Research article

Optimization of CO₂ Adsorption and Physical Properties for Pelletization of Zeolite 5A

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Abstract

Keywords

zeolite 5A; zeolite pellet; CO₂ adsorption; pelletization; powder shaping process This research investigated the effects of compression force, compression time, and addition of bentonite binder on zeolite 5A pelletization. Carbon dioxide (CO₂) adsorption of zeolite 5A pellets was tested in a laboratoryscale packed-bed reactor at 298 K, atmospheric pressure and 2 l/h flow rate. Zeolite 5A pellets were prepared using a pelletization technique at 200-400 MPa compressive force, 5-15 min compression time, and with 0-15% wt. of bentonite binder. The specific surface area and density of zeolite 5A pellets increased with increase of compression force. Compression force led to increase in specific surface area and resulted in an agglomeration of zeolite pellets, making CO₂ molecules more difficult to become active sorbent. The addition of bentonite into zeolite 5A pellets with more compression time resulted in the reduction of specific surface area. The compression force and mass fraction of the binder were found to offer significant control over CO2 adsorption capacity. No addition of binder, 200 MPa compression force and 5 min compression time resulted in a maximum CO₂ adsorption capacity of 3.64 mmol CO₂/g. This research indicated that zeolite 5A pellets have a beneficial effect and high potential as an adsorbent, especially in terms of CO2 adsorption and environmental applications.

1. Introduction

Current research indicates that within months of the novel coronavirus outbreak, a dramatic reduction in CO₂ emissions occurred. As a result, the world's energy demand has drastically reduced. The International Energy Agency (IEA) noted that global CO₂ emissions were 30.6 Gt for 2020, down nearly 8% from 2019 [1]. However, global land and ocean surface temperatures were the highest in 141 years.

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[2]. According to global carbon dioxide emission data in 2020, industrial plants had the highest levels of CO₂ emissions (22%), therefore, industrial plants have been seen as beneficial places to research, and to develop technology to be used in managing and reducing CO₂ in the future [3]. The most common adsorbents used for CO₂ emission reduction are activated carbon, metal organic frameworks (MOFs), polymers, and zeolite.

Zeolite is a highly stable solid that is more environmentally resistant than other materials. The most interesting thing about zeolite is its open, cage-like framework structures that can trap other molecules inside it. Generally, zeolite is in the form of powder, and this causes various restrictions on its use in industry such as loss as dust, high pressure drops through a reactor, changes in flow properties, and caking and lump formation [4, 5]. The shaping process of the zeolite into pellets can produce a uniform pack that allows an optimal use of the tank volume. The pellets have better mechanical properties, are hard and friction resistant, and can be handled easily. Production of adsorbent materials in industrial processes is a major challenge in facilitating the use of materials and making the process closer to commercialization.

Previous pelletization research has shown that the absorbent material that incorporates PEI impregnated MCM-41, when pelletized has a CO₂ adsorption capacity that is approximately 10% lower than that of the powder adsorbent when the adsorbent is pelleted at 18-35 mesh [6]. The efficiency of SBA-15 supported PEI pellets were evaluated for their selective CO₂ capture. The powder material was pelletized under pressure of 7600 psig for 10 min. The pelletization results of the pelletized SBA-PEI material having the same adsorption kinetics as the powder sorbent slightly decreased the adsorption capacity of approximately 18% [7]. A recent study carried out by Peterson et al. [8] showed the effects of pelletization pressure on the physical and chemical properties of MOF, Cu₃(BTC) and UiO-66. Both Cu₃(BTC) and UiO-66 which had been pressed at 1,000 and 10,000 psig pressure into pellets; they were also partially degraded in porosity. Rezaei et al. [9] showed that surface area and pore volume were significantly reduced in amine-based pellet samples at 5,000 psig compared to the adsorbent powders due to pore blockage and collapse of pore structures under pressing. There were slow absorption kinetics and poor internal mass transfer for CO₂ adsorption at 1,000 psig, which were similar to those observed at 5,000 psig pressure. For pelleting under 1,000 psig pressure, the resulting pellets exhibited adsorption properties similar to adsorbent powder. Despite the preliminary investigations described above, there is no systematic study in the literature that shows to what extent pelletization pressure affects the physical properties of zeolite adsorbents. This research is therefore concerned with establishing the suitable factors and conditions for zeolite pelletization in order to promote optimum CO₂ adsorption efficiency.

