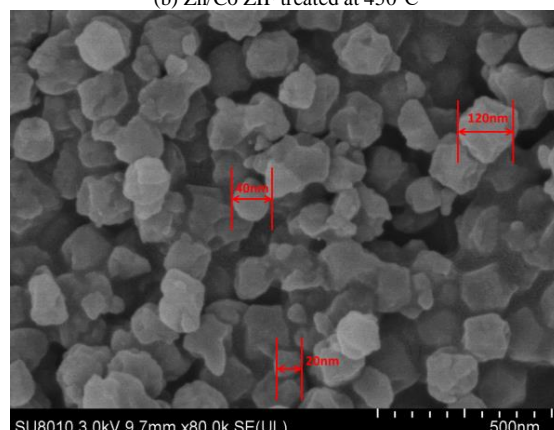
Figure 1 N₂-adsorption desorption isotherm (A) and pore size distributions (B) of Zn/Co ZIF adsorbents treated at various temperature.



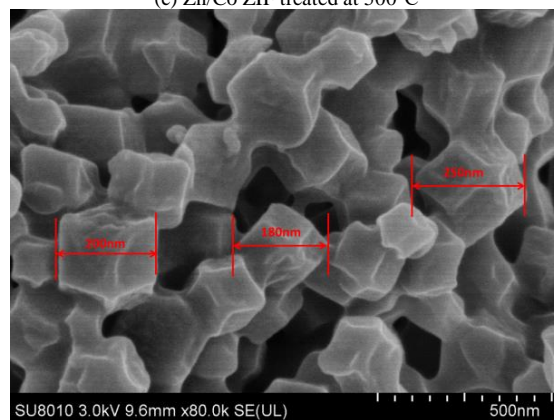
(a) raw Zn/Co ZIF



(b) Zn/Co ZIF treated at 450°C



(c) Zn/Co ZIF treated at 500°C



(d) Zn/Co ZIF (treated at 450°C) impregnated with polyethyleneimine (PEI)

Fig 2. SEM images of Zn/Co ZIF adsorbents treated at various temperatures

In order to obtain the optimum temperature for treating the Zn/Co ZIF samples, three different temperatures (400, 450, and 500 °C) were used for the initial Zn/Co ZIF. The CO₂ adsorption isotherms of the samples were measured at 298 K, Fig. 3 (a). Undoubtedly, the optimized structure of Zn/Co ZIF samples after the thermal treated produced a remarkable enhancement of the CO₂ adsorption capacity. MOFs having open metal centers (such as Mg-MOF-74 and, HKUST-1) exhibited significantly higher working capacities compared to fully coordinated metal MOFs (e.g., ZIF-8, ZIF-67, and MOF-5)[12,16]. The metals (Zn or Co) in the raw Zn/Co ZIF were fully coordinated (Me-N₄, each metal center coordinate to four nitrogen atoms of four discrete ligands). After the thermally treated, part of the Zn-N and Co-N bonds were broken, and the bonding mode between the metal and nitrogen shifted from Me-N₄ to Me-N₂ (each metal center coordinated to two nitrogen atoms of two discrete ligands). Hence, the enhancement of the CO₂ working capacity for Zn/Co ZIF after the thermal treatment could be mainly explained by the presence of exposed Zn and Co sites[20]. The CO₂ adsorption capacity of the Zn/Co ZIF sample treated at 450 °C increased by 53% (from 0.70 mmol/g to 1.07 mmol/g) compared to the raw Zn/Co ZIF. As the treated temperature increased to 500 °C, the framework decomposed and this was reveal by the marked reduction of the CO₂ uptake, (only 0.75mmol/g at 298 K and, 1 bar). This high temperature let to the decomposition of the main framework structure, negatively affecting the CO₂ adsorption performance. Fig. 3 (b) shows the CO₂ adsorption isotherm of PEI-thermally treated Zn/Co ZIF samples with different loadings measured by our homemade experiment instrument at 298 K and, 1bar. CO₂ adsorption capacity of the samples first increased and then decreased with the increasing of PEI loading. The CO₂ working capacity of the 20, 30, 40, 50, 60 wt% PEI impregnated samples were 1.27mmol/g(0.27mol CO₂/mol NH₂ group), 1.48mmol/g(0.21mol CO₂/ mol NH₂ group), 1.82 mmol/g (0.20mol CO₂/ mol NH₂ group), 1.39mmol/g(0.12mol CO₂/ mol NH₂ group), 1.35mmol/g(0.10mol CO₂/ mol NH₂) group, respectively, exhibiting higher working capacities than the non-impregnated samples.

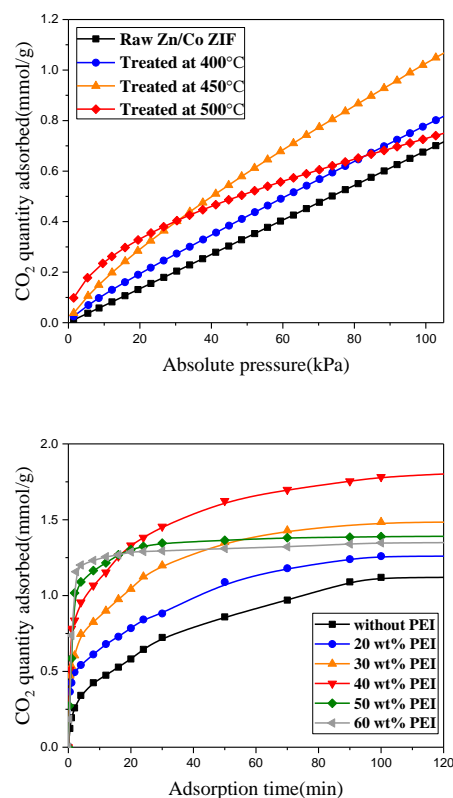


Fig.3 CO₂ adsorption isotherms (at 298 K): Zn/Co ZIF adsorbents treated at various temperatures(a), Zn/Co ZIF adsorbents (treated at 450 °C) impregnated with polyethyleneimine (PEI) (b)

III Conclusions and recommendations

A novel PEI- thermally treated Zn/Co ZIF adsorbent through postsynthetic functionalization was synthesized for the capture of CO₂. This solid was firstly treated below the decomposition temperature and then functionalized with amine groups (PEI) to enhance the CO₂ working capacity. The CO₂ adsorption capacity of Zn/Co ZIF improved significantly (by 53%), from 0.7 mmol/g of raw Zn/Co ZIF to 1.07 mmol/g at 1bar and 298K, under the optimal treatment temperature condition at 450 °C. The CO₂ working capacity increased with PEI loading and reached a maximum for 40wt% PEI (1.82mmol/g at 298 K, 1 bar) , 2.6 times higher than that of the raw Zn/Co ZIF.

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