Study of the effect of organic binders on 13X zeolite agglomeration and their CO$_2$ adsorption properties

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ABSTRACT

The aim of the present research is the shaping of zeolite 13X and study the effect of singular and binary system of binders. For this purpose, zeolite 13X was successfully synthesized under hydrothermal conditions. Different combinations of polyvinyl alcohol (PVA) and polyethylene glycol (PEG) have been used for shaping. Physical properties of granules were measured by nitrogen adsorption-desorption and results showed that increasing the binder content up to a certain amount, enhanced the physical properties but with a further increase in binder content surface area decreases. Also it was found that mechanical strength was decreased with increasing binder content after burnout.

Keywords: Zeolite 13X, Agglomeration, Organic binder, Mechanical strength, CO$_2$ adsorption

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1. Introduction

Zeolites are crystalline porous aluminosilicates having pores and channels. Zeolite structure is made of alumina and silica tetrahedra. These tetrahedra share their oxygen atoms and make three dimensional framework [1]. Each Alumina tetrahedron in the framework has a negative charge which is balanced by alkali and alkaline earth cations present in the voids of zeolite [2]. These cations are mobile due to their weak attraction and can be exchanged [3]. Silica to alumina ratio is a very effective parameter in properties of zeolite and it can vary considerably between one to about 100 or more [4]. Zeolite 13X is a type of zeolite with Silica to alumina ratio of about 1-1.5 and have Na\(^+\) ions in its structure [5].

13X zeolite has the faujasite structure which consists of ten sodalite cages connected by hexagonal prisms. This structure forms an inner cavity of 7.4 Å that is called supercage [6] due to high aluminum presence and the appropriate number of cations. Therefore it has high ion exchange capacity and high affinity to polar molecules [7]. Zeolite X is of particular interest because of its remarkable properties and use as adsorbent [8-10], catalyst [11, 12], molecular sieve [13] and ion-exchanger [14, 15]. Zeolite X has attracted widespread attention in many applications of modern science and technology, including removal of metal ions [16, 17] adsorption of gasses such as hydrogen [18, 19], methane [20], oxygen [21], and carbon dioxide [22-26].

CO\(_2\) is one of the natural gas component, which is produced by combustion of fossil fuels and as by-product in industrial processes. This gas plays an important role in global warming, so capturing it by adsorption is one of the most important approaches in industrial applications [27].
There are several options for CO₂ adsorption [28-30] but zeolite 13X due to its high adsorption capacity, high adsorption rate and high selectivity is one of the appropriate adsorbents [31].

Synthesized zeolites are in powder form and must be agglomerated and make granules having high mechanical strength and high adsorption capacity to be used in industrial processes. Granulation is the process of joining particles together using a binder and form granules. Binders are added to mixture in low quantities which create bridges between particles and hold them together [32].

Binders can be classified into two different types: inorganic binders and organic binders [33]. Kaolin, bentonite, kaolinite and montmorillonite are aluminosilicate clays that are traditionally used as a binder but influence the properties of shaped zeolites [34]. The preference of organic binders is that unlike inorganic binders they decompose under oxidizing conditions and leave no residue so that don’t block micropores.

To optimize the properties of granules, different organic binders in several percentages were used and then mechanical and physical properties of products studied. In this project we used polyvinyl alcohol (PVA) and polyethylene glycol (PEG) as organic binders.

2. Materials and Methods

2.1. Synthesis of zeolite 13X

Colloidal silica (Aldrich, 30 wt.% suspension in water), sodium aluminate (Merck), sodium hydroxide (Merck) and deionized water were used to get a hydrogel solution having the molar
composition of $3.5\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:2.9\text{SiO}_2:150\text{H}_2\text{O}$ [35] for the hydrothermal synthesis of zeolite 13X. The mixture was aged at room temperature for 40 minutes while it was mixing with a magnetic stirrer and was transferred into a Teflon lined hydrothermal synthesis autoclave reactor and was heated at 90 ℃ for 48 hours. The product was filtered and washed with deionized water until the pH value reaches to about 9. It was dried at room temperature and finally milled in an agate mortar.