Zeolite pellets are commercially prepared by mixing zeolite powder and inorganic binders such as bentonite clays, which provide structural mechanical stability during and after preparation [10]. Silicalite, ZSM-5 and zeolite A monoliths were also prepared using bentonite as a binder, and air separation efficiency was assessed [11-13]. However, the binder reduced the purity and degraded the effectiveness of the sorbent by blocking adsorbate access to zeolite crystals [11, 14-19]. Puccini *et al.* [20] studied the ratios of layered graphite binder and zeolite to provide good hardness and structure. The binder content in excess of 40 wt% reduced the good properties. In addition, zeolite NaY nanoparticles were shaped into spherical beads using bentonite clay. It is intended to improve the mechanical stability of the spherical beads. However, adding the binder reduces the N₂ adsorption capacity by 19.2% at 77 K and reduces the maximum Sr²⁺ adsorption per granulation by 35% [21]. Pelletization is commonly compression or formation prior to size enlargement and applied mechanical forces [22-24]. However, mechanical forces and hold time will affect the properties of the pellet such as pore volume.

Therefore, it is worthwhile to investigate the adsorption characteristics of pelletized materials to explain how they compare with their powders. The motivation behind the current work is therefore to identify suitable pressures for pressing zeolite 5A adsorbents and making zeolite-binder pellets that can facilitate the utilization of such materials in practical CO₂ adsorption processes. This research

investigated key factors for physical properties and CO₂ adsorption capacity of the zeolite pellet, including 200-400 MPa compression forces, 5-15 min compression times and 0-15% wt. of bentonite.

2. Materials and Methods

Commercially available zeolite 5A powder used for pelletization in this research was purchased from Thaisilicate Chemicals Co., Ltd., Thailand. The bentonite clay used as a binder of zeolite pellets was purchased from NIC Interchem Co., Ltd., Thailand. The pelletization processes were conducted in three parts: 1) shaping without binder and different compression forces, 2) shaping with optimum force and different wt.% of binder, and 3) shaping with optimum binder and different compression time.

2.1 Shaping without binder and different compression forces

Shaping zeolite pellets without binder and different compression forces was used to find the optimum compression force of the pelletization process. Zeolite powder without binder was poured into each hole of the mold and then pressed by a hydraulic press at 200, 300 and 400 kPa for 10 min. The zeolite pellet was then dried to remove moisture at 378 K for 4 h. This was continued at 773 K for 3 h (Figure 1).

2.2 Shaping with optimum force and different wt.% of binder

The zeolite powder was mixed with water and 5, 9 and 15 wt. % bentonite, respectively. The mixture was kneaded to obtain a paste mixture. The paste was pelletized into the form of pellets, using a hydraulic press at optimum compression force for 5 min. The zeolite pellet was then dried and calcined at 773 K for 3 h, as shown in Figure 1b.

2.3 Shaping with optimum binder and different compression time

The zeolite powder was mixed with optimum wt. % of bentonite binder and water. The pelletization with the hydraulic press machine was compressed at 300 kPa force for 5, 10 and 15 min. The zeolite pellet was dried and calcined as shown in Figure 1.

The resulting zeolite pellets were cylindrical shaped with 0.5 cm diameter and 0.5 cm height (Figure 1). The zeolite pellet samples were named according to their pelletizing condition; B0P2T5, B0P3T5, B0P4T5, B5P3T5, B9P3T5, B15P3T5, B5P3T10 and B5P3T15. The number after each letter B denoted wt.% of bentonite binder, after each P denoted compression force, and after each T represented the compression time.

