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Study of the synthesis and characterization of SAPO-34 zeolite: a promising material for application in gas separation membranes

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Abstract

Different strategies for the gas separation and capture, such as carbon dioxide (CO_2) and nitrogen gas (N_2), have been developed over the past decades, including cryogenic distillation, absorption, adsorption, and membrane separation techniques. Due to simplicity, energy efficiency, compactness, and regenerability, there has been a growing interest in recent years in studies related to the use of inorganic materials in membrane. These studies have generated promising alternatives for the industry.[1,2] The incorporation of molecular sieves, such as zeolites, in these devices has led to significant improvements in the performance for the separation of different gases when compared to polymeric membranes. Zeolites exhibit a unique chemical composition, diverse pore size distributions (depending on the type of zeolite), and varied physicochemical and ion exchange properties. The zeolite SAPO-34 has proven to be highly promising for membrane applications. Its composition is of the $Si_XAl_YP_ZO_2$ type, belonging to the silicoaluminophosphate family, where X = 0.98; Y = 0.01-0.60, and Z = 0.01-0.52. It has a chabazite (CHA) crystal structure, formed by the substitution of silicon with phosphorus ($AlPO_4$). Its intracrystalline structure is composed of 8-membered rings with diameters of 0.94 nm (0.38 x 0.38 nm). Additionally, its average pore size is compatible with the kinetic diameter of different gases, such as CH_4 (0.38 nm), N_2 (0.36 nm), CO_2 (0.33 nm), etc.[1–4] Due to presenting promising characteristics for application in membranes, this work proposes a study to evaluate the influence of synthesis parameters (thermal treatment time and heating power) on the properties of the SAPO-34 zeolite formed at the end of the process. For this purpose, two crystallization methodologies were used (Fig. 1): hydrothermal (HT) in an autoclave and microwave-assisted reaction (MW). In both approaches, the reaction ratio of 1 Al_2O_3 : 2 P_2O_5 : 0.6 SiO_2 : 4 TEAOH : 150 H_2O was applied based on the methodologies of Li *et al*., Zheng *et al*., Zong *et al*., and Álvaro-Muñoz *et al*.[1-4] The HT reaction was carried out in the following steps: 1) Preparation of the synthesis gel by adding, in a 50 mL beaker, the deionized water, aluminum source (aluminum isopropoxide - Alip), phosphorus source (phosphoric acid – H_3PO_4), colloidal silica (LUDOX AS-40), and the organic structure-directing agent (tetraethylammonium hydroxide – TEAOH). The material was stirred overnight; 2) After stirring, the synthesis gel was placed in a Teflon container, sealed and positioned inside a 50 mL autoclave. The autoclave was placed in a muffle furnace at 200°C for different times of thermal treatment, ranging from 24h to 96h; 3) Following the hydrothermal reaction, the crystals were washed, vacuum-filtered and dried in an oven at 100°C; 4) Finally, the dried SAPO-34 crystals underwent a calcination process in a muffle furnace (550°C, 4h, heating rate of 1°C/min) to remove organic residues and adsorbed water. The MW reaction was conducted in a similar way to the HT methodology, however, the heat treatment, elucidated in step 2, was carried out in microwave oven, at 180°C for times between 30min and 24h. Additionally, the washing and separation of the material had to be carried out through cycles of centrifugation (8000 r.p.m) with solvent exchange, as conventional vacuum filtration was not efficient in separating the zeolite crystals. Selected samples were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and N_2 gas adsorption. XRD results showed that, for both methodologies, the SAPO-34 zeolite was formed, in which there was an increase in crystallinity as the heat treatment time of the material increased. All samples led to crystals with preferential growth in planes from family (101) at 2θ = 9,5° with crystallite sizes in the range of 37-58 nm. Additionally, results obtained through microwave synthesis indicated that with just 6 hours of treatment it is possible to obtain a material with crystallinity comparable to that achieved with 72 hours in an autoclave. It is conceivable that this microwave treatment time could be further reduced by incorporating seed usage to expedite the nucleation and growth processes involved in SAPO-34 formation.[6,7] The FTIR results revealed the presence of characteristic bands of zeolite, such as the bending of Si-O bonds (683 cm^{-1}) belonging to D-6 rings that confirms the formation of the CHA structure. Vibration bands near to 740 cm^{-1} and 1090 cm^{-1} were also observed, attributed respectively to the symmetric stretching of P-O or Al-O and the asymmetric stretching of O-P-O. In the region of 3000–4000 cm^{-1}, a broad vibrational stretching band was visualized, attributed to the bridged hydroxyl groups, Si-OH-Al, responsible for generating the Brønsted acidity of SAPO-34. The SEM micrographs show the formation of cubic and alongated structures for all materials. However, samples synthesized via microwave exhibited smaller crystal sizes (≈850 nm) than those produced through hydrothermal treatment (≈2 µm), with a prevalence of

