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Design of ZIF-8/ion copolymer hierarchically porous material: Coordination effect on the adsorption and diffusion for carbon dioxide

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ABSTRACT

The novel CO_2 adsorbent (ZPMAC) was constructed by a facile in-situ growth of ZIF-8 onto the surface of a mesoporous amino-functionalized ion copolymer (PMAC). The existence of coordination effect between Zn^{2+} from ZIF-8 and nitrogen atom from the amino-alkyl chain in PMAC changed the pore structure of substrate for enhancing the amount of CO_2 capture and accelerated the rate of CO_2 adsorption. The ion copolymer PMAC, pristine ZIF-8 and hierarchically porous hybrid material ZPMAC were characterized by SEM, TEM, TGA, N_2 adsorption-desorption, FT-IR, XRD, UV, and XPS techniques. It was observed that ZIF-8 loaded on the surface of PMAC uniformly and tightly. In the growth process of ZIF-8 nanoparticles, zinc ions were firstly coordinated with nitrogen atoms of the amino-alkyl chain in PMAC sample, and subsequently reacted with 2-methylimidazole to generate ZIF-8 nanoparticles. Obviously, the surface areas of ZPMAC increased and smaller peak value of micropore distribution was generated by the strong coordination interaction between ZIF-8 and PMAC after ZIF-8 modified. Meanwhile, the appearance of hierarchically porous structure was conducive to the transportation and adsorption of CO_2 molecules, thus enhancing the amount of CO_2 capture and the rate of adsorption effectively. This study was intended to design a new kind of hybrid materials by the means of in-situ growth of MOF materials onto the IL-type polymers and further study the influences of the structure and properties of ionic-type hybrid materials on the absorption capacity to meet the requirements of various applications.

1. Introduction

Global warming is a problem of great urgency because of extreme climate change [1]. CO_2, one of the primary greenhouse gas, is emitted into the atmosphere increasingly owing to the continuous combustion of fossil fuel. Considering the incessant pressure for economic growth among developed and developing nations, despite increasing utilization of renewable energy, inexpensive and accessible fossil fuel is still the mainstream of energy consumption [2–5]. Therefore, the need for effective CO_2 adsorbents is of critical importance.

Speaking of the CO_2 capture, common methods are physical adsorption and chemical absorption. Alkaline amine based solutions, such as monoethanolamide (MEA) [6–8], are currently utilized for CO_2 absorption that chemical interaction between amino groups and CO_2 molecules occurs. However, several drawbacks including the regenerations of higher energy consumption and chemical instability, together with equipment corrosion worry the researchers [9,10]. The same as liquid absorbent, ionic liquids (IL), room temperature molten salt consisting of cations and anions, exhibits several advantages including higher chemical and thermal stability, negligible vapor pressure, wider liquid range and better ion conduction relative to amine solutions [11–14]. Hence, ILs have widespread applied in many fields [15–18], and it could overcome the weaknesses of amino solutions mentioned above in the process of CO_2 adsorption. Recently, researchers have made amine-functionalized ILs (AILs) to capture CO_2 dependent on its outstanding designability properties [19–21]. Zhang's group designed a dual amino-functionalized cation-tethered IL and was investigated as a potential absorbent for CO_2 capture. The results demonstrated that the CO_2 uptake of per mole AILs could reach up to 1.08 mol at 20 °C under ambient pressure [22]. However, the high viscosity of AILs restricts its extensive application.

Solidification of IL monomers into corresponding solid polymers is an effective approach. Polymer ionic liquids, known as poly(ionic liquid)s (PIL), shows prominent characteristics of both IL and

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macromolecule polymers, which makes them excellent CO_2 adsorbents combining these properties of two materials [23–25]. Mesoporous poly (ionic liquid)s (MPILs), as a well-developed pore structure solid material, exhibit much higher CO_2 absorption capability, faster absorption or desorption rate compared with IL monomers [26,27]. Meanwhile, their admirable designability characteristic, the same as temperature ILs, tailor materials to enhance CO_2 adsorption capacity. Wang et al. reported that a basic amine-functionalized mesoporous imidazolium-PIL exhibited high CO_2 adsorption capacity up to 1.4 mmol g^{-1} at 0 °C under atmospheric pressure [28]. Nevertheless, the CO_2 adsorption capability is still not strong, and the study on heightening this performance is of great necessity.

