Temperature Influence in the Deactivation of LTA Commercial Zeolites

Beatriz O. Nascimento[a], Bianca F. dos Santos, Débora A. S. Maia[a], Darley C. Melo[b], Enrique Vilarrasa-García[a], Moisés Bastos-Neto[a], Diana C. S. de Azevedo[a*]

[a] GPSA, Departamento de Engenharia Química – Universidade Federal do Ceará, Campus do Pici, bl. 731 – 60760-400, Fortaleza Ceará, Brasil
[b] PETROBRAS/CENPES, Rio de Janeiro, Brazil *email: diana@gpsa.ufc.br

Abstract

In an industrial process it is common the utilization of adsorption fixed bed with zeolitic material for gas drying and the adsorbent regeneration may be conducted using a TSA process, which in its turn, can cause the loss of activity, like an aging process. So, the goal of this study is promoting the premature aging of a commercial zeolite, LTA type, by cycles of heating and cooling at two different temperatures, 523 and 573 K. It was made the crystallinity study, textural characterization, FTIR spectroscopy, TGA and carbon dioxide isotherms at 298 K as the probe molecule, to evaluate the adsorption capacity. The crystallinity study does not show any changes in the crystal structure of the zeolite. So, the reduction in the adsorption capacity could be associated to an organic compound deposit in the porous of the material, which might cause the block effect. The temperature study presents a slight variation in the results, but this is not the only factor in the aging process. The number or the duration of the cycles might be key variables in the optimization of this study.

Keywords: Deactivation; LTA Zeolite; TSA Process.

1. Introduction

The high capacity water adsorption on microporous zeolites of low Si/Al ratio make them the best adsorbent for gas drying. This process occurs because of the highly polar surface of this material, which promote the physisorption of polar substances, like water, even at very low concentrations. This process is industrially conducted in a fixed bed with pelletized material [1]. The Temperature Swing Adsorption (TSA) is a common way to regenerate the adsorbent manly for the strongly adsorbed species, but with the repetition this may cause a reduction in the adsorption capacity due the loss of crystallinity or coke formation when the regeneration step is carried out in presence heavy of hydrocarbons [2].

The use of the TSA process goes back to the 50's, where that was employed in the natural gas purification. After this the TSA had a rapid growth and, today, can be found in systems with two or three fixed beds. In a plant's operation one of the fixed beds was maintained in the adsorption temperature and the interest compound are accumulated in the porous material. In the same time another fixed bed, which was previously saturated by the adsorptive, is regenerated by a hot purge [3].

At last, the goal of this work is promoting the accelerate aging in a commercial zeolite, using TSA cycles at two different temperatures. Then investigate the mechanism of this deactivation and its impact in CO_2 adsorption capacity.

2. Experimental

2.1. Material

The adsorbent used in this work is a zeolite LTA type with sodium as the exchange cation in pellets shape of 1.6 mm of diameter. The crystal form of

the same zeolite, was used in the crystallinity study. Both materials were supplied by Sigma Aldrich.

2.2. Aging Test

The aging test was conducted following the methodology showed by Santiago *et al.* in 2018 [4]. That consists in placing 25 g of the zeolite in a stainless steel reactor (Parr Instrument Company, USA) with volume of 500 mL. The sample had passed by a pre-stage, where it was humidified by a stream of nitrogen bubbled in water for 24 h, at 303 K and 1 bar of pressure. After this stage it was added 0.6 mL of n-heptane per gram of zeolite and the reactor was pressurized at 30 bar with a mix of carbon dioxide and methane in the proportion of 1:4 for an hour. At last, the heating/cooling cycles were initiated. The Sample was heated until 523 K and kept for 3 hours and it was cooled to 303 K by natural convection. This process was repeated and aliquots was collected in 14, 24 and 35 cycles, that samples being called A1, A2 and A3, respectively. The same process was made changing the temperature to 573 K in the heating/cooling process. In this case the samples were called by B1, B2 and B3, in the same order, that is, samples collected after to 14, 24 and 35 cycles, respectively.