The morphology of the zeolite pellet was examined by SEM photographs taken with a FEI model QUANTA 450 SEM system. It was operated at an accelerating voltage of 15 kV. The obtained pellets with good shape were analyzed via SEM. The zeolite pellet samples for SEM analysis were prepared by immersing the pellets in liquid nitrogen and cutting them in half to examine the inside of the pellets. The specific surface area was evaluated from nitrogen adsorption isotherm measurements. The surface area and porosity analysis were done using a BELL model BELSORP-MINI apparatus. The surface area and porosity analyzer were measured on whole broken pellets.

Zeolite 5A pellets of 1 g were packed into the adsorption column. The adsorption column was heated in a furnace connected with a CO_2 analyzer (Handheld carbon dioxide meter, GM 70). The CO_2 adsorption of each zeolite pellet was tested at atmospheric pressure, 298 K and 2 l/h CO_2 flow rate. The CO_2 adsorption capacity was defined in equation (1).

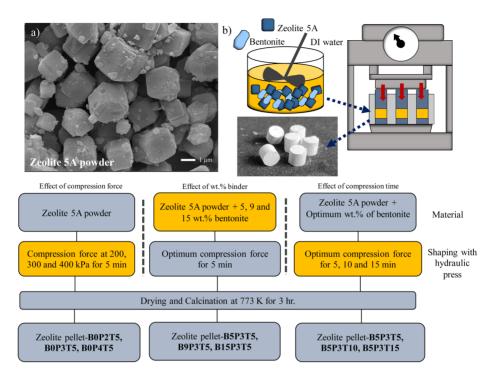


Figure 1. Schematics of the pelletization process of zeolite 5A and bentonite binder by hydraulic press

$$q_e = \left(\frac{C_0 - C}{W}\right) * \frac{vt}{M_w} \tag{1}$$

Where q_e is the equilibrium adsorption capacity, C_0 and C are the concentrations initial and equilibrium of CO_2 respectively; v is CO_2 flow rate; M_W is the molecular weight of CO_2 ; W is the weight of zeolite pellet and t is time.

3. Results and Discussion

3.1 Effect of compression forces

Compression force is one of the main pelletization factors that affect the physical properties and CO_2 adsorption capacity of zeolite 5A pellets. The characterization results from SEM photographs shown in Figure 2 indicate that increase in compression force made the zeolite 5A particles within the pellet come very close together. This resulted in CO_2 adsorption capacity decreasing to 3.64, 3.37 and 1.89 mmol/g at compression force of 200, 300 and 400 kPa, respectively.

The inconsistent results suggested that the surface area of pellets was increased but the CO₂ adsorption was reduced due to the increasing compression force. Because the zeolite 5A particles were compressed and broken into small pieces, the zeolite 5A particles were smaller than the original ones and the resultant density of the zeolite 5A pellets was increased from 1294 to 1593 kg/m³. Zeolites 5A

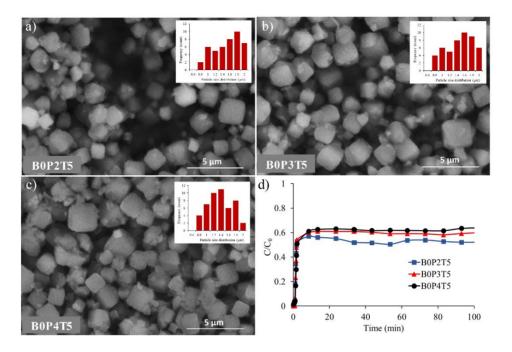


Figure 2. Scanning electron micrograph of zeolite pellets with different compression forces (a) 200, (b) 300 and (c) 400 kPa, (d) breakthrough curves of zeolite pellet with different compression forces

was inferred to be of 1.9 μ m average crystals size. When zeolite pellets were compressed at 400 kPa, the particle size was reduced to 1.3 μ m size approximately, as shown in Figure 2. When the zeolite particle size was reduced, the surface area increased; however, the zeolite particles were also closed up. Therefore, it was difficult for CO₂ molecules to reach the zeolite particles. Lower mass transfer resulted in lower CO₂ adsorption efficiency at 400 kPa compression force.

