17th International Conference on Inorganic Membranes
New Frontiers for Inorganic Membranes
July 1 - 5, 2024
Oceania Convention Center - Florianópolis - Brasil

Analysis of hydrothermal synthesis parameters for production of SSZ-13 seeds for membrane-based N_2/CH_4 separation

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Abstract

Zeolite membranes have presented promising results for membrane-based gas separation, such as natural gas treatment [1], as it shows the capacity to tune the pore size based on the zeolite composition. The SSZ-13 zeolite, for instance, presents a chabazite structure with 0.38 nm pores resulting in molecular sieving effect for efficient gas separations of CO_2/CH_4 and N_2/CH_4 [2]. Synthesis of the SSZ-13 is typically by hydrothermal synthesis at high temperatures and pressures for periods within 3-10 days [3]. Despite the intense effort on production of SSZ-13 membranes recently, deeper understanding of the influence of the Si precursor on hydrothermal synthesis for shorter synthesis periods is fundamental for future developments on membrane science.

This study explores the microstructural characterization of SSZ-13 seeds synthesized with tetraethyorthosilicate (TEOS) and colloidal silica (Ludox – AS4) as silicon precursors through hydrothermal synthesis lasting 1-4 days, focusing on the comparison of the obtained seeds and discussion of the influence that zeolite properties will have on the secondary growth of SSZ-13 membranes. The solution was produced with NaOH, $Al(OH)_3$ and N,N,N-trimethyl-1-adamantylammonium hydroxide (TMAdaOH). Components were mixed for 1h and poured inside an autoclave. The sealed autoclave was placed in an oven at 160 °C for periods varying within 1-4 days. The obtained white powder was washed and the dry powder was heat treated at 600 °c for 6 h with 5 °C/min heating rate. The calcined powder was characterized by X-Ray Diffraction (XRD), Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA) and Gas Sorption Analysis (with Argon). SSZ-13 membranes and mixed-matrix membranes (PDMS/SSZ-13) were also produced using the SSZ-13 seeds from this study, both will be simultaneously presented in other abstracts during the 17th ICIM 2024, as this abstract focused on the microstructural comparison of SSZ-13 seeds.

All the samples produced with TEOS were highly crystalline showing the typical SSZ-13 structure, even the sample with only 1 day hydrothermal synthesis. The synthesis yields revealed that the use of different Si precursors had a stronger influence on the mass yields than the duration of the hydrothermal synthesis. For instance, when TEOS was used the high yields (~85%) were attained for synthesis within 2-4 days, with a slight decreas to 76% when the material was synthesized within 1 day. As for the samples with Ludox as Si precursor, the samples within 2-4 days showed highly crystalline SSZ-13 structure, however the sample with 1 day hydrothermal synthesis displayed low degree of crystallinity due to the presence SSZ-13 and amorphous Si and Al compounds. The mass yields did not show a clear trend on the influence of the duration of the hydrothermal synthesis, although all samples showed significantly lower yields (46-61%) when compared to the samples with TEOS.

The samples obtained by each Si precursors showed significantly different morphologies (shown in Fig. 1a), samples produced from TEOS resulted in cubic structures with increasing particle size (1.5 µm to 3.0 µm, average size) for longer hydrothermal synthesis, whereas the Ludox resulted in larger particles (5-30 µm, Fig. 1b) with random shapes and polycrystalline structures. The only exception was the sample produced with Ludox and synthesized within 1 day, which resulted in large agglomerates composed of nanometric particles, probably a Si-based amorphous phase.

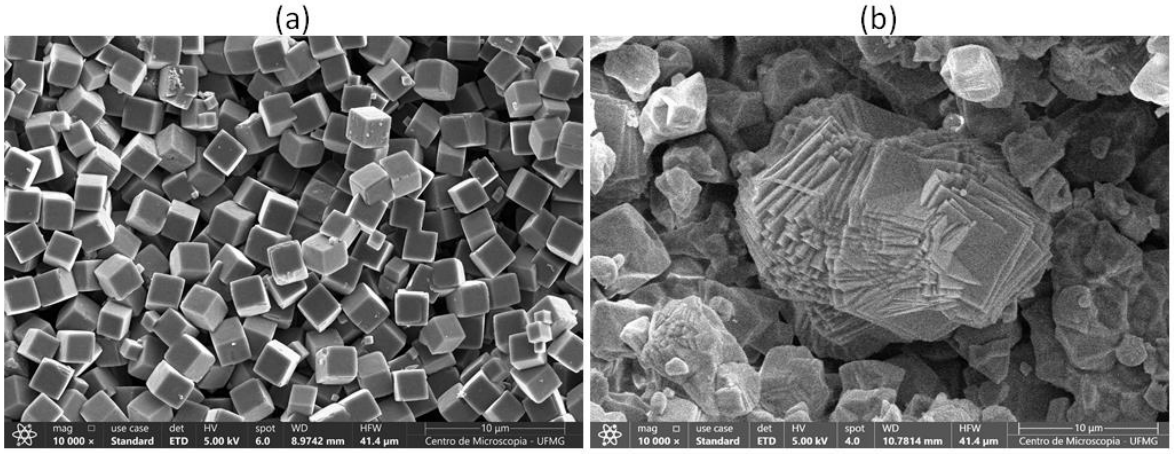

Fig. 1 – SEM micrographs of the obtained samples, detailing the samples obtained with 4 days hydrothermal synthesis and using different Si precursors: (a) TEOS and (b) Ludox AS-40. The scale bars read 10 µm for all micrographs.

The Ar isotherms showed an interesting behavior, in which samples produced with TEOS were all microporous (average pore width of 0.755 nm, typical of chabazite 3D cage with 0.38 windows) with decreasing specific surface area (749 to 609 m^2/g) and pore volume (0.437 to 0.362 cm^3/g) as the synthesis was performed for longer periods. On the other hand, the samples with Ludox revealed that the sample produced during 1 day has micro and mesopores on its structure. For samples obtained with synthesis longer than 2 days, they were all microporous with increasing specific surface area (599 to 858 m^2/g) and pore volume (0.340 to 0.500 cm^3/g) as longer synthesis were performed. These results suggest that the samples with TEOS are initially formed by a structure with rough surface and hollow structure, which are then filled as the synthesis is carried out for longer periods until the formation of a perfectly cubic shape with well-defined vertices and edges. Regarding the samples with Ludox, the initial nanometric and amorphous particles allow the development of the SSZ-13 structure simultaneous to the particle growth forming polycrystalline particles with sizes around 5-30 µm.

Future studies will focus on utilizing these seeds for SSZ-13 film formation for membrane manufacture. The authors have hypothesized that the use of smaller and rougher particles are more appropriate for the secondary growth of SSZ-13 membrane, since the surfaces (including internal surface for hollow particles) of these particles are more highly energetic. Consequently, there will be a higher thermodynamic trend for crystal growth around these seeds than the perfectly shaped SSZ-13 seeds, making it a more adequate seed for secondary growth. Moreover, higher packing of these seeds has already been reported to allow production of thinner membranes [2], which is advantageous for membrane performance. Therefore, the comparison of SSZ-13 membranes using different seeds is paramount for complete understanding for membrane manufacture.

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