2.3. X-Ray Diffraction (XRD)

The X-ray diffraction analysis for the fresh samples, A3 and B3 were carried out with X'PERT PRO Powder diffractometer (PANalytical, UK) equipped with a Co-Kα anode. The samples were analyzed in the range of 2θ between 5 and 70° and with steps of 0,013°.

The diffraction patterns were used to determine the crystallinity based on in a standard sample, in this case the commercial LTA in crystal form. The equation 1 was used to calculate this parameter:

$$Crystallinity(\%) = \frac{S_x}{S_s} \cdot 100 \qquad (1)$$

Where S_x is the average of the area of the selected peaks of the sample and S_s is the average of the area of the selected peaks of the standard sample. The peaks correspond to the crystalline planes 222, 420, 442, 620, 642 and 644 [5].

2.4. Textural Characterization

The BET area and total pore volume was determined by the adsorption/desorption nitrogen isotherms at 77 K and this was conducted in an Autosorb-iQ3 (Quantachrome, EUA). The samples were degassed before the measurements by application of 10^{-6} bar of vacuum and temperature of 573 K by 8 h.

2.5. Fourier-Transform Infrared Spectroscopy (FTIR)

The FTIR analyses were conducted in a spectrometer VERTES 70 (Bruker, UK), with sensibility of 2 cm^{-1}. The samples were conformed in KBr pellets.

2.6. Thermogravimetric Analysis (TGA)

The thermal stability and the release of volatile compounds were analyzed in STA 409 CD/403/5/G SKIMMER (Netzsch, Germany). The samples were submitted to a final temperature of 1072 K through a 10 K min^{-1} heating hate. The inert atmosphere was obtained by constant flux of nitrogen at 20 ml min^{-1}.

2.7. CO$_2$ Adsorption Isotherm

The CO$_2$ isotherms at 298 K were obtained in a volumetric system, the Autosorb-iQ3 (Quantachrome, EUA). The samples were degassed before the analysis under vacuum and 573 K for 8 h.

3. Results and discussion

3.1. X-Ray Diffraction (XRD)

This technique was used to determinate the crystallinity and purity of the zeolite type LTA. Figure 1 shows the diffractogram of the standard material, the fresh samples, A3 and B3. The diffraction pattern results agree with the literature patterns [6]. These results show that there were no changes in the zeolite main structure with the aging cycles.
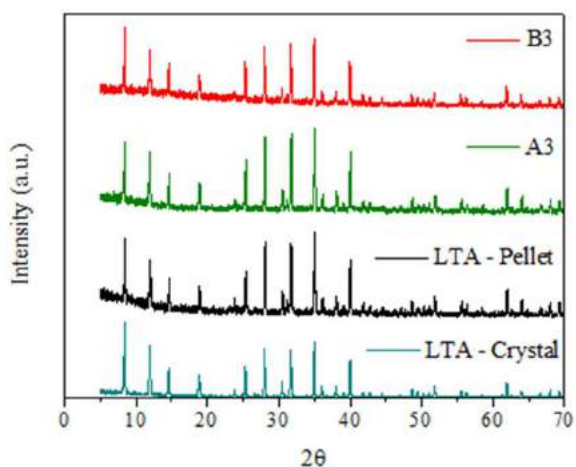
Fig. 1. The diffraction patterns to the fresh sample in crystal and pellet form, A3 and B3.

This is confirmed by the crystallinity data presented in the Table 1, the results show any significantly change with the cycles. The values are in the error range of the method.

Table 1. Crystallinity data of the samples.