3.2 Effect of bentonite binder

The adsorbent material is very important in the adsorption process. Fluid flow through the adsorbent during operating may break or degrade the adsorbent material chemically. Moreover, attrition/abrasion occurs between the adsorbent materials and also between the adsorbent material and reactor wall. As mentioned above, dust problems such as blocking of valves have occurred while running an adsorption process. In order to avoid dust formation, binders must be used appropriately. However, an excess amount of binder may affect the CO₂ adsorption efficiency, physical properties, pore volume and surface area, and also compressive strength of zeolite pellets. Therefore, the optimum conditions for adding binder to zeolite 5A powder to form zeolite 5A pellets were carried out. The pelletization of zeolite pellets was done at 300 kPa compressive force since the results in section 3.1 had shown that there was a large gap between the zeolite crystals in the pellets at 200 kPa (Figure 2a), and zeolite crystals were broken into smaller pieces at 400 kPa (Figure 2c). Figure 3 showed the results of adding bentonite binder. In fact, the pore size must be appropriate to allow the adsorbed molecules to penetrate within. Increasing the bentonite binder at 5, 9, 15 wt.% decreased pore volume of pure zeolite 5A starting from the variant with no added binder from 0.2208 cm³/g to 0.1606, 0.1601 and 0.1869 cm³/g, respectively. The characteristics of the zeolite 5A powder were cubic shaped crystals of smooth surface, as shown in Figure 1a. When the bentonite binder was added, the bentonite adhered to the external surface of zeolite 5A particle, which then appeared as fibers bound between zeolite particles, as SEM micrographs shown in Figures 3a, 3b and 3c. The red dotted circles indicate the formation of "bentonite-bridges" on the zeolite interface that formed after the calcination resulted in pore volume reduction with an increase of bentonite content.

In addition, previous research on bentonite and CO_2 adsorption found that the CO_2 adsorption capacity varied from 0.11 to 0.32 mmol/g at 298-318 K and 1 atm [25-27]. It was seen that there was very low adsorption capacity due to the structure of bentonite, which was composed of H_2O and cations. These molecules that were involved in high relative humidity hindered the access of CO_2 molecules within the interlayer spacing. Furthermore, the CO_2 adsorption capacity on zeolite 5A powder in this research was 3.8 mmol/g at 298 K, 1 atm. When shaping zeolite powder into the pellets with bentonite, there was a pressure drop in the column, and the product could be easily regenerated and stored. However, zeolites with binder showed a slight decrease in CO_2 adsorption efficiency compared to those without binder.

The percentage of bentonite was varied and ranged from 5 to 15 wt.%. This was done in order to identify the optimal amount needed to produce good hardness and ensure the porous structure of the pellets. However, when the bentonite binder was increased, there was a drop in CO₂ adsorption, as shown in Figure 3d. In any case, the zeolite pellets require a suitable mixing of zeolite powder and binder to provide sufficient mechanical strength to resist attrition loss for most commercial applications. The optimum binder content was at 5 wt.%, which produced enough compressive strength when compared with 9 wt.% binder additions because the increased binder at 9 wt.% increased the compressive strength by 60 kPa. Moreover, increases in binder result in higher production costs and lower adsorption capacity.

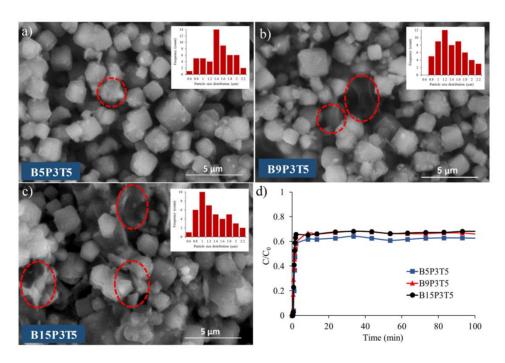


Figure 3. Scanning electron micrograph of zeolite pellet with different wt.% bentonite binder (a) 5, (b) 9 and (c) 15 wt.% bentonite, (d) breakthrough curves of zeolite pellet with different wt.% bentonite binder

