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A comparative study of ZSM-5 embryonic and crystalline zeolites synthesis through two methodologies

Ana L. A. Simões,[1] Sara S. Vieira,[2] Emanuel B. C. D. Elias,[3] Mariele I. S. de Mello,[3] Sibele B. C. Pergher[3] and Maria H. Araujo[1]

[1]Departmento de Química, Universidade Federal de Minas Gerais, Belo Horizonte, Brasil
[2] Instituto de Química, Departamento de Química Inorgânica, Universidade Federal Fluminense, Niterói, Brasil
[3]Instituto de Química, Universidade Federal do Rio Grande do Norte, Natal, Brasil
e-mail: aninhaasimoes@yahoo.com.br

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Zeolites are a group of materials defined by Martínez and Corma[1] as inorganic solids, typically microporous, composed of tetrahedral structures made up of TO_4 units, where T generally corresponds to Si and Al atoms. In the 2000s, zeolitic materials with nanometric dimensions became a subject of interest for numerous researchers, thus, the quest for materials with larger surface areas and more accessible active sites led to the exploration of hierarchical and embryonic zeolites.[2] These partially formed zeolites lack the typical crystallinity of fully developed zeolitic structures but exhibit short-range ordering. In these embryonic zeolites, the pores are more open, and the active sites are fully accessible, reducing the reactants' diffusion path and facilitating their use as catalysts.[3] This work aimed to investigate the formation of embryonic and crystalline ZSM-5 zeolites. We compared two different adapted methodologies and varied parameters to better understand the formation of embryonic zeolites and compare the materials obtained from each method. In series A, two samples were synthesized, varying only in the presence or absence of the hydrothermal step, resulting in ZA150 and ZA, respectively. XRD, FTIR, and N_2 adsorption results indicated the presence of an embryonic structure in sample ZA, whereas ZA150 exhibited a crystalline structure. In series B, three samples were meticulously synthesized, varying the hydrothermal step: sample ZB3B without the hydrothermal step and samples ZB1 and ZB3 with hydrothermal steps of different durations (1 and 3 days, respectively). XRD profiles and N_2 adsorption results suggested the formation of some embryonic nuclei in sample ZB3B, although in smaller quantities than intended, along with the possible presence of a macroporous amorphous aluminosilicate matrix. The hydrothermal treatment at 150°C for both 1 and 3 days was sufficient to promote the development of zeolitic crystals with the ZSM-5 structure. However, XRD and FTIR results indicated that crystallization was not complete. For methodology A, an area above 600 $m^2\ g^{-1}$ was achieved for the embryonic zeolite with a 4-hour aging step at room temperature, a value much higher than the 139 $m^2\ g^{-1}$ area of sample ZB3B, which was left at room temperature for three days. This difference was also observed in crystalline zeolites. The primary factor for the observed differences was using a larger quantity of the directing agent TPAOH in methodology A compared to methodology B. The $(TPA)_2O/SiO_2$ ratio for A was 0.18, 60 times greater than that used for B, 0.003. The presence of the directing agent favors the nucleation stage, facilitating the formation of embryonic zeolites at lower temperatures and yielding smaller zeolite crystals, potentially leading to significant advancements in the field.

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