

Preparation and characterization of NaLTA zeolite/polydimethylsiloxane composites for CO₂/N₂ adsorption and separation

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Abstract

This study aims to prepare and characterize a NaLTA zeolite and polydimethylsiloxane composite in a pellet shape, with high CO₂ selectivity, in a CO₂/N₂ gas mixture. The composite was prepared by mixing the NaLTA zeolite prepared using metakaolin as precursor, with polydimethylsiloxane silicon rubber. Different composite with varying proportions of polymeric matrix were synthesized to assess how the polymer acts as a selective barrier for gaseous molecules during the adsorption process. The zeolite and composites were characterized using SEM, XRD, EDS, BET area, and porosity, the NaLTA zeolite, the polydimethylsiloxane, and the composites were submitted to sorption tests with pure CO₂ and N₂ gases, at temperature of 20°C ± 2 °C, with pressure from 0 to 7500 mmHg. The XRD results indicate that the synthesized NaLTA zeolite has a great structural formation with high crystallinity, and the SEM images and EDS mapping shows that the zeolite was successfully charged into the polymeric matrix, which indicating a positive interfacial interaction between the zeolite crystals and the polymeric matrix. Finally, as a result of the sorption tests, the composite containing 44% by mass of NaLTA zeolite (C44), showed the best result in terms of structural characteristics, CO₂ adsorption capacity, and selectivity.

Keywords: polydimethylsiloxane; zeolite NaLTA; CO₂ capture; CO₂ adsorption; gas separation.

1. Introduction

The phenomenon of global warming represents the main contemporary environmental issue, consequently, in recent years, research involving the capture, storage, and utilization of CO₂ has emerged as an alternative to mitigate adverse environmental impacts on life [1,2]. Currently, strategies of incorporating inorganic loads such as molecular sieves into polymers with good chemical and mechanical stability is a well-established practice in the preparation of hybrid materials for gas separation [3,4]. For application in large scale it is also expected that the adsorbents can selectively adsorb CO₂ from the flue gases [5,6,7,8,9]. Thereby, zeolites have been extensively studied for CO₂/N₂ separation, due to their crystalline and microporous structures, high surface area, thermal stability, and high CO₂ adsorption selectivity. They can be synthesized using low-cost aluminosilicates [5,9,10,11]. The use of polydimethylsiloxane (PDMS) as polymeric base is related to its permeation properties, thermal stability, chemical inertness, and good chemical and physical

compatibility with other materials [4,5,6,12,13]. Therefore, the production of zeolite and PDMS composites is considered promising for applications in CO₂/N₂ separation processes [5,12,13,14], and for this purpose, a good interfacial interaction between molecular sieve and polymer must be considered, as it directly influences the performance of the hybrid composite [12,13,14,15]. Thus, the objective of this study is to prepare and analyze NaLTA zeolite/PDMS composites in pellet form, aiming for high CO₂ adsorption and selectivity in a CO₂/N₂ gas mixture.

2. Methodology

The process used to synthesize NaLTA zeolite and prepare the NaLTA/PDMS composite was based on Souza (2012) and Adnadjevis; Jovanoc (2000). For the zeolite synthesis, the kaolin was first calcined at 800°C for 2 hours, then it was mixed with sodium hydroxide using a magnetic stirrer. The mixture was left at room temperature for 24 hours and then was treated using the hydrothermal method for 6 hours at 150°C for aging. After that, the crystallization process was interrupted

by cooling the material. Finally, the zeolite was washed until reached a pH close to 9, the sample was then dried in an oven at 100°C for 48 hours. To prepare the composites Bluesil RTV 3720 silicone rubber was used, the material presents two components, A (a blend of liquid PDMS polymers and silicones terminated with vinyl groups) and B (hydroxymethylsiloxane, serving as a crosslinking agent), which were mixed together to obtain the PDMS. Three composites were produced with 30 wt% (C30), 44 wt% (C44), and 52 wt% (C50) of NaLTA zeolite. So, the composites were prepared in a beaker by manually mixing the zeolite and PDMS until homogeneous. Finally, the mixture was placed into molds (dimensions 3.0 cm x 0.2 cm x 0.2 cm) to form pellets and then was vulcanized at room temperature ($\sim 23^{\circ}\text{C} \pm 2^{\circ}\text{C}$). For the sorption tests, the Micromeritics ASAP 2050 equipment was used.

3. Results and discussion

3.1. Zeolite NaLTA morphology

The sample exhibited a high formation of cubic crystals, typical of the LTA zeolite structures, with average edge sizes of around 5 μm with the presence of intergrowth cubic zeolitic crystals. The influence of the aging stage during the synthesis process is by the crystal size, which affects the separation or partial separation of nucleation and growth stages in crystal size [5,16]. The morphology of the zeolite is shown in Figure 1, which displays crystalline structures of the sodalite zeolite phase in spherical clusters, this may indicate that the crystallization temperature used initiated the formation of a phase with greater stability than Na-LTA zeolite [5,10].