3.3 Effect of compression time

Compression time is another factor that affects the physical properties of zeolite pellets. When compression time was too low, the zeolite powder pelletized had a low density that led to easy cracking. Figure 4 shows the morphology of zeolite pellets made with different compression times. From the SEM photographs in Figures 4a, 4b and 4c, there was no different size for pellets made with different compression times of 5, 10 and 15 min. However, when the compression time was increased to 15 min, the CO₂ adsorption capacity decreased, as shown in Figure 4d. This was due to the restriction of movement of molecules permanently from long-compression time. It could be one reason for the lower adsorption efficiency compared to zeolite powder.

Figures 2d, 3d and 4d show the breakthrough curves with different conditions of compressive forces, bentonite binder, and compressive time, respectively. Interestingly, at low compression force, a low amount of bentonite binder content and short compression time, the breakthrough curve might not have reached equilibrium, but these conditions still provided good CO₂ adsorption. This was due to the density of zeolite pellet, as shown in Table 1. With less bulk density, the pore size within the pellet was larger than the effective pore size in high density pellet. The immediate breakthrough curves at high compression force, high amount of bentonite binder content and long compression time suggested that CO₂ molecules were not able to access the pores of the zeolite 5A pellets.

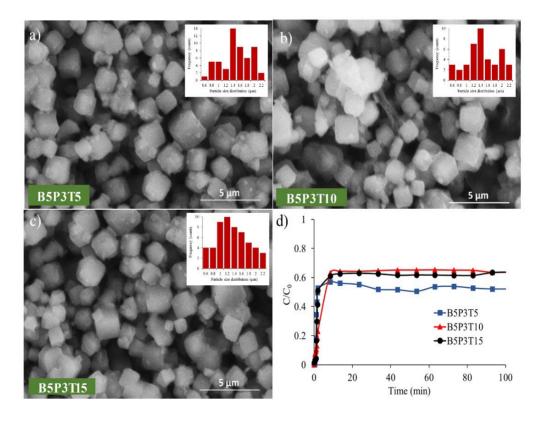


Figure 4. Scanning electron micrograph of zeolite pellet with different compression times (a) 5, (b) 10 and (c) 15 min, (d) breakthrough curves of zeolite pellet with different compression times

Table 1. Bulk density of zeolite 5A pellet

Zeolite 5A pellet	Bulk density (kg/m³)
B0P2T5	1294
B0P3T5	1324
B0P4T5	1593
B5P3T5	1630
B5P3T10	1640
B5P3T15	1898
B9P3T5	1719
B15P3T5	1823

Interestingly, the CO₂ adsorption capacity on the zeolite pellets decreased when the compressive force was increased from 200 to 400 kPa. Meanwhile, the surface area slightly increased from 353.43 to and 365.22 m²/g (Figure 5a) as discussed in section 3.1. From Figure 5d, the increase of bentonite binder content at 5, 9 and 15 wt.% bentonite resulted in increased pellet compressive strength of 505.3, 562.2 and 705.8 kPa, respectively, while the surface area and CO₂ adsorption capacity decreased (Figure 5b). For compression times of 5, 10 and 15 min, the density of the zeolite pellet increased by 1630, 1640 and 1898 kg/m³, respectively. Additionally, the BET surface area and CO₂ adsorption capacity values did not follow the theoretical trend. This suggested that at 15 min compression time, the BET surface area was greatly reduced and the CO₂ adsorption capacity had decreased when compared to the result at 5 min, as shown in Figure 5c. It was owing to the reduction of the amount of active sorbent and blocked pores [20, 21].

