Chinese Journal of Chemical Engineering 23 (2015) 1275–1282

Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJChE

Separation Science and Engineering

Gas adsorption in shaped zeolitic imidazolate framework-8☆

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ARTICLE INFO

Article history:
Received 23 April 2014
Received in revised form 4 December 2014
Accepted 11 January 2015
Available online 2 April 2015

Keywords:
ZIF-8
Shaping
Gas adsorption
Model reduction
Materials

ABSTRACT

Zeolitic imidazolate framework-8 (ZIF-8) was prepared through a solve-thermal reaction method and then shaped using different additives. The influence of the shaping conditions on the microstructure of the shaped samples was characterized by the XRD, BET, and SEM techniques. The results demonstrate that the compressive strength of the various shaped tablets is greatly increased and capable of meeting the industrial requirements compared to the unshaped ZIF-8 and that the loss rate of specific surface areas was maintained at 10% after the addition of 10%(by mass) binder and 10%(by mass) solvent. The adsorption isotherms of CO_2, CH_4, C_3H_8, and C_3H_6 on powdery ZIF-8 and the shaped tablets (T-shaped ZIF-8, C-shaped ZIF-8, and N-shaped ZIF-8) were determined through volumetric measurements under different pressures and temperatures (298.2, 323.2, and 348.2 K). The adsorption capacities of the gases on both the ZIF-8 powder and the shaped tablets follow the order $C_3H_6 > C_3H_8 > CO_2 > CH_4$. Furthermore, the results show that the adsorption capacities of the gases on the shaped tablets are lower by approximately 10%–20% than those on the powdery ZIF-8. In fact, the adsorption equilibrium isotherms for CO_2, CH_4, C_3H_8, and C_3H_6 on both powdery and shaped ZIF-8 can be well described by the Langmuir equation.

1. Introduction

Zeolitic imidazolate frameworks (ZIFs), which are a new type of porous materials, possess several remarkable features, such as controllable structures, adjustable pore size, enormous specific surface area, and particularly good hydrothermal stability. The application of ZIFs in gas adsorption, membrane separation, energy storage, and catalysis has gradually aroused extensive attention [1–5]. In the family of ZIFs, ZIF-8 is a typical compound with a sodalite (SOD) zeolitic-type structure, in which the tetrahedral Si (Al) sites are replaced by transitional metal Zn and coordinated by dimethyl imidazoles as ligands to form four-ring and six-ring ZnN_4 clusters. The aperture size of ZIF-8 is 0.34 nm, and the diameter of the largest sphere is 1.16 nm [6–8]. Unlike traditional zeolites, which have rigid frameworks and stable and small pore sizes, ZIF-8 is capable of capturing molecules with pore diameters larger than 0.34 nm [9–12]. Hu *et al.* [13] characterized the physical structure, chemical stability, and adsorption and separation performances of ZIF-8 adsorbent and emphasized that ZIF-8 is likely more promising for practical applications. Yamamoto *et al.* [14] examined the adsorption properties of the synthesized ZIF-8 nanoparticles in a T-type micromixer and found that the amount of adsorbed N_2 gas is higher than that obtained with a conventional ZIF-8 sample. Huang *et al.* [15] investigated the effect of temperature on the adsorption of gases in ZIF-8 using a combination of experimental measurements and molecular simulations and demonstrated that the effect of temperature is significant for pure gas adsorption. Hu *et al.* [16] explored the storage behavior of ZIF-8 and found that is it strongly dependent on pressure. Liu *et al.* [17] measured single-gas permeation data for ZIF-8 membranes and found that the diffusivity value decreases with increasing molecular size. Zhang *et al.* [18] modified the ZIF-8 powder to ED-ZIF-8, which exhibits improved selectivity for CO_2/N_2 separation. In addition, Evangelia *et al.* [19] simulated the self-diffusivity and the collective diffusivities of a gas mixture of CO_2 and CH_4 with the ZIF-8 and revealed that the ZIF-8 ligands had a significant influence on the adsorbate transportation.