Sample	Crystallinity (%)
LTA	58.6
A3	61.1
B3	66.9

3.2. Textural Characterization

Figure 2 shows the adsorption and desorption isotherms of nitrogen at 77 K. The isotherms are the Type II according the IUPAC classification, which are characteristic of macroporous and non-porous materials [7]. These indicate that nitrogen adsorption occurred in the macroporous of the binder. Zavareh, Farrokhzad and Darvishi have tried in 2018 measure the BET area of the zeolite 4A, but they had no success because the "window" size of the crystal cage was smaller than the diameter of the nitrogen molecules [8].
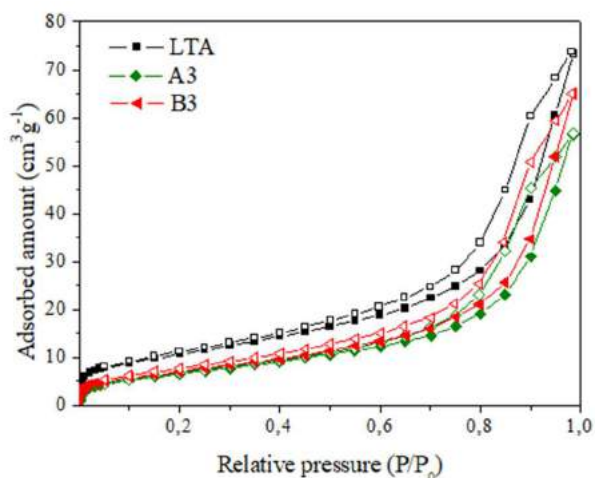

Fig. 2. Nitrogen adsorption and desorption isotherm at 77 K to the fresh sample, A3 and B3.

Table 2 resumes the textural characterization. We can observe a reduction in the textural properties of the zeolite, which can suggest a block effect by the coke formation in the macroporous during heating/cooling cycles.

Table 2. Textural characterization.

Sample	BET area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	DR volume ($cm^3 g^{-1}$)
LTA	39	0.094	0.010
A1	29	0.079	0.007
A2	26	0.088	0.006
A3	25	0.087	0.006
B1	35	0.093	0.007
B2	33	0.090	0.007
B3	26	0.080	0.006

This technique is not recommended to characterize polar surfaces due to the quadrupolar moment. The nature of nitrogen has influenced the molecule orientation on the adsorption and in the micropore filling pressure. The equilibrium of the isotherm was difficulted by the specific interactions of the nitrogen with the material surface [7].

3.3. Fourier-Transform Infrared Spectroscopy (FTIR)

The FTIR spectroscopy was used to determine if any functional groups were present in the sample before and after the aging tests. The Figure 3 show the spectra for the fresh LTA.
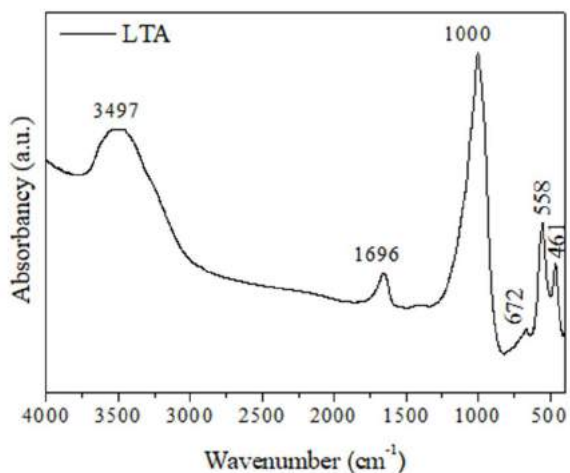
Fig. 3. The FTIR spectrum for fresh sample.

The fresh sample presents bands at 3500 and 1650 cm^{-1} that indicate the presence of water. In the first, we had the stretch vibrations of the groups OH and in the second the adsorbed water. The bands around of 1000, 660 and 460 cm^{-1} demonstrate the aluminosilicate structure that indicates, respectively, the asymmetric and symmetric stretch and deformation of the TO_4, where T is a silicon or aluminum atom. The band at 557 cm^{-1} was associated with the external vibration of a secondary structure of the zeolite A, the DR4 (the rings of four members in the secondary structure of the LTA) [9].