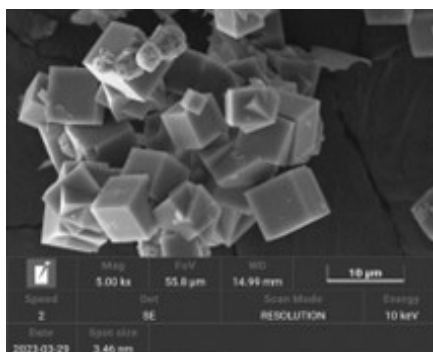


Fig 1. SEM image of the synthesized NaLTA zeolite.

3.2. Mineralogical composition and crystallinity of the NaLTA zeolite

Through the XRD pattern of the NaLTA, presented in Figure 2, it is possible to observe significant peaks corresponding to the well-crystallized zeolite NaLTA “A” (ICSD: 024901) with high intensity. Small proportions of sodalite “S” (ICSD: 015336) and cancrinite “C” (ICSD: 039920) phases were also observed, the presence of these phases in reduced proportions was expected, considering that NaLTA zeolite is a metastable phase in the formation process of sodalite and cancrinite. Peaks corresponding to illite “I” (ICSD: 090144) and quartz “Q” (ICSD: 083849) are attributed to impurities present in the kaolin, even after thermal treatment. Peaks of fluorite “F” (ICSD: 060369), which were also identified, are part of the internal standard used for the quantitative analysis of phases present in the samples.

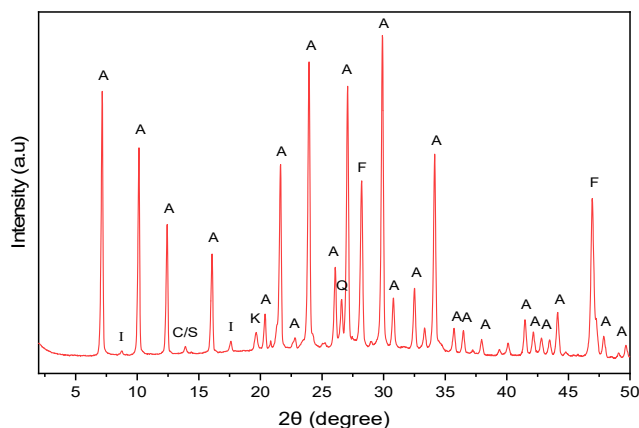


Fig.2. XRD pattern of NaLTA zeolite.

3.3. CO₂ and N₂ adsorption

Figure 3 shows that the carbon dioxide adsorption capacity increases with the zeolite proportion in the composite. At maximum pressure (~ 7500 mmHg), the C30, C44, and C50 composites achieved adsorptions capacity of 2.55, 2.65, and 2.91 mmol/g, respectively, the zeolite NaLTA and PDMS presented an adsorption capacity of 4.66 and 0,84 mmol/g, respectively. This correlation of increasing the adsorption as the zeolite concentration increases is well-documented in the literature for hybrid materials used in gas separation applications [12,13,15]. The difference in adsorption values for the NaLTA zeolite and the composites is expected due to the constructive interaction between the materials. In the composite, the zeolite provides molecular sieve effects, while the polymer acts as a selective barrier to gas transport [5, 13], so the amount

of gas adsorbed by the composite occurs due to the zeolite inserted into the matrix [5].

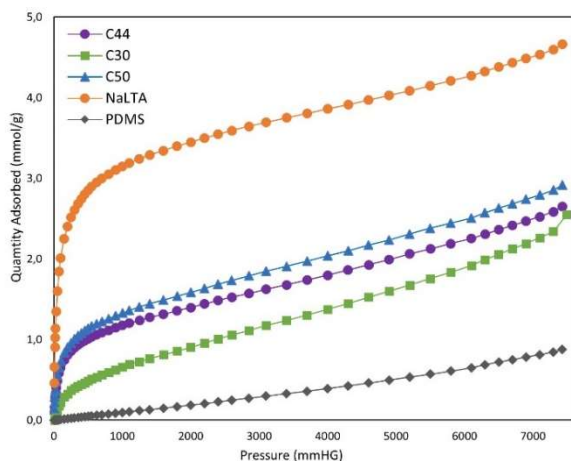


Fig. 3. CO₂ adsorption isotherms of the C30, C44, C50, NaLTA zeolite, and PDMS samples at temperature of 20°C ± 2 °C.

