MACEIÓ - ALAGOAS
EBA 15
15° ENCONTRO BRASILEIRO SOBRE ADSORÇÃO
15th Brazilian Meeting about Adsorption

Microcalorimetric Study of LTA/Bentonite Shaped Pellets

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Abstract

The shaping of adsorbent materials is crucial not only to reduce pressure drop in adsorbent beds, but also to enhance the thermal and mechanical properties. In this work, commercial sodium-based zeolite Linde Type A (Na-LTA) in powder was shaped by extrusion into cylindrical beads using bentonite binder followed by calcination at 673 K for 24 h. The 2-mm beads were labeled as LTABEN15, LTABEN20 and LTABEN25 with the addition of 15, 20 and 25% of binder (w/w), respectively. Adsorption equilibrium isotherms and enthalpy of CO_2 at 298 K were measured to characterize the shaped samples and assess the adsorption mechanism.

Keywords: adsorbent shaping; LTA; bentonite; adsorption enthalpy.

1. Introduction

Adsorbent materials have a wide range of applications in separation and purification of gases [1]. Powdered adsorbents, whether synthesized or naturally mined, are often impractical for industrial use due to the difficulties of handling fine powders, which can cause significant pressure drops. To address these issues, researchers have focused on shaping adsorbents into pellets or other forms [2]. This not only improves handling but also enhances mechanical and thermal resistance, making them more suitable for industrial applications [3]. Several techniques, such as extrusion, 3D-printing, and granulation, can be employed to shape crystalline powders into different forms and sizes [4], including granules, beads, spherical or cylindrical pellets, monoliths and rods. Inorganic binders like alumina, silica, and clay play a crucial role in creating robust structures during the shaping process [5].

In this work, LTA zeolite pellets were extruded into cylindrical beads using a bentonite binder followed by calcination and tested for their mechanical and adsorption properties. The objective of this work is to assess the CO_2 adsorption mechanism on LTA/Bentonite shaped pellets using microcalorimetry.

2. Materials and Methods

2.1. Materials

The pellets were prepared using powdered 4A LTA zeolite (labeled LTA), supplied by Sigma Aldrich, as adsorbent, and the binder compound was bentonite, supplied by T-Minas Minerais Ind. Distilled water was added to obtain a moldable paste. The pellets have 2 mm of diameter and 2 to 6 mm in length, depending on how much time the extrusion was performed [5].

2.2. Methods

2.2.1. Preparation of pellets

The scheme presented in Figure 1 shows the equipment used in the preparation of the pellets.

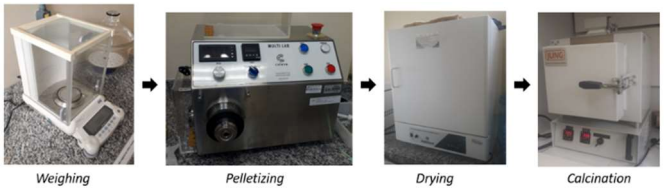

Fig. 1. Scheme of the conformation process. From left to right: *1- Analytical balance; 2- Pelletizer; 3- Stove; 4-Muffle. *Adapted from [4].*

In the first step of the extrusion process the adsorbent and the binder in powder are weighted

and then mechanically mixed with addition of distilled water, which acts as a wetting agent in the composition, giving the mixture an aspect of paste. After that, the mixture is introduced in a Multi Lab pelletizing machine from Caleva Process Solutions (United Kingdom), where pressure is applied by a rotating screw at 75 rpm in a confined space, obtaining the pellets [1]. Lastly, the pellets receive two thermal treatments: first, the water excess is dried in a stove at 373 K for 48 hours, and then the produced pellets are calcinated in a Muffle at 673 K for 24 hours, with a rate of 2 K/min.

2.2.2 Durometry

The mechanical resistance of the pellets was analyzed in an HDP-20CP Durometer from DUROControl© according to ASTM D6175. This equipment measures the max force applied to break the pellet, giving the value in kgf. A total of 15 measurements was performed for each sample, excluding the outliers (biggest and lowest values) to have a more accurate media result. After that, the values obtained were converted to MPa.

2.2.3 CO_2 Adsorption Enthalpy

The samples were also characterized using adsorption microcalorimetry at 298 K, which provides a direct measurement of the adsorption enthalpy as a function of CO_2 coverage [6].

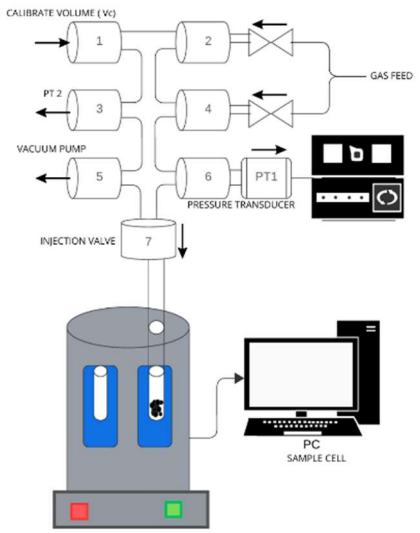

Fig. 2. Microcalorimetric setup.

This technique uses heat data to measure the parameters and effects of adsorption through the layer of CO_2 that surrounds it. This equipment consists in a manometric system which is coupled to a C80 microcalorimeter (SETARAM, France) [7]. It is an extremely sensitive experiment in which all the heat flow from the sample is captured and measured using (3D) heat sensors and data acquisition software with a resolution of 0.12 µW.