Metal organic frameworks (MOFs) is a class of inorganic-organic porous coordination polymer with ligands connecting metal-containing units [29–31], attracting large attention because of its large surface area, high porosity and facile synthesis, which offer potential in high CO_2 uptake [32–34]. Yaghi et al. reported a zinc-based MOF, MOF-210, was synthesized successfully with ultrahigh CO_2 storage capacity of 2870 mg g^{-1}, since its Brunauer-Emmett-Teller (BET) and Langmuir surface areas were capable of reaching 6240 and 10400 m^2 g^{-1}, respectively [35]. Zeolite imidazolate frameworks (ZIFs), a kind of MOFs, not only possesses the advantages of MOFs, but also exhibits high chemical and thermal stability like inorganic zeolites [36,37]. Moreover, smaller crystal size of ZIFs, such as ZIF-8, make it easier to be supported on another solid matrix in order to exhibit the advantages of a certain portion in the hybrid materials adequately or improve the performance of both two, while retain the original morphology [38,39]. For example, Zhu et al. showed that synthetic MOFs-alginate composite kept the shape of alginate and played an effective role in removal of dye from water in the meanwhile, largely due to the characteristics of MOFs [40]. In our previous works [41], we constructed the composite by the means of in site self-assembly of metal organic framework HKUST-1 with mesoporous SBA-15 after metal ions coordinating with the surface silanol groups. The interaction between metal ions and surface silanol groups induced structural changes and was in favor of increasing CO_2 uptake. Nonetheless, there are few studies on enhancing the CO_2 uptake of solid adsorbents utilizing the IL-copolymers and MOFs hybrid materials, especially the further investigation on the effects of the coordination interactions and micropore channels on the CO_2 adsorption capacity.

Herein, a hydrophobic mesoporous ionic copolymer (PMAC) was prepared via radical copolymerization of amine-functionalized imidazolium-IL monomer and divinylbenzene (DVB), and subsequently was modified by ZIF-8 on the surface of PMAC through a facile in-situ growth. The modified copolymer (ZPMAC) with the hierarchically porous construction showed excellent adsorption and diffusion properties in comparison to pure support PMAC. In particularly, smaller peak value of micropore distribution was generated in the growth process due to the interaction between PMAC and ZIF-8, which was conductive to store CO_2 molecule in the low pressure. The adsorption kinetic data further verified the characteristic of hierarchically porous structure on fast CO_2 capture.

2. Experimental

2.1. Synthesis of ionic liquid monomer

The ionic liquid monomer, 1-aminoethyl-3-vinylimidazolium bromide hydrobromide ([AVIM]Br·HBr) was prepared following the literature [42]. 1-vinylimidazole (4.71 g, 0.5 mol) and 2-bromoethylamine hydrobromide (10.25 g, 0.5 mol) were dissolved in acetonitrile (50 ml). The solution reacted at 78 °C for 24 h under the protection of nitrogen atmosphere then with a magnetic stirrer. Afterwards, the supernatant liquid of reaction mixture was poured out and the remaining parts was washed with anhydrous ethanol three times. The ionic liquid monomer was obtained after drying at 60 °C under vacuum. ^{1}H NMR (D_2O, 298 K, 300MHz, ppm) δ: 3.56 (t, 2H, -*Im***CH**2-), 4.61 (t, 2H, -NC**H**2-), 5.41 (dd, 1H, = CH**H**), 5.79 (dd, 1H, = C**H**H), 7.14 (dd, = **CH**-*Im*), 7.66 (s, 1H, C-**CH**-N of *Im*), 7.82 (s, 1H, N-**CH**-C of *Im*), 9.18 (s, 1H, N-**CH**-C of *Im*). The symbol *Im* stands for imidazole ring, and the ^{1}H NMR spectra was shown in Fig. S1.