2.2. Granulation by using PVA

The aqueous solution containing 2, 4, 6, 8 and 10 wt.% of PVA (Merck, 72000 g/mol, hydrolyzed >98%) with respect to zeolite powder were made. After that were mixed with milled zeolite powder and appropriate amount of deionized water, to converting the mixture into the paste. Prepared pastes were shaped into the spherical granules having the average diameter of 3.2 mm using lab sized disc type granulator and were dried at room temperature for 24 hours. In order to remove of the water and prevent appearance of cracks in the products, granules were dried in an electric oven at 70 ℃ for 2 hours. Finally, samples were placed in a ceramic crucibles and debinded and calcined in the muffle furnace at thermal program according to figure 1.

Insert here figure 1

2.3. Granulation by using PVA and PEG
The effect of adding PEG (Merck, 20000g/mol) as a binder plasticizer was studied. The aqueous solutions containing 0.25, 0.5, 1.5 and 3 wt.% of PEG with respect to zeolite powder were mixed with zeolite 13X powder, 6 wt.% PVA solution and required amount of deionized water and converted the mixture into pastes and were shaped. Then granules were dried at room temperature and after that again were dried at 70 °C for 2 hours. Furnace temperature for Debinding and calcination was as follows: from room temperature increased to 450°C at 7 °C/min, and then held for 1 hours. Finally, the temperature increased to 700°C at 10°Cmin−1 and then was held at 290°C for 2 hours, as shown in figure1.

2.4. Characterization

The X-ray powder diffraction (XRD) patterns of synthesized zeolite 13X and granulated sample containing 6 wt.% PVA (after calcination at 700 °C) were taken by STOE powder diffraction system using Cu- Kα radiation (40 kV, 40 mA) of wavelength 1.54060 Å with a 0.06° step size and 1 second step time from 1 to 40°. The nitrogen adsorption-desorption isotherm, specific surface area and pore size of the samples were measured with a Micromeritics model ASAP2020 surface area and porosity analyzer at 77 K after out gassing the samples at 300 °C for 3 hours. The crush strength of samples was measured according to ASTM D 61 75-03. The morphology analysis of the samples was carried out using a scanning electron microscopy (SEM) (KYKT-EM3200). Samples were gold coated prior to measurement. Thermal analysis of samples was carried out on a Bahr STA-503 instrument. Uncalcined samples were loaded in an alumina crucible and then heated to 1200°C with heating rate of 10 °C/min under air atmosphere with a flow rate of 50 mL/min.
2.5. CO$_2$ adsorption measurement

The volumetric method was used to investigate CO$_2$ adsorption capacity of samples by setup shown in figure 2. 1g of sample was loaded in the adsorption cell and was attached to the system. The existing gas inside the system was swept out with helium. For degassing the system the valves 1, 2 and 4 were closed and other valves were opened then the vacuum pump was turned on and the system was vacuumed at the heating temperature of 250 °C for 90 minutes. Afterward valves 5, 8 and 9 were closed and the system was cooled to ambient temperature. To perform an adsorption test, the valve of ultra-high purity carbon dioxide cylinder (99.999%) and the valve 5 were opened to balance the desire pressure then valve 8 was immediately opened and the pressure in adsorption cell was decreased. The pressure of adsorption cell was decreased due to adsorption dead volume in reactor. The dead volume was measured via helium test and was subtracted from total pressure change and the exact pressure decrease due to carbon dioxide adsorption was calculated.

Insert here figure 2

3. Results and discussion

The X-ray diffraction patterns of synthesized zeolite 13X powder and prepared granules having 6% PVA after calcination at 700 °C for two hours are shown in figure 3. The XRD pattern of zeolite 13X powder matched with that of the Na-X zeolite [36] that represents the successful
synthesis. The location of the reflection lines remains constant for the granulated sample indicating that the structure of zeolite 13X was well preserved but the intensities were slightly reduced that is due to effect of calcination on crystallinity of samples.