Figure 4 (A) presents the FTIR results of the aged samples. One can notice in the aging material the presence of the bands around 2962-2936 and 2877-2449 cm^{-1}, which is characteristic of the CH_3 and CH_2, respectively, asymmetric stretching vibration in aliphatic compounds. In the Figure 4 (B) were showed the deformation vibrations which usually appear. The asymmetric deformation of the group methyl is presented in the region of 1466 cm^{-1}. The deformation of the methylene group might occur between 1347 and 1189 cm^{-1}, but close to carbonyl groups that can appears at 1380 cm^{-1} [10].
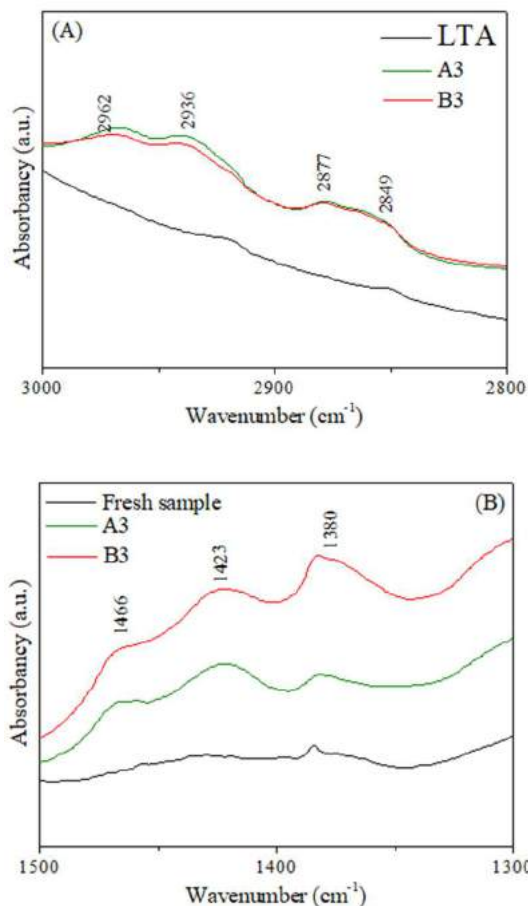

Fig. 4. The FTIR spectra of fresh sample, A3 and B3 samples.

The bands around 1435 were associated to the stretching of the CO_3 ions, which might be presented in both samples [11]. These results suggest that the presence of carbon dioxide in the aging method can change the positions of the bands in the same way to the carbonyl groups. The rock vibrations appear at 724 cm^{-1} in the spectrum. These bands are typical of longs noncyclic CH_2 chains [10]. The absence of these bands can infer the n-heptane might be cracking in smaller compounds.

3.4. Thermogravimetric Analysis (TGA)

The thermogravimetric analysis of the fresh sample and of the most aged samples are exhibited in Figure 5. The patterns of mass losses were different from each other that indicate different kind of compound. The fresh sample presented the mass loss until 200°C. This might be associated to the free water losses [12]. In the aged materials, it was observed another mass loss that was stabilized at

823 K. This might indicate the presence of organic compounds more thermic stable in the zeolite cages after the aging tests.
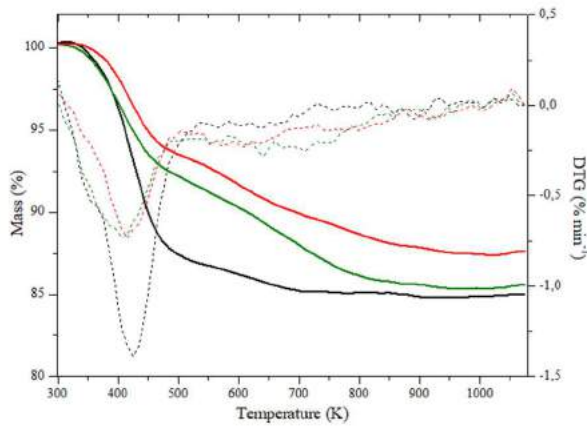

Fig. 5. TGA (continuous line) and DTG (dotted line) of LTA (black), A3 (green) and B3 (red) samples.

