SYNTHESIS AND CHARACTERIZATION OF THE LTA-ZEOLITE FROM BEACH SAND SILICA FOR CARBON DIOXIDE CAPTURE

Adriano M. N. Freitas[1*], Aisha V. S. Pereira[1], Rafael V. Sales[1], Clenildo de Longe[1], Elaine C. de Souza[1], Jordanna L. B. Costa[1], Matheus L. A. Macedo[1], Daniel Plata-Ballesteros[2], Enrique Rodríguez-Castellón[2], Luciene S. de Carvalho[1].

[1]*Universidade Federal do Rio Grande do Norte, Laboratório de Tecnologias Energéticas (LABTEN), Instituto de Química, 59078-900, Natal RN.*
[2]*Universidad de Málaga, Spanish.*
**adriano_mago@hotmail.com.*

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Introduction

In the last decades it has become evident that the environmental impacts caused by human actions are a scientific object of study in order to mitigate its consequences. In between the fields of study there is the green chemistry, which looks for the use of sustainable resources and reduce the environmental impact.

Gases produced through fossil fuels combustion, such as carbon dioxide (CO_2) and hydrogen sulfide (H_2S), plays a huge part on global warming. The last Intergovernmental Panel on Climate Change (IPCC) report, on 2023, warned that the increasing global warming caused by the excessive greenhouse gas emission, mainly CO_2, will rise the annual global temperature by 1,5 ºC, and projects that after 2030 it will be harder to restrain this increase in a ration lower than 2,0 °C per year. Carbon Capture Storage (CCS) is a promising option to help on reducing the CO_2 amount on atmosphere, which is based on the removal of the gas from the air and sticking it to further application on many ways, such as on biogas production and industrial purposes (BUIT et al., 2018; SHAW and MUKHERJEE 2022; TAO et al., 2023).

In addition to CO_2, the sulphur contained in oil is also considered a contaminant (SALES, 2015), and its combustion releases gases such as sulphur dioxide (SO_2) and sulphur trioxide (SO_3), which react with moisture in the atmosphere to form sulphuric acid (H_2SO_4), which precipitates in the form of acid rain, causing harm to the health of humans and animals, as well as acidifying water bodies (GOMES, 2011).

Mesoporous materials can be used to adsorb the gases present in the fuel, making it a less costly process and one that can be synthesized from cleaner materials (TEYMOURI et al., 2013). Zeolites are mesoporous alumina and silicon-based materials surrounded with active sites able to adsorb particles, and are mainly synthesized by hydrothermal method, using highly reactive reagents and lower pressures compared to expensive industrial methods (JIN et al., 2021).

The contribution of this research is to synthesize mesoporous materials in a more sustainable way, using less toxic reagents and alternative sources of silica that are more environmentally friendly. In addition, these synthesized materials also seek better or equal efficiency in relation to commercial models for use in CO_2 adsorption applications.

Material and Methodology

MPI silica was synthesized following CARVALHO, 2015, methodology patented and made by Laboratório de Tecnologias Energéticas – LABTEN (BR102014025283-5), made from beach sand in order to lower the process cost and enhance the sustainability's process.

Firstly, beach sand was collected, sifting and mixed with sodium hydroxide (mass proportion 1:1,6 sand/hydroxide). The mixture was heated for 4 hours and filtered with hot

water. The filtered was treated with HCl until pH was set to the range fairly basic. The precipitated silica was vacuum filtered and dried overnight. This amorphous silica was labeled MPI.

The molecular sieve Linde Type A, LTA, was synthesized via hydrothermal method modified from IZA standard procedure. For the synthesis of LTA using MPI silica, as the silica source, a mixture of sodium aluminate, sodium hydroxide, distilled water and MPI were homogenized under mechanical stirring. Then the system was transferred to a teflon beaker and inserted into a stainless steel autoclave, and then placed in an oven at 100 ºC for aging.

Results and Discussion

MPI amorphous silica crystallinity was characterized through X-ray diffraction (XRD). X-ray patterns of MPI are displayed in Figure 1, showing a wide and broad peak in the range of 2θ = 22,81 º, typical of amorphous solid materials (KALAPHATY et al., 2002).