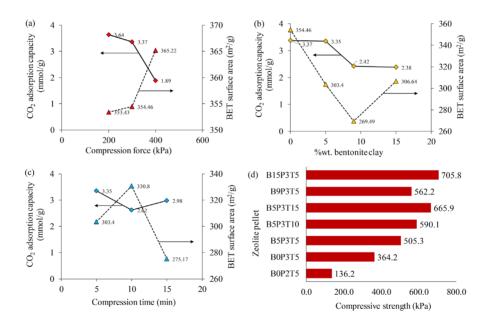


Figure 5. CO₂ adsorption capacity and BET surface area with different pelletized conditions, (a) different compression forces (b) different wt.% bentonite binder (c) different compression times and (d) compressive strength of zeolite pellets

However, excess amounts of binder, compression times and compression forces may have affected the CO₂ adsorption efficiency and physical properties including pore volume, surface area and the compressive strength of zeolite pellets, as shown in Figure 5d.

The CO₂ adsorption capacity of the obtained zeolite 5A pellet in this research reached a maximum at 3.64 mmol CO₂/g. It is considered that CO₂ adsorption efficiency of zeolite 5A pellets was higher than commercial zeolite CaA pellet [28] but it was little lower than the CO₂ adsorption efficiency of zeolites CaA bead [29].

In addition, the structural diversity of the zeolite structure produces a wide range of properties, including geometric characteristics (dimensions of channels, connections and pore space), which are directly related to adsorption applications and physical properties such as mechanical behavior. Indeed, many three-dimensional porous structures have been found in zeolites that display elastic anisotropy properties. Zeolites have elastic properties, and when compression force is applied; the molecules are arranged in a disorganized way due to the slight displacement of the molecules in the zeolite structure. Conversely, when a compression force is removed, these molecules will return to their original position. If the compression force has been applied too long, it can affect the movement of molecules permanently. This could be one reason for getting low adsorption efficiency compared to zeolite powder. Mechanisms of CO₂ adsorption include e physical adsorption and chemical adsorption. This research dealt primarily with physisorption; the target molecules are attracted to the surface of pore walls within a high surface-area sorbent by Van der Waals forces. Therefore, the density of pellets increased (less pore volume) with increasing compression force, amount of binder, and compression time, making it more difficult for CO₂ molecules to reach active sorbents. As a result, the internal mass transfer of CO₂ in zeolite pellet is lower [30, 31]. A schematic illustration of the CO₂ sensing mechanism for the interior of the zeolite pellet ash is shown in Figure 6. Therefore, the optimum conditions for pelletization highlighted in this research can be beneficial for expansion to industrialscale adsorption processes.

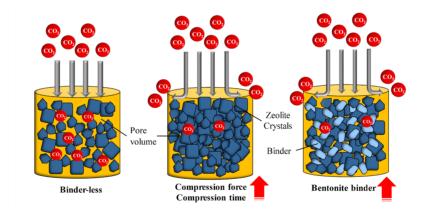


Figure 6. Schematic illustration of CO₂ adsorption mechanism for interior zeolite pellet

4. Conclusions

Zeolite 5A pellets were formed by pelletization with a hydraulic press. The impact of pelletization on the physical properties and CO₂ adsorption of the zeolite pellets were evaluated by comparing zeolite pellets pelletized under 200, 300 and 400 kPa pressure, with compression times of 5, 10 and 15 min and 0, 5, 9 and 15 wt.% of bentonite binders. The B0P2T5, without the binder, gave the highest CO₂

adsorption capacity of 3.64 mmol/g under 200 kPa pressure and 5 min of compression time with 353.43 $\rm m^2/g$ surface area. The binder could increase the mechanical strength of the zeolite pellets but it may block the pores, resulting in reduction of the BET surface area and $\rm CO_2$ adsorption capacity. The addition of 15 wt.% bentonite binder gave the highest compressive strength of 705.8 kPa. Increased compression force at 400 kPa compression force resulted in the zeolite particle size decreasing from 1.9 $\rm \mu m$ in zeolite powder size to 1.3 $\rm \mu m$ in zeolite pellet, and creating a large BET surface area of 365.22 $\rm m^2/g$. On the other hand, the large surface area did not increase the $\rm CO_2$ adsorption capacity. For the reason, the zeolite particles were closer together which reduced the gaps and made it difficult for the $\rm CO_2$ molecules to reach and enter the zeolite pores.

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