3.5. CO_2 Adsorption Isotherm

The Figure 6 shows the carbon dioxide isotherms at 298 K of the aged samples at 523 K. These samples presented a decrease of adsorption CO_2 capacity, where the difference between the samples were equal to 22, 43 and 49%, respectively, to 14, 24 and 35 cycles of heating/cooling. That result was in agreement with the textural characterization, FTIR spectra and thermogravimetric analyses, where it was indicated the loss of the zeolite textural properties by formation of organic compounds inside the material pores.
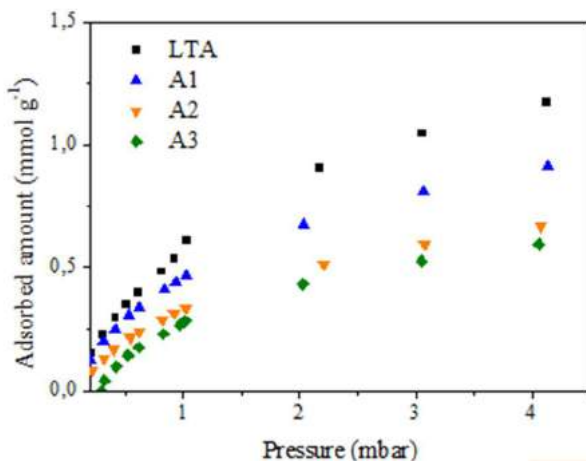

Fig. 6. CO_2 adsorption isotherms at 298 K of the aging samples at 523 K.

Santiago and coworkers studied the deactivation on microporous zeolites by TSA process in 2018 [4]. They found a reduction of the 25% in the CO_2 adsorption capacity at 303 K in the samples aged by 35 heating and cooling cycles. These results indicate the commercial LTA was more susceptible to the deactivation than that another sample in the same conditions.

The samples aged at 573 K are presented in Figure 7. In this temperature, the reduction in the adsorption capacity is the 29% for B1, 37% for B2 and 51% for B3. That is comparable with the values of the experiment at 523 K. These results indicate the change in the temperature is not enough to promote a premature aging test in the zeolite type LTA.
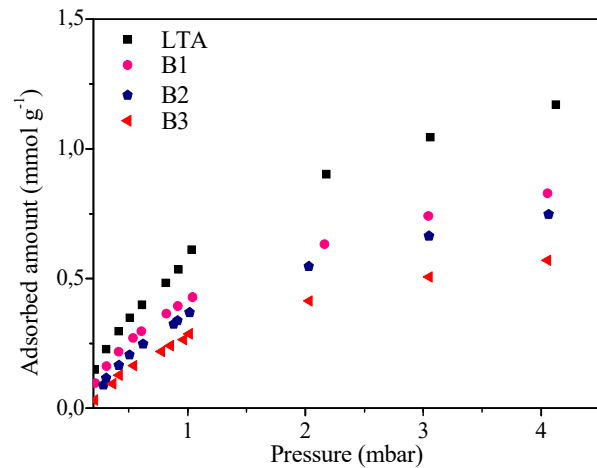

Fig. 7. CO_2 adsorption isotherm at 298 K to the samples B1, B2 and B3.

4. Conclusions

The aging methodology tested is efficient in the deactivation of zeolites type LTA pointed by the reduction in the adsorption capacity of a probe molecule, as the carbon dioxide at 298 K. The crystallinity showed no changes in the zeolite main structure. FTIR has showed that deactivation mechanism could be the accumulation of organic material in the porous. The study presented the temperature as important variable, but not the only one that should be considered in the understanding of the aging process.

Acknowledgements

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