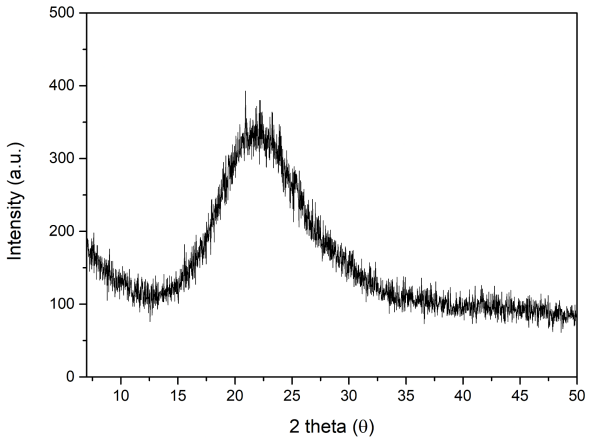

Figure 1. MPI amorphous silica X-ray patterns.

According to the scanning electron micrographs (SEM) obtained for MPI amorphous silica, the sample showed amorphous morphology and absence of well-defined structures, as shown in Figure 2.

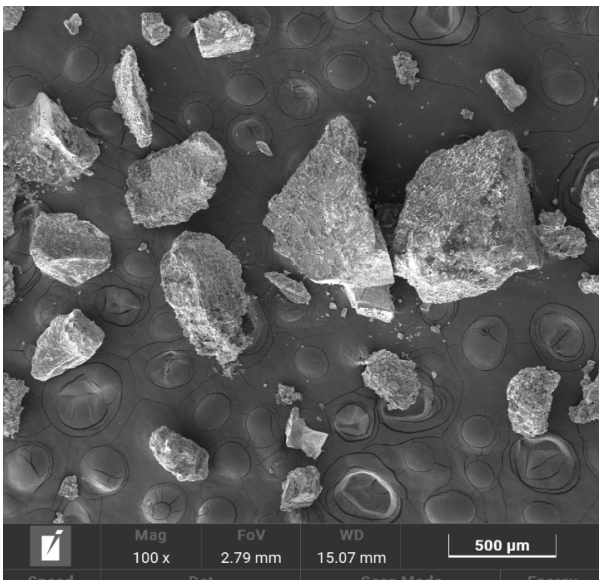

Figure 2. Scanning electron micrograph for MPI silica.

MPI silica was analyzed with energy dispersive X-ray (EDX) attesting presence of oxygen and silicon over the surface of the material, as expected for a silica-based solid. The result is shown in Figure 3, revealing the dispersion of silicon dioxide upon MPI's structure.

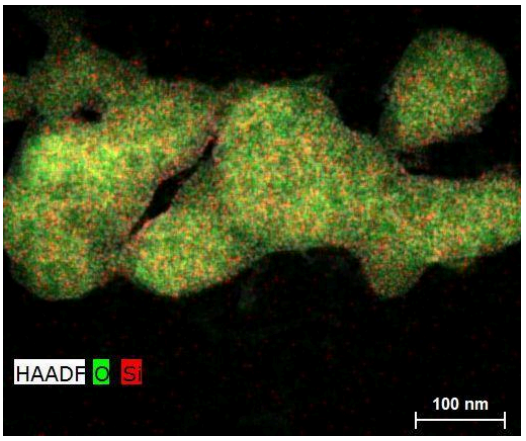

Figure 3. EDX results for MPI silica.

The MPI silica was submitted to thermogravimetric analysis (TG) and the TG and DTG's curves are presented in Figure 4. Three main weight loss steps occurred under the analysis: the first one (Event I), in the range of 30 ºC to 65 ºC, showed weight loss of 7,10 %; the second one (Event II), in the range of 66 ºC to 455 ºC, showed a weight loss of 12,0 % due to loss of physically adsorbed water; and the third one (Event III), occurred in the range of 456 ºC to 736 ºC with 6,0 % weight loss, assigned to the elimination of chemical species used on the material's synthesis, such as sodium and chloride.

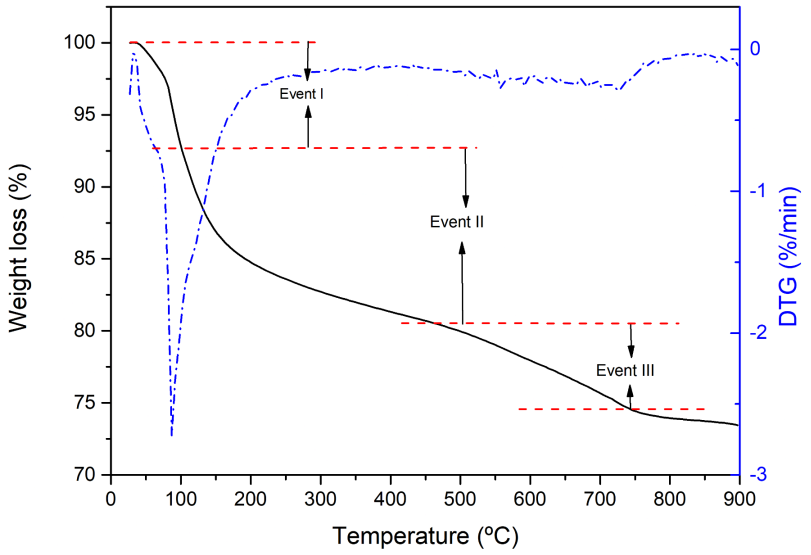

Figure 4. TG and DTG's curves of MPI silica.

