Short Communication

LTA zeolite synthesis using natural materials and its evaluation by Green Star methodology

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Abstract

The industrial costs of zeolite synthesis can be diminished by the substitution of traditional raw materials by natural sources. In this work, we obtained LTA zeolite from four natural materials, three different diatomites and expanded perlite, and characterize them by X-ray diffraction, X-ray fluorescence and scanning electron microscopy. It was possible to observe the formation of the zeolitic materials through the identification of the Bragg reflections and the cubic morphology characteristic of the aluminosilicate. The Si/Al ratio of the samples resulted next to the unit as expected for this topology. We found small differences between the zeolitic products, remarking the possibility of adapting this process using natural materials to industry. These results were used for the Green Star evaluation, calculating the synthesis degree of greenness, resulting greener due to the complete substitution of the traditional silica source.

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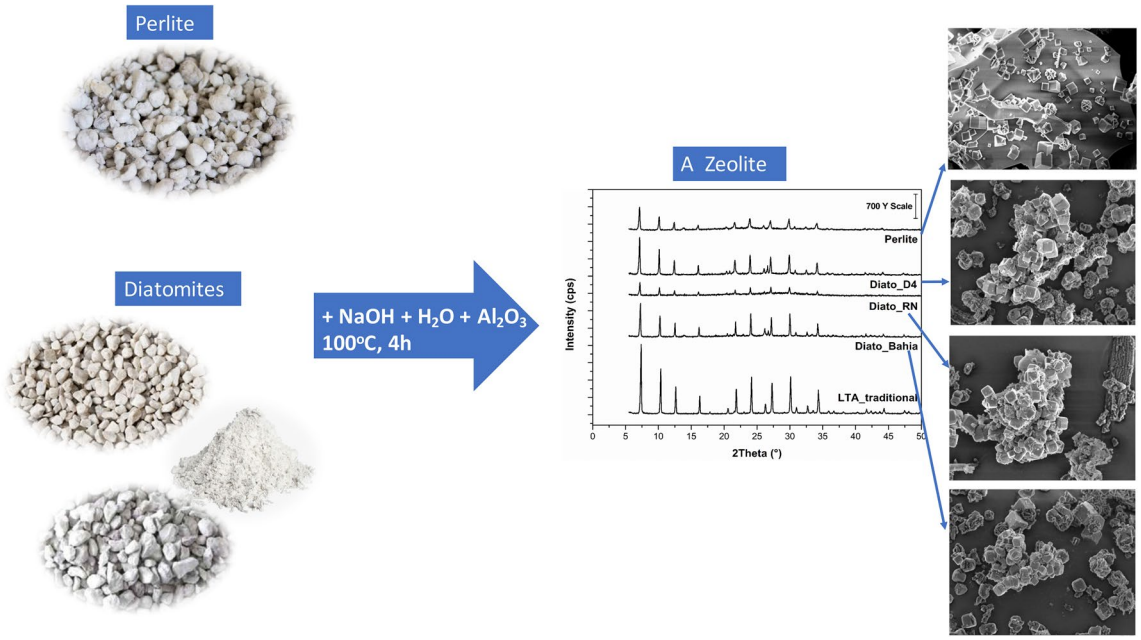
Graphic abstract



Keywords Green Star · Zeolite · Perlite · Diatomite · Eco-synthesis

1 Introduction

Zeolite A is a microporous material belonging to the LTA topology [1]. It is usually synthesized in its sodium form and features a Si/Al ratio equal to 1 [2]. Its surface area varies depending on the cation used for its synthesis, being very low for NaA (around 7–15 m^2g^{-1}) and higher for CaA (around 450–550 m^2g^{-1}) [3, 4]. This zeolite is applied in a variety of industrial processes, for example, forming part of detergents or removing radioactive cations [5, 6]. Its synthesis uses traditional silica sources (i.e. water glass), which are involved in the generation of a large number of residues [7–9]. Then, they should be substituted by alternative sources that add value to materials considered waste for many industries and processes, bringing a new perspective to the production of catalytic materials with an appeal for environmental awareness. It is known from the literature that it is possible to synthesize zeolites from various non-traditional materials containing silicon and aluminium, such as waste porcelain, coal ash or kaolin [10–12].