structures resembling nano-sheets and elongated shapes. This indicates that the microwave-assisted reaction not only increases the reaction rate but also has the potential to influence the nucleation and growth mechanisms of the crystals. These characteristics are desirable for membrane applications, as zeolite crystals with small and uniform dimensions are promising for the production of thinner and less defective membranes, contributing to a better balance between permeability and selectivity. Finally, the results obtained in the adsorption study showed that the increase in synthesis time, for both methodologies, led to: an increase in the BET total surface area (810 m^2/g); an increase in the area and volume of micropores (773 m^2/g | 0.28 cm^3/g); a decrease in external surface area (38 m^2/g); and a decrease in mesopore volume (0.07 cm^3/g). Therefore, it is evident that the SAPO-34 crystals synthesized in this study exhibit excellent potential for application in the production of membranes for gas separation of different configurations (e.g. - mixed matrix membranes). This is particularly true for those produced via microwave, as their structure features a more uniform morphologies and pore size compatible with the kinetic diameter of various commercially relevant gases (CO_2, N_2, CH_4, Xe, etc.), enabling the production of membranes with a more uniform surface and smaller thicknesses.

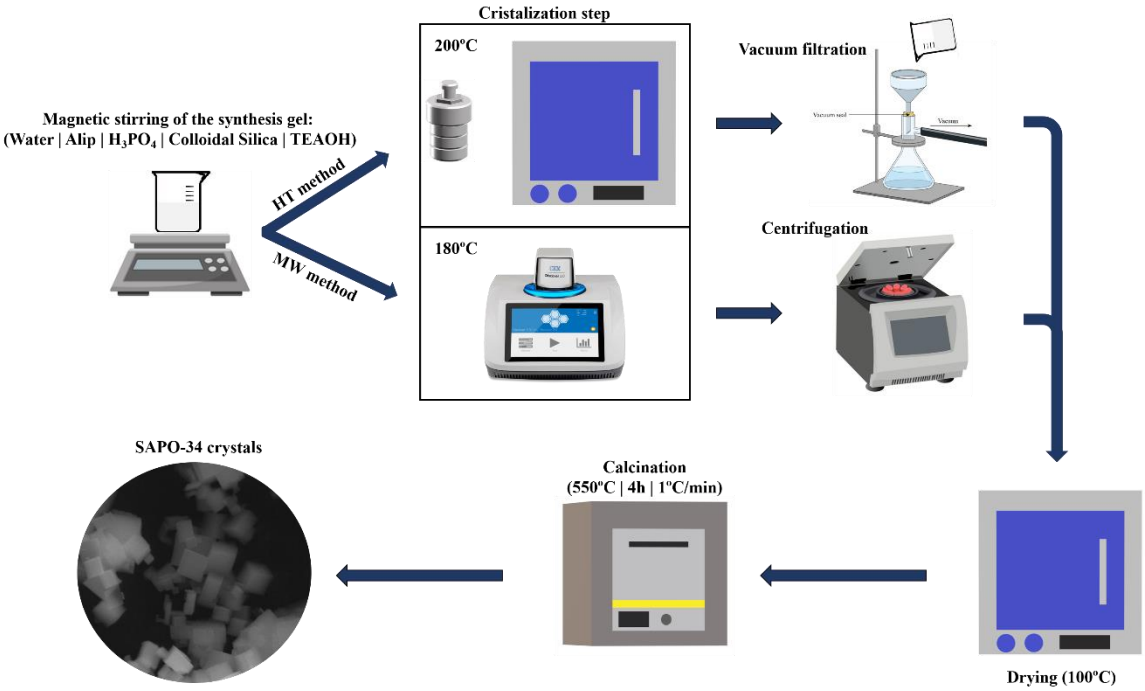

Figure 1. Scheme for synthesis methodologies adopted in the present study.

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