Textural characterization of MPI silica was performed through N_2 adsorption-desorption isothermal analysis, as shown in Figure 5. Furthermore, the data collected from analysis were used to calculate the following parameters: specific surface area = 16,71 m^2/g, by Brunauer-Emett-Teller method (BET); specific external area = 13,92 m^2/g, by t-Plot method; micropores area = 7,82 m^2/g, by t-Plot method; total pore volume = 0,0029 cm^3/g, obtained at p/p_0 = 0,95; total micropore volume = 0,017 cm^3/g, by t-Plot method; and average pore

diameter = 6,93 nm, by Horvath-Kawazeo method. The isotherm shows a type II pattern, attributed to non-porous or macropores materials (THOMMES et al., 2015)

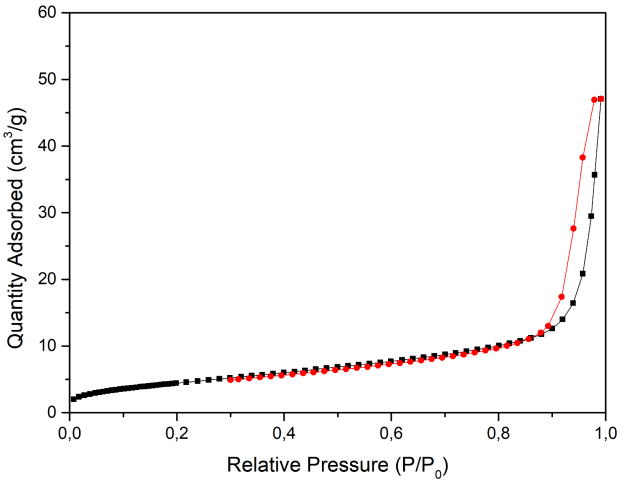

Figure 5. N_2 adsorption-desorption isotherm of MPI.

Zeolite LTA made of MPI silica, upon aging time of 4 hours, denoted matching morphology as reported on literature based on XRD and SEM results.

X-ray pattern of LTA made of MPI are shown in Figure 6, with distinctive peaks in the range of 2θ = 7,17 °, 10,16 °, 12,40 °, 15,44 °, 16,17 °, 21,81 °, 24,19 °, 27,07 °, 30,00 °, 31,00 ° e 34,16 °. The quality and crystallinity of the material is related to the intensity of peaks, in LTA a high crystallinity is attributed to successive processes of dissolution and recrystallization of tethraedrical leaves (CHEN et al., 2020).

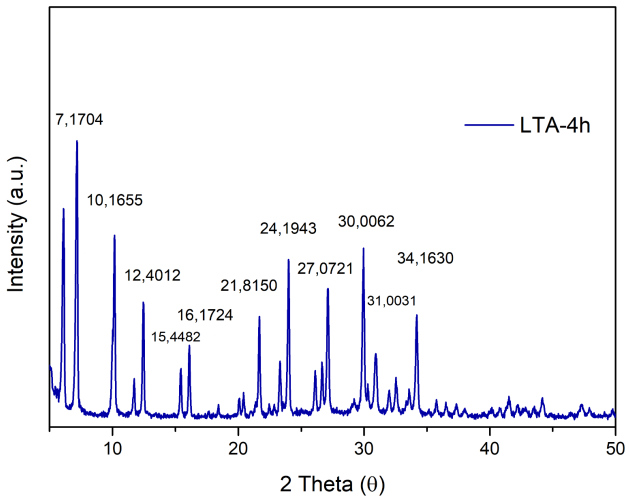

Figure 6. XRD pattern of LTA made of MPI.

LTA made of MPI samples micrographs exhibited cubic structures specific of LTA zeolite, as shown in Figure 7.