Diatomite and perlite are natural materials whose structural properties defined their applications, such as cleaning treatments for polluted soils or dyes adsorption [13–15]. The high levels of silica in their composition also make them attractive to use as an alternative source of silicon in zeolite synthesis [14, 16]. They were already reported as alternative silica sources for the LTA zeolite synthesis. However, they needed calcination pretreatments or had long synthesis times (even with a previous ageing step), or the crystallinity was too low, or the products were mixed with other phases in significant proportions [17–20]. For these reasons, it is interesting to continue studying these materials as alternative sources for zeolite synthesis gels. Also, to evaluate the greenness of the raw sources' substitution procedure, it is interesting to use the Green Star methodology described by Ribeiro et al. [21] consisting on a quantification of the twelve principles.

Therefore, the objective of this research is to obtain the LTA zeolitic topology replacing the traditional silica by Argentinian expanded perlite and Brazilian diatomites without the need of any pretreatment and in a shorter time and to evaluate the greenness of the synthesis with the Green Star methodology.

2 Materials and methods

The traditional LTA zeolite was synthesized according to the standard procedure proposed by the International Zeolite Association (IZA) [22]. In the synthesis using the alternative materials, the different diatomites (RN, Bahia

and D4 from CETEM, zeolitic products named 'Diato_RN', 'Diato_Bahia' and 'Diato_D4', respectively, fully characterized in da Silva Filho et al. [23]) and the expanded perlite (Schumacher Insumos, zeolitic product named 'Perlite', fully characterized in da Silva Filho et al. [24]) directly replaced sodium metasilicate and sodium aluminate. For the synthesis of the zeolitic materials using alternative substances, 1.8 g of NaOH (Química Moderna, 97%) was added in 27 g of H_2O and stirred until complete dissolution. This volume was divided into two equal parts. In the first half, we added variable amounts of sodium aluminate (Sigma-Aldrich, Al—50–56% and Na—40–45%) according to the Si/Al ratio of the natural material employed (RN = 23.6, D4 = 11.9, Bahia = 6.0, Perlite = 4.2), being 2.2 g when used the diatomites RN and D4 and the perlite, and 1.4 g when used the Bahia diatomite. In the second half, we added 1.4 g of diatomite or perlite, and, then, it was stirred magnetically for 15 min. After this step, the second solution was poured quickly into the solution containing the sodium aluminate and was kept stirring for 30 more minutes. Subsequently, the synthesis gel was placed in the autoclaves and maintained at 100 °C in a static oven for 4 h. Once this time finished, the synthesis was left cooling to room temperature, and, then, it was filtered and washed with distilled water until achieving a neutral pH. The resulting materials were characterized by X-ray diffraction (XRD, Bruker D2 Phaser), X-ray fluorescence (XRF, Bruker S2Ranger -raw materials- and Shimadzu EDX-720 -zeolites-) and scanning electron microscopy [SEM, ZEISS-branded Auriga microscope with FEG type emitter (Field Emission Gun)].

3 Results and discussions

The obtention of the LTA topology was proven by comparison of the XRD (Fig. 1) with the reference from IZA database [1]. All the products presented the characteristic Bragg reflections of the LTA topology, ex. the planes (100), (110), (111) and (210) corresponding to the 2θ values of 7.49°, 10.54°, 12.93° and 16.65°, respectively. The products obtained from the diatomites Diato_D4 and Diato_Bahia also presented a small Bragg reflection at a 2θ value of 21.0° and 26.6° corresponding to a quartz impurity present in the initial diatomite (Supplementary Information). We observed a small Bragg reflection at a 2θ value of approximately 14° for the products obtained using perlite and Bahia diatomite, probably due to a small quantity of SOD zeolite impurity. Also, a small amorphous halo was found for the Diato_RN sample probably related to unreacted diatomite. Then, we were able to obtain LTA topology (without quartz nor other zeolitic phases) with Diato_RN, without needing to adjust the Si/Al gel ratio