Insert here figure 3

The SEM image of zeolite 13X powder and granulated samples using 6 wt.% and 10 wt.% PVA after calcination are shown in figure 4. The crystals of zeolite 13X powder confirm the successful synthesis. It can be seen that well regular shape and morphology are in granulated samples. In SEM image of granulated sample using 10 wt.% of PVA (figure 4c), PVA binder near of zeolite crystals indicates that removal of binder is incomplete.

Insert here figure 4

3.1. Granules prepared using PVA:

Figure 5 shows the variation in average pore size with PVA content. As seen in the figure, the average pore size of samples increased by increasing PVA content. Using more PVA amount in the paste results in forming larger pores after calcination and increase in pore size. Average Pore size of samples with 10wt.% PVA increased by 9.41% compared with samples prepared using 2wt.% of PVA binder. (From 1.8561 nm for 2% to 2.0309 nm for 10 wt.%)
It’s clear from figure 6 that for the samples prepared using different PVA percentages, with PVA increase, the specific surface area goes through a maximum and then decreases. Granules with 2 wt.% PVA had the lowest specific surface area (507.8494 m$^2$/g). Increasing binder amount to 4 and 6 wt.% increases the specific surface area to 542.7279 and 612.9750 m$^2$/g respectively. Further increase in PVA amount decreases specific surface area to 575.0992 and 531.7569 m$^2$/g for 8 and 10 wt.% respectively. Increase in specific surface area from 2 to 6 wt.% of PVA is due to vaporization of PVA and left pores after calcination but decrease in specific surface area for samples containing more than 6 wt.% amount of PVA can be related to incomplete burnout of PVA and its residual carbon. Presence of PVA binder in granule prepared using 10 wt.% as result of incomplete binder removal is obvious in figure 4c. Moreover, carbonaceous residue remained after burnout of high PVA content samples, which causes no change in total pore volume, but due to increase in average pore size, specific surface area is decreased. Variation in total pore volume and average pore size by increasing the PVA content in granules are listed in Table 1.
Table 1. Effect of PVA amount on the total pore volume and average pore diameter of granules

| PVA content | Total pore volume (cm$^3$/g) | Average pore diameter (nm) |
|-------------|-------------------------------|----------------------------|
| 2%          | 0.2911                        | 1.8561                     |
| 4%          | 0.2751                        | 1.9063                     |
| 6%          | 0.2689                        | 1.9382                     |
| 8%          | 0.2651                        | 1.9756                     |
| 10%         | 0.2640                        | 2.0303                     |

As can be seen in Figure 7, by increasing the PVA amount in the mixture the crushing strength gradually decreased. It seems that the decrease in strength is due to difference in porosity level of the samples. Pore size distribution curves of these samples are shown in Figure 8. Granules prepared using more PVA amounts, have more porosity after calcination and removing of binder and existence of more cavities in this samples reduces the mechanical strength. Crushing strength for samples having 2-10 wt.% PVA is 114.22, 63.02, 33.79, 23.03 and 19.40 N respectively.

In order to investigate the effect of PVA amount on gas adsorption of produced granules, the result of N$_2$ adsorption-desorption isotherms and CO$_2$ adsorption capacities are illustrated in
figures 9 and 10, respectively. The N\textsubscript{2} adsorption isotherms of granulated samples are a typical type I isotherm, a signature characteristics of microporous materials. As seen, N\textsubscript{2} adsorption capacity increases with PVA content up to 6 wt.% and then decreases by more increase in PVA content that this can be due to variation in specific surface area. Also, CO\textsubscript{2} adsorption capacity shows the same trend. The higher values of the CO\textsubscript{2} adsorption capacity were obtained for the granules having the highest N\textsubscript{2} adsorption capacity and specific surface area (6 wt.% of PVA).