Initially, the samples are degassed, a pressure is dosed into the gauge system and then injected into the cell, with several dosages being made at different pressures, which makes it a discontinuous process. The heat peaks were integrated using Calisto® software (v1.043 AKTS-SETARAM). Figure 2 shows a schematic view of the equipment.

3. Results and Discussion

The nomenclature of the produced samples is given according to the amount of binder used, as presented in Table 1.

Table 1. Composition of the shaped samples.

sample	LTA (g)	bentonite (g)
LTABEN15	10	1.5
LTABEN20	10	2.0
LTABEN25	10	2.5

Table 2 shows the results of mechanical resistance of the produced samples. Regarding the influence of the binder content in the studied samples, it has been observed that the increase from 15 to 20% in bentonite content generated a difference of almost 10% in resistance before reaching the first point of rupture. However, a further increase in the content of binder leads to a decrease in mechanical strength, indicating that the correlation is not linear and there might be an optimum amount of binder that can be used.

Table 2. Mechanical resistance of the samples.

sample	resistance to compression (MPa)
LTABEN15	12.75
LTABEN20	13.83
LTABEN25	6.56

The shape of the CO_2 isotherms does not undergo any significant change after the pelletization (Figure 3). Furthermore, the impact of

the shaping on the CO_2 adsorption capacity is not proportional to the amount of bentonite binder, as expected. While the increase from 15 to 20% in bentonite leads to similar capacities, the increase from 20 to 25% leads to a considerable loss in CO_2 adsorption capacity. Although there seems to be no direct relationship among composition and capacity for the mixture of LTA with bentonite, binder contents beyond the optimum might obstruct part of the pore network during the palletization process [8].

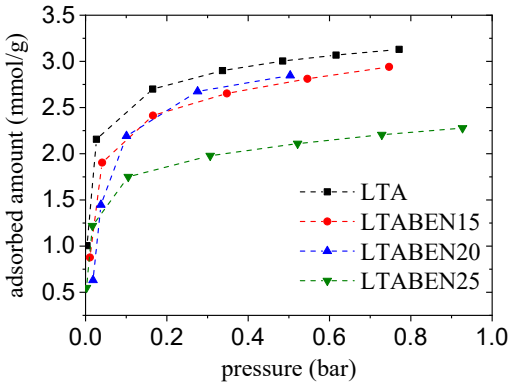

Fig. 3. CO_2 adsorption isotherms at 298 K for the zeolite powder (LTA) and LTA/bentonite pellets.

Figure 4 presents the CO_2 adsorption enthalpy of the studied samples. The decreasing enthalpy with the increasing sorbate loading suggests that the materials have heterogeneous surfaces according to the classification proposed by Llewellyn [9]. When comparing only the shaped pellets, it is noteworthy that LTABEN25 enthalpy decreases more steeply, which indicates that the amount of bentonite in the samples has changed the surface characteristics, corroborating the behavior of the isotherms shown in Fig. 3. The first sites to be occupied are those having greater CO_2 attractive forces, probably where the zeolite cations are placed [10]. After reaching the most energetically favorable sites (zero coverage), the curve levels off, indicating the occupation of weaker adsorption sites. The results demonstrate that, while LTA powder shows a small plateau at 40 kJ/mol, the enthalpy decreases with increasing CO_2 uptake for all pellets.

The probable adsorption mechanism is that as the micropores are filled by CO_2 molecules at low pressures, the presence of mesoporosity granted by the binder on the pellets changes the amount of energy released and consequently the shape of the enthalpy curve. The interactions between the binder and the zeolitic matrix could be associated to a mechanism of cation exchange within the intercrystalline network, a process influenced by the quantity of binder in the pellet. Literature suggests that a higher binder content can intensify cation exchange, potentially causing cations to be allocated within the micropores or obstruct their access [5]. This corroborates with the LTABEN25 sample had the lowest CO_2 adsorption capacity (see Fig. 3). The results also show how the microcalorimetric curves are sensitive to the shaping formulation.

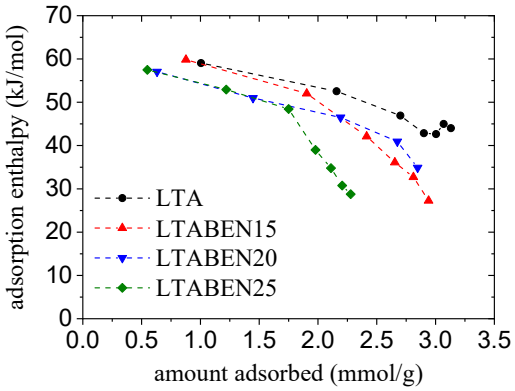

Fig. 4. CO_2 adsorption enthalpy curves at 298 K for the zeolite powder (LTA) and LTA/bentonite pellets.

4. Conclusion

There is an optimal content of binder (bentonite) that can be added to a zeolitic matrix in order to produce pellets, providing a desirable trade-off between mechanical and adsorption capacity. Calorimetric data suggest that the CO_2 adsorption mechanism is related to the mesopores granted by the addition of binder. However, a deeper understanding of the phenomena in each case requires additional chemical and structural analyses (e.g. elemental analysis, XRD, RMN).

Acknowledgements

The authors acknowledge financial support from CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), FUNCAP (Fundação Cearense de Apoio ao Desenvolvimento Científico e Tecnológico) and

CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior).

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