2023

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6th International Conference

september 6-8 | 2023
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EFFECT OF SILICON SOURCE AND TEMPERATURE ON THE FORMATION OF ZEOLITES OBTAINED FROM SALT SLAG

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ABSTRACT
Considering its numerous applications and searching for alternatives to reduce production costs and alleviate environmental impacts, the manufacture of zeolites from waste has increased in recent years. In the present study, the effect of the silicon source and temperature on the formation of waste-based zeolites are reported. Hazardous aluminum salt slag and rice husk ash as silicon source were used as alternative raw materials for synthesize zeolites through a sustainable single-step hydrothermal process. It was found that the variation on the silicon source (rice husk ash or Na_2SiO_3) greatly affects the zeolite crystallization process, as well as temperatures variations, whose increase (80-120 ºC) leads to the formation of more stable and crystalline zeolitic materials. The synthesis of zeolites represents a promising route for recycling hazardous aluminum- and agri-food wastes, generating added-value products and reducing process costs and environmental impacts.

Keywords: waste-based zeolites, aluminum salt slag, rice husk ash, sustainable zeolite synthesis

INTRODUCTION
Zeolites are aluminosilicates that due to their regular porous structure and properties have been used in many industrial applications, including catalysis, water remediation and gas purification [1]. Zeolites can be found in nature or synthesized from a great variety of Si and Al sources. In the last decades, the use of waste materials as low-cost precursors for the preparation of zeolites has been increasing, driven by the need to minimize the waste disposal into landfills and to address associated environmental impacts [2]. In this regard, aluminum wastes can be considered promising secondary raw materials for the zeolite synthesis. One of the most important wastes generated in the secondary aluminum recycling process is salt slag, a highly reactive hazardous waste that can cause serious effects on living beings [3]. However, its aluminum-rich composition has encouraged its recovery and application. More recent research has turned its attention on the synthesis of zeolites using rice husk ash (RHA) [4]. This silicon-rich material is one of the most abundant agro-industrial wastes, resulting of the thermal transformation of rice husks, easily available and inexpensive material. Thus, zeolite synthesis from RHA opens a new route for the use of this waste, avoiding its landfill disposal and alleviating the related environmental impacts. In the present investigation, the effect of both the silicon source and temperature on the zeolite synthesis are reported. Hazardous salt slag was used as the aluminum source in the zeolite synthesis through a sustainable single-step hydrothermal process. Thus, the use of these industrial and agri-food wastes as unconventional materials is presented as a sustainable alternative for the production of zeolites, minimizing the consumption of raw materials, reducing costs and contributing to the environmental preservation.

MATERIALS AND METHODS
Materials and Analytical Techniques

The main raw material for the synthesis of zeolites was salt slag, used as aluminum source. The as-received sample consisted of a dark-grayish granular solid, with grain sizes ranging between 1 and 4mm. A commercial sodium silicate (Na_2SiO_3), also known as waterglass (WG), and RHA were used as silicon source. The RHA consisted of a dark powdered solid with grain size <1mm. X-ray Fluorescence (XRF), in a wavelength-dispersive spectrophotometer (Bruker, S8 Tiger), was used to determine the chemical composition of the wastes and synthesized zeolites. The mineralogical characterization was carried out in a Bruker D8 Advanced Diffractometer by X-ray diffraction (XRD), using CuK radiation with a scan rate of 0.5 s by step in an interval 2θ = 5-60º.

Synthesis of Zeolites

The zeolites were synthesized through a single-step hydrothermal process in a Teflon-lined autoclave reactor. All reactants, including solid wastes, NaOH solution and distilled water, in the required amounts, were placed at the time into the reactor and kept under continuous stirring. The experiments were performed with a fixed Si/Al molar ratio of ~2.0. In order to evaluate the effect of the silicon source on the zeolite synthesis, WG and RHA were tested. The temperature was varied between 80-120 ºC. All experiments were conducted at a fixed reaction time. After the synthesis, the solid products were filtrated, washed with distilled water and dried at 100 ºC.

RESULTS AND DISCUSSION

XDR patterns of the solid wastes are presented in **Fig. 1**. The mineralogical profile of the salt slag (**Fig. 1a**), consistent with its chemical composition, shows the aluminum content (35 wt%) distributed in different phases, principally, corundum (Al_2O_3), aluminum nitride (AlN) and spinel (Al_2MgO_4) (see magnification of **Fig. 1a**). The salt slag exhibits pronounced peaks related to sodium chloride, derived to the high amounts of salt used in the aluminum scrap melting process. The XRD pattern of RHA (**Fig. 1b)** exhibits the profile characteristic of cristobalite (SiO_2) as the only crystalline phase.

