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Aluminum Content on the Crystallization of Zeolite Beta

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The zeolite beta is a very important material for catalytic processes; it was described for the first time in 1.967 according to patent [1]. It is a microporous solid that can be synthesized in an extensive range of Si/Al ratios, its structure is formed by an intergrowth of two or three polymorphs [2,3]. The stacking disorder obtained by the presence of different proportions of these polymorphs affects the sorption and catalytic properties.

The understanding of the physical and catalytic properties of these materials is dependent on the knowledge of the structural features of the framework. These properties are mainly affected by crystal size, faulting, and Si/Al ratio. Therefore, in the present work a detailed study of the effect of the aluminum content on these variables and on the crystallization behavior of beta zeolite was studied.

The synthesis was carried out following a modification of the recipe given by Camblor et al. [4]. $Al(OH)_3$ was first dissolved in tetraethylammonium hydroxide (20% aqueous solution, Merck). This solution was then added to a mixture made by dispersing Ludox HS-40 colloidal silica, 40% suspension in water in a solution of tetraethylammonium hydroxide and the mixture was homogenized by stirring. Crystallization was performed with and without agitation at 140ºC in a stainless steel autoclave for different periods. The solids obtained were separated by centrifugation, washed with distilled water and calcined at 600ºC. Gels with different SiO_2/Al_2O_3 ratios (200, 100, 25) were prepared. Characterization was carried out in a CM10 Philips transmission electron microscope operating at 80keV and a Field emission scanning electron microscope Hitachi FE 4500 operating at 8-10 kV

The aluminum addition has a strong effect on crystallization behavior, crystal size and morphology. As it is expected the concentration of alumina in the reactant gel affects the rate of crystallization and the crystal size. As the Al content increases the crystallization time increases and the crystal size decreases due to the disruptive effect of the Al on the structure. For high aluminum content (SiO_2/Al_2O_3 =25), complete crystallization is reached after 14 days with very a long induction period. As the aluminum content decreases shorter crystallization periods are observed with shorter induction periods. For low aluminum content (SiO_2/Al_2O_3 =200) crystallization is reached in less than 6 days.

The kinetics of crystallization was followed by XRD for the different SiO_2/Al_2O_3 ratios. The sample with the lowest SiO_2/Al_2O_3 ratio fully crystallized after 14d. However a close analysis by TEM showed very small crystallites after 10days indicating the initial crystallization stages (Fig. 1). The Al content has also a marked effect on crystal morphology, Fig. 1 shows the TEM images and Fig. 2 the SEM images for the different SiO_2/Al_2O_3 ratios. For low Al content (SiO_2/Al_2O_3 = 200) the crystals were rounded with an average crystal size of 250 nm. As the Al content increases (SiO_2/Al_2O_3 = 100) the crystal morphology changes to an elliptical rice-like morphology with an average crystal size of 120 nm. For even higher Al contents (SiO_2/Al_2O_3 = 25) nanometric beta zeolite was obtained with an average crystal size 15 nm. A direct linear dependence between crystal size and SiO_2/Al_2O_3 ratio was observed.

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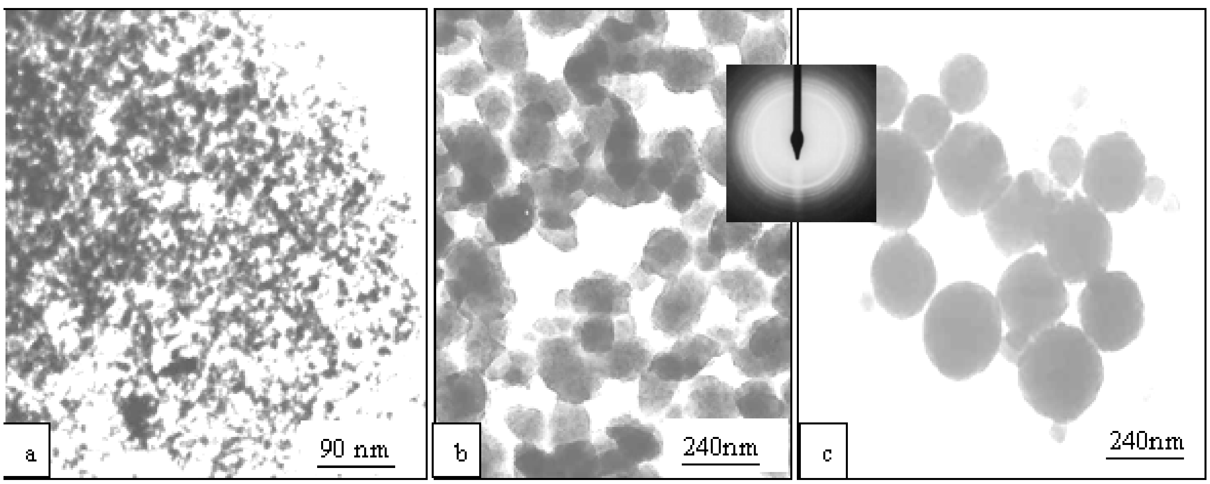

Fig. 1 TEM bright field images for crystallization period of 10 d for different SiO_2/Al_2O_3 ratios; a. x= 25; b. x=100; c. x=200

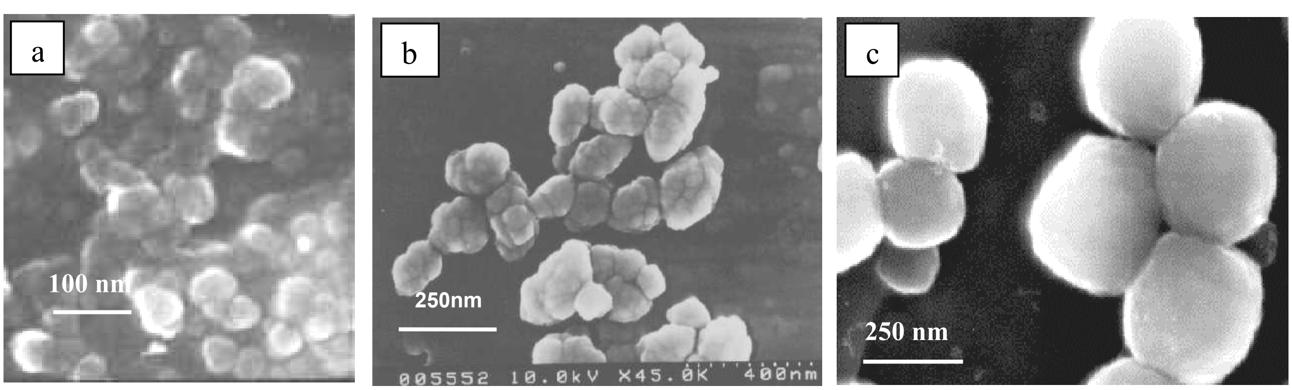

Fig. 2 SEM images of zeolite beta with different SiO_2/Al_2O_3 ratios; a. x=25; b. x=100; c. x=200.

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