Although ZIF materials have been widely studied in the field of gas separation, almost all of these studies were limited to the use of powdery particles, which may face large fluid resistance in practice due to the limitation associated with the pressure drop [20]. Thus, powdery ZIF-8 needs to be shaped prior to its usage for adsorption purposes. Thus, we decided to study different shaping methods with respect to ZIF-8. It has been noted that the shaping process reduced the surface area of the original material and may lead to a partial collapse of the structure [21]. Therefore, a shaping technology that can retain the micro-structure of ZIF-8 is urgently needed. In this regard, Sumida *et al.* [22] used activated carbons and zeolite 13×, which were loaded with MEA and TEA through solution processing, to study the performance achieved with capturing CO_2 and found that both materials exhibited a decreased CO_2 capacity compared with the bare material.

☆ Supported by the National Natural Science Foundation of China (21176010, 21476009, 21406007, and U1462104).
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http://dx.doi.org/10.1016/j.cjche.2015.01.015
1004-9541/

Ferreira *et al.* [23] noted that Cu-BTC extrudates presented a reduction of 63% in their adsorption capacities for C_3H_8 and C_3H_6 compared with Cu-BTC powder. Finsy *et al.* [24] indicated that the adsorption capacities of N_2 decreased by 32% in contrast to the pure MIL-53 powder. These findings indicate that the shaping process may have significant influence on the properties of the resulting material.

The purpose of this work was to resolve the key bottlenecks limiting the practical application of ZIF-8 by screening suitable additives and determining the superior shaping conditions. The adsorption isotherms of various single gases (CO_2, CH_4, C_3H_8, and C_3H_6) on powdery ZIF-8 and shaped tablets were measured at different temperatures and pressures to investigate the influence of the shaping conditions on the adsorption performance.

2. Experimental

2.1. Preparation of ZIF-8

The ZIF-8 nano-crystal was prepared according to reported procedures [7] with certain modifications. The molar ratio of 2-methylimidazole to zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$] was adjusted to 3:1 with several attempts. The solid mixtures of 2-methylimidazole (0.791 g) and $Zn(NO_3)_2 \cdot 6H_2O$ (0.955 g) were dissolved in *N,N*-dimethylformamide (DMF, 72 ml) in a PTFE-lined container. The mixed solution was sealed, heated to 140 °C in an oven, maintained at this temperature for 24 h, and cooled naturally to room temperature. After the mother liquor was removed from the mixture in the filtration bottle, white powders were collected from the upper layer. These powders were then washed three times with absolute methanol and dried in air for 30 min.

2.2. Shaping process of ZIF-8

In this work, the process used to shape ZIF-8 was implemented based on tableting technology. Methylcellulose, bentonite, silica, alumina, SB powder (high-quality pseudoboehmite, Sasol, Germany), talc powder, and sesbania powder were chosen as binders, and deionized water, nitric acid, citric acid, and trichloroacetic acid were chosen as solvents. Accurately weighed ZIF-8 powder (sieved through a 120 mesh) was mixed with different amounts of one of the binders and solvents at room temperature and then pressed at 1.5 kN in the TDP-1.5 single push tablet pressing machine. The shaped ZIF-8 tablets, which exhibited a diameter of 9 mm and a thickness of 6 mm, were dried naturally for 30 min and heated at 120 °C for 2 h in the oven.

2.3. Characterization

Scanning electron microscopy (SEM) images were acquired on a Hitachi S4700 instrument (Hitachi Ltd., Tokyo, Japan) using an accelerating voltage of 20 kV. The pretreated sample was coated onto the silicon wafer and sprayed with gold.

The X-ray diffraction (XRD) patterns were measured on a Bruker D8ADVANCE X-ray diffractometer (40 kV, 40 mA) using CuK_α ($\lambda = 0.15418$ nm) radiation at a scanning rate of $1(°)\cdot min^{-1}$ from 5° to 50°.

The BET specific surface areas and were determined through an N_2 adsorption–desorption experiment using an ASAP2020 physical sorption instrument at 77 K. Prior to the adsorption experiment, the sample was heated at 200 °C for 8 h, and the BET specific surface area was measured by a Brunauer–Emmett–Teller model.

