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Synthesis and characterization of K^+_SSZ-13 as an active phase for gas separation membranes

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Abstract

Zeolitic materials, such as SSZ-13 zeolite, have a three-dimensional structure with well-defined channels and cavities in which the micropores present in this structure allows efficient separation as molecules diffuse through this material [1 – 4]. The three-dimensional network structure of the SSZ-13 zeolite (CHA topology) consists of $[AlO_4]^{5-}$ and $[SiO_4]^{4-}$ tetrahedrons that are interconnected by oxygen bridges that form a large ellipsoidal cage (CHA) and double six-membered ring (d6r) as composite building units [4]. It has a pore diameter of 0.38 nm, which makes it a promising material for separation of gases such as CH_4, N_2 and CO_2 which have a kinetic diameter of 0.38 nm, 0.36 nm and 0.33 nm, respectively [1, 2].

SSZ-13 zeolite is usually obtained by the hydrothermal method, using the sodium ion (Na^+) as the counter-ion of the structure [1, 4]. However, with the aim of optimizing the synthesis of this material and based on studies by Iorio *et al*. [3], changing the counter-ion of the structure can lead to a structural improvement of the material [2, 3]. The use of monovalent counterions such as potassium ion (K^+) provides structures richer in silicon when compared to structures that use bivalent cations [2]. Furthermore, as K^+ has a larger ionic radius than Na^+, this allows for an improvement in the stabilization of the intersections of pore channels existing in zeolite structures, as the addition of the K^+ ion together with the organic structure-directing agent N,N,N-trimethyl-1-adamantammonium hydroxide (TMAdaOH), provided evidence that three K^+ cations displace one $TMAda^+$ from occupying a cage, so that they influence the location and distribution of Al atoms of the structure, in which there are predominantly isolated Al sites in the rings of 6 members (6-MR) [3]. Thus, the objective of this study was the synthesis and characterization of the K^+_SSZ-13 structure by X-Ray Diffraction (XRD), Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Gas Sorption Analysis (with nitrogen). The synthesis gel was produced from a mixture of the reagents KOH, $Al(OH)_3$, TMAdaOH and Ludox AS 40 in the molar ratio of 100 SiO_2: 5 $Al(OH)_3$: 20 TMAdaOH: 20 KOH: 4400 H_2O [1,2]. The gel was poured inside an autoclave and sealed. The autoclave was placed in an oven at 160 °C for periods varying within 1-4 days. The obtained white powder was washed with distilled water and the dry powder was heat treated at 600 °C for 6 h with 1 °C/min heating rate.

The characterizations indicated that the synthesis of K^+_SSZ-13 zeolite was successful for 3 and 4 days of synthesis. The syntheses carried out with 1 and 2 days showed the initial stages of polymerization, with the formation of an amorphous gel of oligomers and the beginning of the presence of the crystalline phase due to the dissolution of these oligomeric precursors into smaller units, which will form the nuclei that will grow until the definitive formation of the zeolitic crystals [1 – 4]. For the syntheses carried out with 3 and 4 days, the formation of characteristic peaks (Fig. 1) of the rhombohedral SSZ-13 crystal structure [1 - 3] was observed, with a crystallite size of 33.8 nm. The results of the FTIR analysis confirmed the presence of the 6-membered rings present in the SSZ-13 zeolite structure [4].

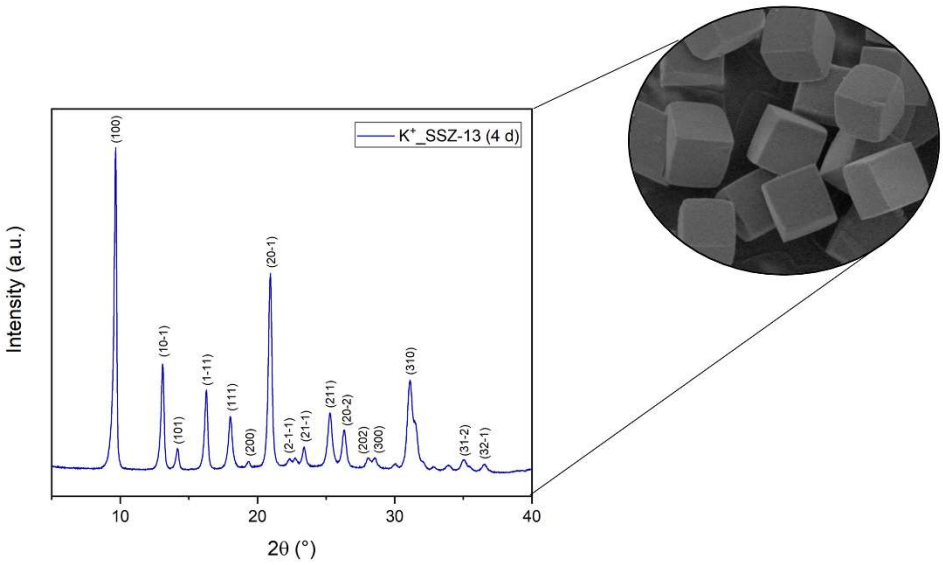

Fig. 1 XRD diffraction and SEM image of the K^+_SSZ-13 produced in four days.

As the K^+_SSZ-13 synthesis time increased, the cubic crystals characteristic of this structure [1, 2], became perfectly cubic shape, indicating an average particle size of 4 – 5 µm, with a Si/Al ratio around of 12 (the Si/Al ratio of Na^+_SSZ-13 was 10). Also, the gas adsorption analysis in N_2 indicated the formation of a microporous material [1, 5], and the estimated BET specific surface area was 926 m^2/g, slightly higher than expected for SSZ-13. In general, the K^+_SSZ-13 zeolite showed the formation of better-defined crystals, with a higher Si/Al ratio and a relative increase of 86% in BET specific surface area than the zeolite produced with the sodium counter-ion (Na^+_SSZ-13). These results demonstrated that the switch in the counterion promoted structural changes that could provide advantages in the application of this material. For instance, the use of particles with higher specific surface area may lead to improved membrane performance, whereas the higher Si/Al ratio of SSZ-13 has already been reported to increase the stability of membranes in the presence of humidity [1]. As a future application perspective, the K^+_SSZ-13 seeds produced in this study will be used to form an active zeolite film in the formation of inorganic membranes intended for gas separation.

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