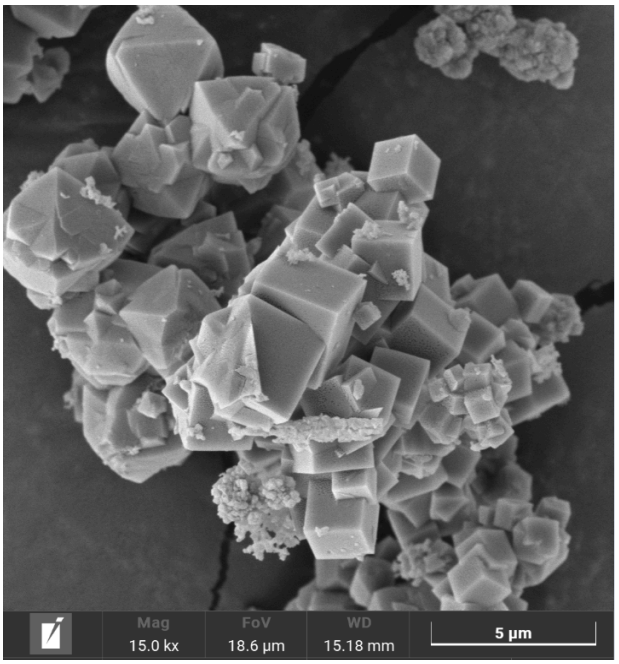

Figure 7. SEM micrograph of LTA zeolite made of MPI.

LTA zeolite made of MPI silica was analyzed with energy dispersive X-ray (EDX) revealing presence of oxygen, silicon, sodium and aluminum over the surface of the material as shown in Figure 8.

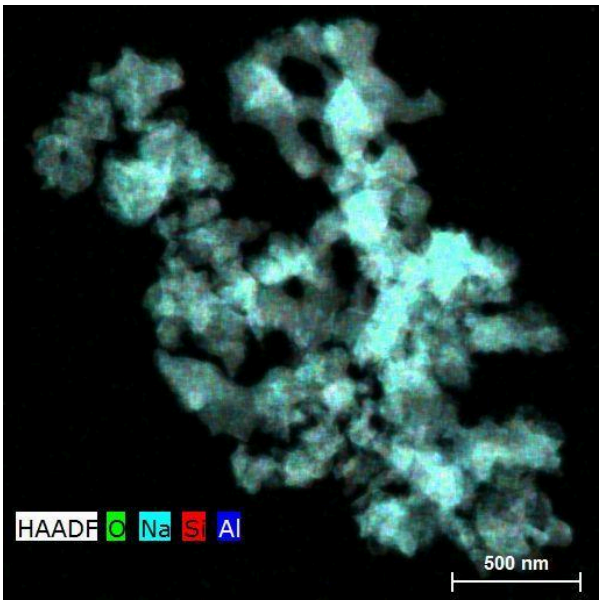

Figure 8. EDX results of LTA zeolite made of MPI.

The chemical bonds between atoms and chemical groups were obtained through the bands detected by FTIR, as shown in Figure 9. The material proved to be compatible with the characteristics of LTA zeolite through the bands measured. There are bands in the region of 3696, 2964 and 1562 cm^{-1}, attributed to the stretching of the group of adsorbed water molecules (OH), as well as bands in the region of 959 and 632 cm^{-1},attributed to the asymmetric stretching of the Si-O-Si bonds of the internal tetrahedral structure of TO_4. The band at 578 cm^{-1} is due to the external vibration of the 4 double rings of the D4R zeolitic

structure (Si-O-Si e O-Si-O). The band at 427 cm^{-1} is due to the bending vibration of the O-Si-O bonds.

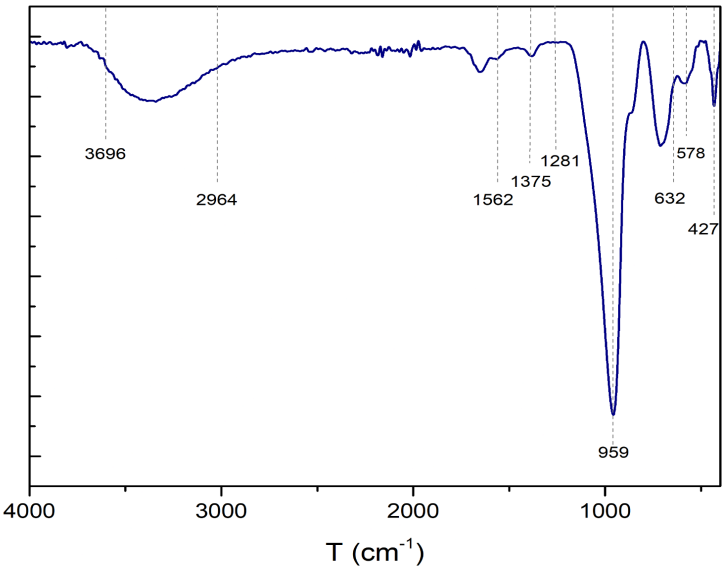

Figure 9. FTIR spectra of LTA zeolite made of MPI.