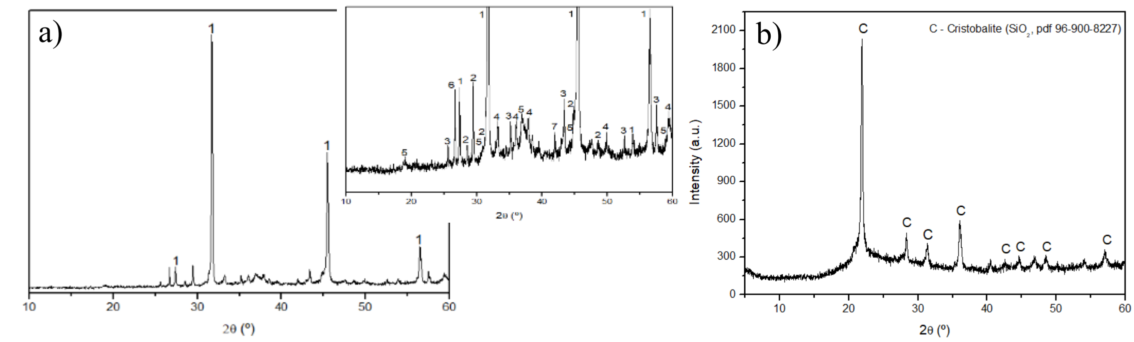

Fig. 1. XRD pattern of the a) salt slag (1 = halite (NaCl, pdf 96-430-0181), 2 = sodium nitrite ($NaNO_2$, pdf 96-152-8101), 3 = corundun (Al_2O_3, pdf 96-900-9672), 4 = aluminum nitride (AlN, pdf 96-901-1658), 5 = spinel (Al_2MgO_4, pdf 96-900-2098), 6 = quartz (SiO_2, pdf 96-153-6390), 7 = periclase (MgO, pdf 96-900-6763), and b) RHA (C = cristoballite).

Fig. 2 shows the XRD pattern of the synthesized zeolites at different experimental conditions. The diffractogram of the zeolite synthesized with WG (**Fig. 2a**) exhibits a diffraction profile characteristic of zeolite type-P (NaP1, $Na_6Al_6Si_{10}O_{32}.12H_2O$, cubic), according to the reference file (ICCD PDF = 96-810-3735). This phase exhibits well-defined and narrow peaks with the most intense reflection centred at 28º (2θ).

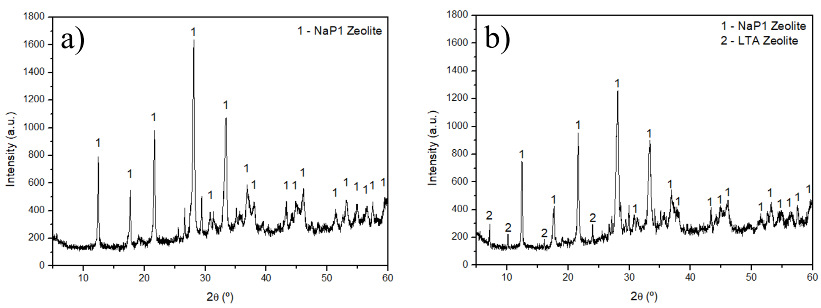

Fig. 2. XRD pattern of zeolites synthesized with a) WG and b) RHA.

The zeolite synthesized with RHA (**Fig. 2b**) also exhibits an XRD profile characteristic of NaP1 zeolite; however, the intensity of peaks is lower than that of the zeolite obtained with WG. In addition, some weak peaks of Linde Type-A (LTA) zeolite (ICCD PDF = 96-412-4674) are also observed. Crystallized zeolitic phases greatly depend on the type of silicon source, since its variation (including its textural and chemical properties) can modify the nucleation and crystal growth of zeolites [5]. The easier solid-liquid interaction can explain the better crystallization of the sample from WG rather than solid RHA, which can be attributed to the more rapidly depolymerization of the silica with NaOH solution, resulting in inducing faster nucleation [6].
Considering that the present work focuses on waste-based zeolites, the effect of the temperature in their synthesis using salt slag and RHA was studied. Diffractograms shows that at 80 ºC (**Fig. 3a**), the peaks of NaP1 and LTA zeolites are weakly intense, indicating low crystallographic development. Furthermore, the amorphous background pattern indicates that part of the waste compounds was not able to react under these conditions. At 100 ºC (**Fig. 3b**), the sample exhibits a pattern with sharper and slightly better defined peaks. From the **Fig. 3c**, it is notable that at 120 ºC the chemical reaction between salt slag and RHA has taken place to a significant extent, and led to the formation of crystalline product, highlighted with sharp and narrow diffraction peaks, forming Analcime (ANA) zeolite (ICCD PDF = 96-900-9956). It is observed that the increase in temperature leads to the development of more crystalline and stable zeolites.

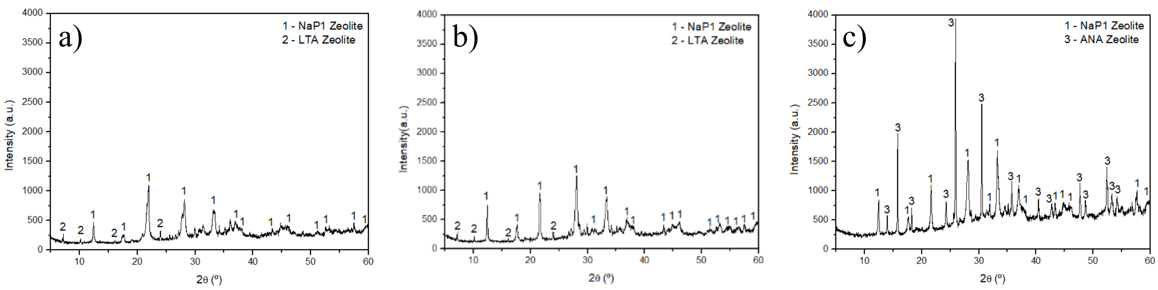

Fig. 3. XRD pattern of zeolites synthesized at a) 80 ºC, b) 100 ºC and b) 120 ºC.

CONCLUSION

The waste-based synthesis led to the formation of NaP1, LTA and ANA zeolites. It was evident the great influence of the silicon source, affecting the nucleation and crystal growth processes of zeolites. Increasing the temperature promoted the development of crystalline phases and the formation of more thermally stable zeolites. The waste conversion into zeolitic material can be considered a sustainable alternative to the waste management, generating value-added materials with promising applications, reducing the process costs, and greatly contributing to environmental preservation.

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