The compressive strength of the shaped tablets was assessed using the DL-II type intelligent particle strength tester (Penghui Ltd., Dalian, China), which recorded the pressure value at which the shaped tablet started to exhibit crazing. Eight samples for each shaping condition were randomly measured, and the average value was considered the final compressive strength.

2.4. Gas adsorption experiments

The adsorption equilibrium isotherms of CO_2, CH_4, C_3H_8, and C_3H_6 on the powdery ZIF-8 and three types of shaped tablets (using different solvents during the shaping process) were measured at temperatures of 298.2, 323.2, and 348.2 K by a static adsorption device as presented in Fig. 1.

The volume of the adsorption cell was measured by charging the helium gas at different pressures and calculating the volume ratio relative to the reference cell *via* the second-order Virial equation. In this way, the volumes of reference cell and adsorption cell are determined to be 122.1 and 78.0 cm^3, respectively. Prior to the adsorption measurement, the adsorbent must be evacuated at 423.2 K until no mass loss was observed. A certain amount (about 10 g) of adsorbent was then carefully loaded into the adsorption cell in an attempt to reduce the adhesive attrition and ensure the precise determination of the free volume. The single adsorbed gas was then introduced into the reference cell under a given pressure and passed through the adsorption cell. Both the adsorption and reference cells were immersed in a water bath controlled by an advanced digital temperature controlling system with an uncertainty of 0.1 K. The adsorption equilibrium was assumed to have been reached when the system pressure measured by a pressure gauge (ExSAF) with an uncertainty of ± 1 kPa was invariable. A typical equilibrium was 30 min per point. During the measurement, the dead volume of the gas pipeline between the adsorption cell and reference cell was also taken into account to improve the accuracy of the experimental data, and this volume was calculated from the internal volumes of the valves and pipeline and found to be approximately 3.51 cm^3.

3. Results and Discussion

3.1. Structure of ZIF-8

Fig. 2(a) and (b) presents the surface morphologies of the powdery ZIF-8 and shows the clear outer cubic surface of the ZIF-8 unit cells. The XRD pattern of ZIF-8 is displayed in Fig. 2(c), and the characteristic peaks match well with those reported by Park *et al.* [7], who clearly indicate the existence of ZIF-8 crystals. Fig. 2(d) presents the N_2 adsorption-desorption analysis, which showed a high adsorption capability for N_2 of up to 400 $cm^3\cdot g^{-1}$. The adsorption curve belongs to Type I, in line with the Langmuir model. Moreover, the N_2 adsorption–desorption analysis displayed that the BET surface area of ZIF-8 is 1186.5 $m^2\cdot g^{-1}$, and the Langmuir surface area is 1746.7 $m^2\cdot g^{-1}$. These values are consistent with those reported in previous studies [7,25], in which ZIF-8 was synthesized in a reactor that was 20 ml smaller than that used in the present study. The pore size distribution was obtained by BJH and DFT methods, as shown in Fig. 2(e) and (f). The pore diameters mainly locate at the range of 1.0–1.4 nm, and the volumes of micro and total pores are 0.5933 and 0.8087 $cm^3\cdot g^{-1}$, respectively.

3.2. Selection of shaping binders and solvents

3.2.1. Influence of binders on specific surface areas of the shaped samples

In this work, seven types of binders (methyl cellulose, silica, bentonite, alumina, SB powder, talc powder, and sesbania powder) were selected. Moreover, the influence of solvent concentration (using SB and talc powders as binder, and nitric acid as solvent at different concentrations) on specific surface area of shaped ZIF-8 was investigated, and the results are listed in Table 1. It can be seen that BET surface area is the highest when using 10% (by mass) nitric acid as solvent for both SB and talc powders.

Each binder, as well as 10% (by mass) nitric acid, was combined with powdery ZIF-8. The experimental results are given in Table 2. Due to the minimal loss of specific surface areas obtained with talc powder and SB powder, one of these binders was used as the single binder in the subsequent experiments. In addition, the specific areas obtained with silica or