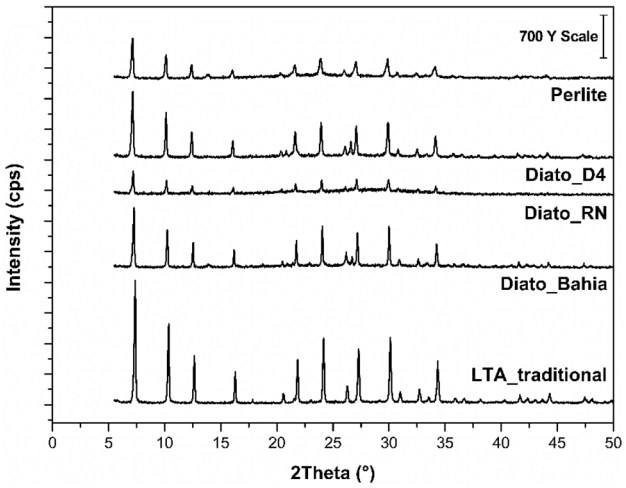


Fig. 1 X-ray diffractograms of the final zeolitic products in comparison with the LTA traditional powder pattern

with other raw sources, in contrast with the existing literature on LTA zeolite with alternative raw materials [18, 25]. Besides, we remark that neither diatomites nor perlite were pre-treated in this synthesis, being an advantage to the use of kaolinite or rice husk [26, 27]. It is important to notice too that this is the shortest time reported with untreated diatomite, as the recent articles reporting other hydrothermal synthesis conditions reached the LTA topology in 24 h [16, 28].

We also performed a comparison of the alternative synthesis products with a relative crystallinity calculus [29]. Diato_D4 (100%) was the most crystalline of the samples, followed by Diato_Bahia (87.2%) and Perlite (60.8%). Meanwhile, the less crystalline product was Diato_RN (23.5%), probably due to the unreacted diatomite.

The resulting materials were also studied by X-ray fluorescence (Table 1). We observed the appearance of the same elements in the zeolitic products as in the raw materials (ex. Si, Al or Fe). The proportions varied as the incorporation of these elements were different. It was also added some new elements, as Na, to perform the synthesis, increasing its final concentration in the samples. With these data, we calculated the Si/Al ratio of the zeolitic samples, being 1.6. 1.6, 1.5 and 1.1 for the samples Perlite, Diato_RN, Diato_D4 and Diato_Bahia respectively. These results were greater than 1, probably due to the existence of a small proportion of unreacted material/impurities.

The morphologies of the samples were analysed by scanning electron microscopy (Fig. 2). The zeolite LTA presented a cubic morphology, in the four samples, appearing some remains of the natural materials without reacting in the case of Diato_D4 and Perlite. The average sizes of the zeolites were 1.7, 2.0, 2.5 and 1.8 μm for the samples Diato_RN, Diato_D4, Diato_Bahia and Perlite, respectively.

Table 1 Detailed composition in oxide form of the natural materials (perlite and diatomites) and of the zeolites obtained by X-ray fluorescence

	Raw materials (values in %)				Zeolites (values in %)			
	Perlite[a]	RN[b]	D4[b]	Bahia[b]	Perlite	RN	D4	Bahia
SiO_2	73.6	94.4	90.0	81.0	48.0	56.7	51.2	41.8
Al_2O_3	14.9	3.4	6.4	11.5	25.0	29.7	29.8	31.1
K_2O	6.0	–	–	–	7.8	–	–	–
Fe_2O_3	1.3	0.3	0.6	1.5	9.4	3.0	6.5	15.1
Na_2O	2.6	0.3	0.4	1.5	6.9	9.4	8.7	7.9
MgO	0.6	1.2	1.3	1.7	–	–	–	–
Others	1.0	0.2	0.2	2.0	2.9	1.2	3.8	4.1
Si/Al	4.2	23.6	11.9	6.0	1.6	1.6	1.5	1.1

[a]Previously reported in: da Silva Filho et al. [24]

[b]Previously reported in: da Silva Filho et al. [23]