Moreover, the thermal properties of granules containing 6 wt.% of PVA was investigated by TG/DTA analysis and the results are shown in figure 11. DTA plot of sample at 10°C/min shows a broad endothermic peak between 50 and 200°C that is due to water present in cages and channels of the zeolite framework and water trapped within the binder. This exothermic peak is associated with the mass loss at this temperature range in TGA graph. A big but sharp exothermic peak occurring from 250 to 500°C and centering at 274°C is thought to be caused by burn out of PVA. This phenomenon is shown with a small weight loss stage in TGA profile. At 889 and 943°C there are two exothermic peaks in DTA curve that are not associated with any weight loss. Therefore, these peaks should correspond to collapse of zeolite framework in two stages.
3.2. **Granules prepared using PVA and PEG**

Figures 12 and 13 illustrate the effect of PEG amount on the average pore size and specific surface area, respectively. Both average pore size and specific surface area increased with increase of plasticizer content. The values of average pore size and specific surface area for different percentages of PEG were found to be 1.9382, 1.9419, 1.9466, 1.9519, 1.9931nm and 612.9750, 622.7558, 631.4400, 645.0985, 667.2166 \( m^2/g \) for 0, 0.25, 0.5, 1 and 3 wt.% of PEG, respectively. This increase is attributed to PEG burnout after calcination.

![Insert here figure 12](image12)

![Insert here figure 13](image13)

The variation in the crushing strength with PEG amount in mixture is presented in Figure 14. As can be seen, crushing strength gradually decreases with increase in PEG content. The effect of PEG in reduction of mechanical strength is the same as PVA but since PEG is added in less amounts, causes less reduction in crushing strength. Crushing strength for samples having 0, 0.25, 0.5, 1 and 3 wt.% PEG are 33.79, 32.05, 29.91, 25.33 and 19.80 N, respectively.
The effect of PEG amount on the N\textsubscript{2} adsorption-desorption curves is illustrated in Figure 15. All samples exhibit very close isotherms and all of them correspond to typical type I. N\textsubscript{2} adsorption capacity slightly increases by increasing PEG and so increase in surface area.

Figure 16 shows the adsorption isotherms of CO\textsubscript{2} on granules prepared with different PEG amounts. By increase in PEG content value of the CO\textsubscript{2} adsorption capacity is partially increased. This increase is negligible for samples containing 0.25, 0.5 and 1wt.% of PEG.

4. Conclusions

Organic binders were used to shape the NaX zeolite powder into spherical granules. The binder content in the mixture strongly affects the properties of adsorbents. Since organic binders decompose in thermal processes, so appropriate amounts of organic binders cause to increase in average pore size, surface area and CO\textsubscript{2} adsorption capacity. Although incomplete debinding for further binder amounts, decrease in average pore size, surface area and CO\textsubscript{2} adsorption capacity
is observed. Applying large amounts of binder is considered unfavorable from mechanical strength viewpoint.

The best condition for the spherical adsorbents close to the mechanical and physical properties of products can be obtained when the amount of PVA is 6 wt.%. For samples prepared using both PVA and PEG, the 0.25 wt.% showed the best properties.
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**Table Caption:**

**Table 1.** Effect of PVA amount on the total pore volume and average pore diameter of granules

**Figure Captions:**

**Figure 1.** Thermal program of debinding and calcining

**Figure 2.** Setup for CO$_2$ adsorption measurement

**Figure 3.** XRD patterns of zeolite 13X powder (a) granule prepared using 6 wt.% PVA after calcination (b)

**Figure 4.** SEM image of zeolite 13X Powder (a) granule prepared using 6 wt.% PVA (b) and 10 wt.% PVA (c) after calcination

**Figure 5.** Effect of PVA amount on the average pore size of granules

**Figure 6.** Effect of PVA amount on the specific surface area of granules

**Figure 7.** Effect of PVA amount on the crushing strength of granules

**Figure 8.** Pore size distribution of samples prepared using different PVA percentages

**Figure 9.** Effect of PVA amount on N$_2$ adsorption-desorption isotherm

**Figure 10.** Effect of PVA amount on CO$_2$ adsorption capacity

**Figure 11.** TGA and DTA profiles of granules containing 6 wt.% of PVA.

**Figure 12.** Effect of PEG amount on the average pore size of granules

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