2.2. Synthesis of mesoporous amino-functionalized copolymer

The hydrophobic mesoporous amino-functionalized copolymer (PMAC) was synthesized by radical copolymerization of [AVIM]Br·HBr and DVB with azobisisobutyronitrile (AIBN) as a initiator [43]. We took the molar composition of IL/DVB/AIBN/ethanol/water = 1:1:0.05:100:110 for synthesis. Here, [AVIM]Br·HBr (1.5 g, 5mmol) and DVB (0.65 g, 5mmol) were dissolved in the mixed solvent of ethanol/water (40 ml), where the mixture of ethanol/water with volume ratio was 3:1. The AIBN (0.04 g) was added when the two precursors above dissolved absolutely. The mixture was stirred at 80 °C for 24 h under reflux with nitrogen atmosphere. The mesoporous amine-functionalized copolymer PMAC was obtained by being filtrated and washed with ethanol and water each three times, dried at 60 °C under vacuum soon afterwards. Scheme for the synthesis of PMAC was shown in Fig. S2.

2.3. Synthesis of ZIF-8 nanoparticles

ZIF-8 nanoparticles were prepared following the previous report [44]. In brief, 0.6 g of zinc nitrate hexahydrate and 1.32 g of 2-methylimidazole were both dissolved in 22.6 g of methanol respectively, named as A solution and B solution. ZIF-8 nanoparticles were finally obtained by stirring the mixture of A solution and B solution with 24 h, washing with methanol and drying at 75 °C overnight.

2.4. Synthesis of ZIF-8 modified amino-functionalized copolymer

We prepared ZIF-8 modified hierarchically porous amino-Functionalized copolymer (ZPMAC) through facile in-situ growth following the synthetic method of ZIF-8. The obtained PMAC (0.4 g) was dispersed into excess zinc solution (dissolving zinc nitrate hydrate (4 g) in ethanol) thoroughly by ultrasound with the purpose of dispersing Zn^{2+} on the surface of PMAC. The suspension liquid was then washed with methanol three times to remove the redundant Zn^{2+}, and the intermediate product PMAC@Zn^{2+} was got. The obtained mixed solid PMAC@Zn^{2+} was then added into 2-methylimidazole solution (dissolving 2- methylimidazole (0.825 g) in methanol (35 ml)) and stirred for 24 h so that ZIF-8 nanocrystal could grow onto the surface of mesoporous copolymer successfully. We would get the composite modified by ZIF-8 after centrifuging and washing three times with ethanol, drying at 60 °C under vacuum overnight finally.

2.5. Adsorbent characterization

Scanning electron microscope (SEM) images were taken from HITACHI S-4800 field emission scanning electron microscope. Thermogravimetric analysis (TG) was performed on a STA449 thermal analyzer at a heating rate of 10 °C/min in air with the temperature range of 30–900 °C. Fourier transform infrared (FT-IR) spectra was obtained by a Thermo Nicolet 6700 spectrometer (United States) in the 4000-400cm^{-1} region (KBr discs). Transmission electron microscope (TEM) images were provided with the JEM-2100 (JEOL) electron microscope. X-ray diffraction (XRD) measurements were carried out with a Smartlab TM 9KW from 5° to 80° with a scan rate of 10°/min. N_2 adsorption-desorption isotherms were performed at −196 °C on the BELSORP-MINI analyzer to provide Brunauer-Emmett-Teller (BET) surface area, pore volumes and pore size distribution. The samples were pretreated at 120 °C for 4 h under vacuum before measurement. ^{1}H nuclear magnetic resonance (NMR) spectra were performed om a