Textural characterization of zeolite LTA, made of MPI, was performed through N_2 adsorption-desorption isothermal analysis, as shown in Figure 10. Furthermore, the data collected from analysis were used to calculate the following parameters: specific surface area = 20,67 m^2/g, by Brunauer-Emett-Teller method (BET); specific external area = 18,16 m^2/g, by t-Plot method; micropores area = 2,51 m^2/g, by t-Plot method; total pore volume = 0,036 cm^3/g, obtained at p/p_0 = 0,95; total micropore volume = 0,0013 cm^3/g, by t-Plot method; and average pore diameter = 6,93 nm, by Horvath-Kawazeo method. The isotherm shows a type II pattern, attributed to non-porous or macropores materials (THOMMES et al., 2015)

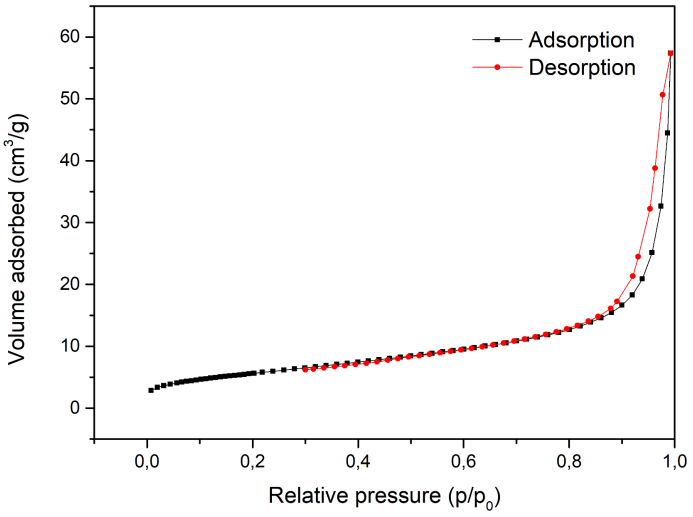

Figure 10. N_2 adsorption-desorption isotherm of LTA made of MPI.

The CO_2 adsorption and desorption isotherms were obtained generating a maximum adsorption of 1.5 mmol/g, as shown in Figure 11.

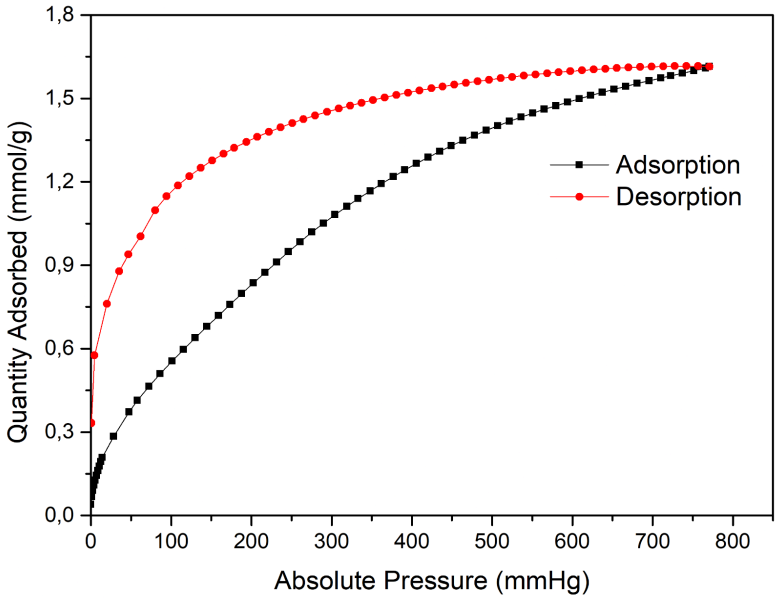

Figure 11. CO_2 adsorption-desorption isotherm of LTA made of MPI.

Conclusion

It can be concluded that the methodology used for the synthesis of MPI silica is effective in producing an amorphous silica for the production of mesoporous materials, such as the LTA molecular sieve produced in this work. As it comes from an alternative, sustainable source, its use benefits the environment and it is considered a green material.

CO_2 adsorption isotherms obtained for zeolite LTA, made of MPI amorphous silica, presented satisfactory results for the adsorption of this gas. Furthermore, the use of the molecular sieve synthesized in this work to capture CO_2 through adsorption contributes to reducing the environmental impacts and pollution caused by the excessive release of this gas.

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