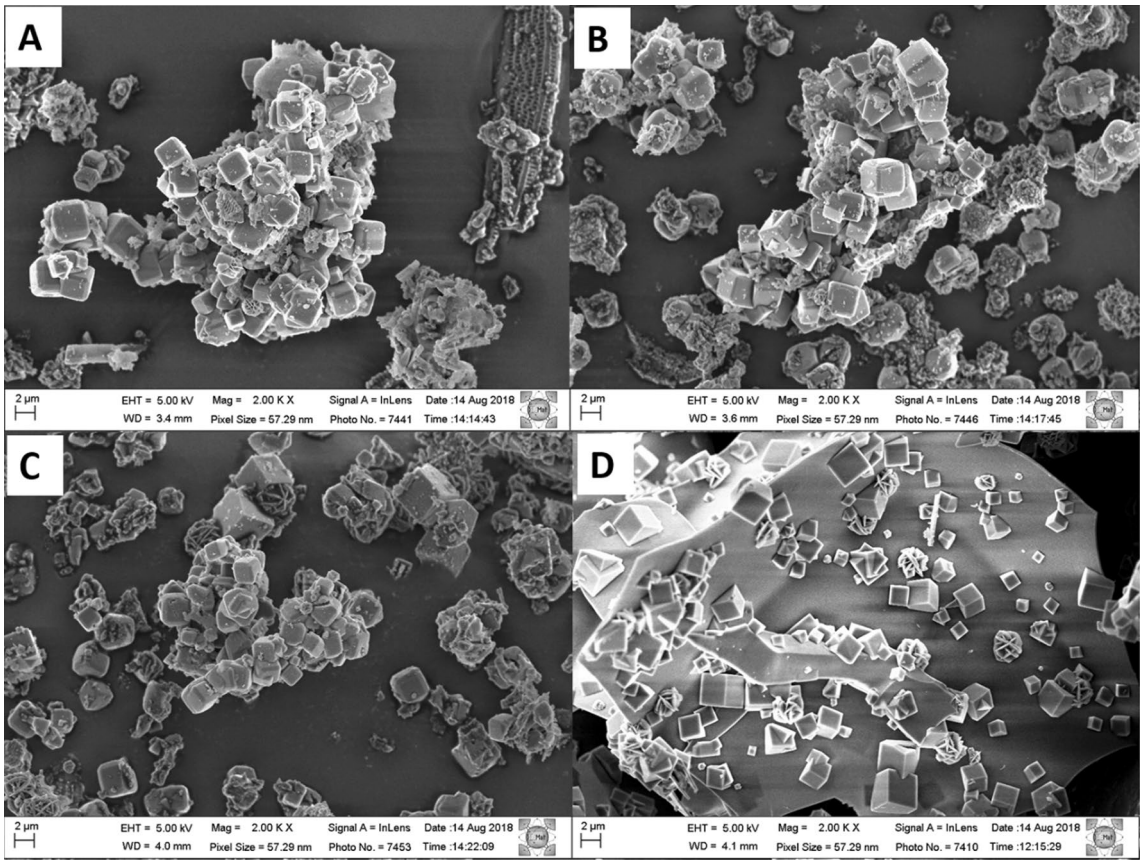


Fig. 2 SEM micrographs (2kx magnification) of the LTA zeolitic samples: **a** diato_RN, **b** diato_D4, **c** diato_Bahia, and **d** perlite

These size differences probably resulted from the variations of the crystallization rate, having the biggest crystal size the faster synthesis and the smallest crystal size the slowest synthesis.

Finally, we performed a Green Star analysis based on the methodology described by Ribeiro et al. and evaluated the results according to the literature [21, 30]. The results represented in Fig. 3 showed an improvement in the greenness of the reaction due to the complete substitution of the silica source, increasing to 2 the punctuation given to the third parameter (P3—less hazardous chemical synthesis). The other parameters were identical, as the same conditions applied in both syntheses.

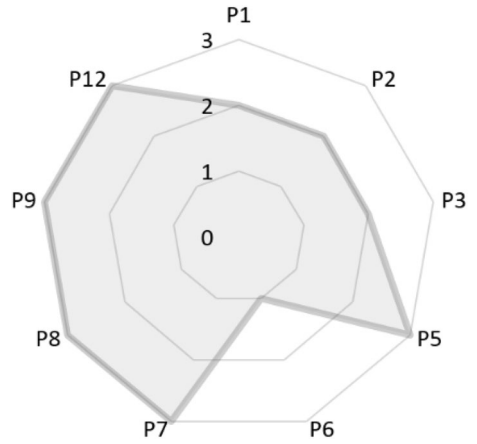


Fig. 3 Green Star chart for the synthesis of LTA using diatomite and perlite

4 Conclusions

In this research work the synthesis of the LTA zeolite employing alternative sources, such as perlite and diatomites from different sources, was successfully performed. The products presented the Bragg reflections and characteristic morphology of the topology. The evaluation through the Green Star process showed an improvement in the greenness through the complete substitution of the traditional silica source. In resume, the final products resulted comparable to the traditional zeolite.

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Compliance with ethical standards

Conflicts of interest The authors declare no conflict of interest.

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