Figure 4 presents the N₂ adsorption isotherms on the samples. As expected, the amount of N₂ adsorption capacity is lower than the amount of CO₂ adsorbed. The lower adsorption occurs due to the larger kinetic diameter of N₂ compared to CO₂ and the limited gas diffusion caused by the distribution of cations in the zeolite structure [11], and the PDMS has a dense morphology and presents low interaction with gas, unlike microporous materials [6]. However, the facilitated permeation of CO₂ in comparison to the N₂ through the small voids between entangled polymeric chains is a consequence of the smaller kinetic diameter of the CO₂ [6,7].

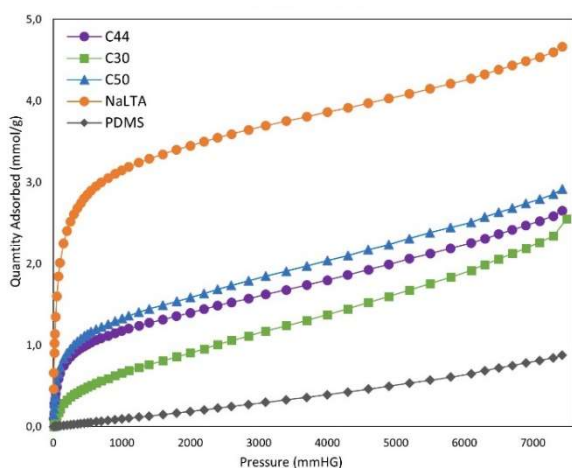


Fig. 4. N₂ adsorption isotherms of the C30, C44, C50, NaLTA zeolite, and PDMS samples at temperature of 20°C ± 2 °C.

3.4. Characterization of C44 composite

Aiming to produce cohesive adsorbent pellets and based on the adsorption capacity results, the C44 composite, with 44 wt% of NaLTA zeolite, presented the best performance. In contrast, the C30 sample did not present adsorption capacity, and the C50 composite, with 52 wt% of zeolite, exceeded the optimal ratio between filler (zeolite) and polymeric matrix, resulting in a granular physical appearance. Thus, Figure 5 presents the SEM images and EDS mapping of the cross-section of the C44 sample after cryogenic fracture. The images reveal a uniform distribution of zeolite within the PDMS matrix, indicating good interfacial compatibility between the polymeric matrix and particles [13,14,15].

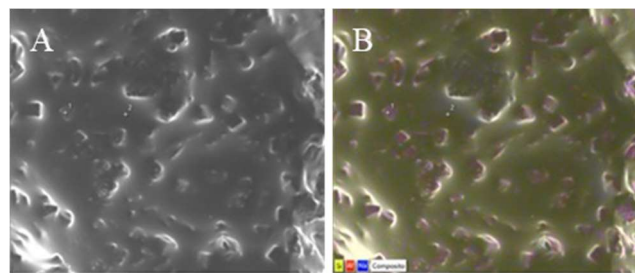


Fig. 5. SEM image (A) and EDS map (B) of the C44 sample.

With the data obtained from CO₂ and N₂ adsorption isotherms at pressures of 1000, 4000, and 7000 mmHG, Figure 6 was plotted aiming to compare the selectivity for CO₂/N₂ of pure zeolite and PDMS with the C44 composite. The results indicate that the interaction between the composite components results in an increase in the selectivity compared to the zeolite and PDMS only.

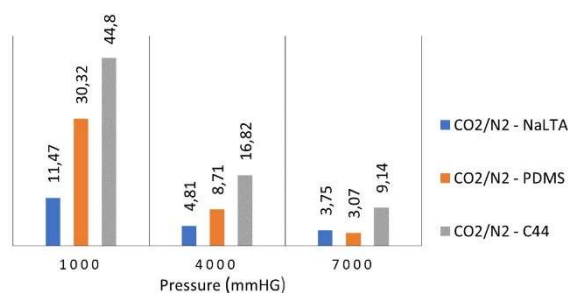


Fig. 6. CO₂/N₂ selectivity for NaLTA, PDMS and C44 samples.

4. Conclusions

The NaLTA zeolite/PDMS adsorbent composites prepared in this study demonstrated the ability to increase the selectivities for CO₂ in relation to N₂. The

good interfacial interaction between zeolite and polymeric matrix was evidenced, with homogeneous dispersion and no aggregation of zeolites in the matrix. This fact indicates that the mixture of polymer and molecular sieve had an optimal interphase morphology, which added to the gas transport properties. The C44 composite presented the best composite performer, considering the parameters of morphology, CO₂ adsorption and CO₂/N₂ selectivity, emerging as a highly promising material for gas capture and separation.

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6. References

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