Supplementary Material

Monitoring of the crystallization of Zeolite LTA using Raman and chemometric tools

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Zeolite synthesis optimization

In order to obtain the best conditions to synthesize zeolite LTA nanocrystals, some investigations were performed on the influence of the alkalinity, crystallization time, crystallization temperature and aging time. The best synthesis condition was monitored using Raman spectroscopy with at-line sampling and the dataset was analyzed by PCA.

Effect of alkalinity. In order to investigate the effect of alkalinity, syntheses were performed using the ratios Na_2O/Al_2O_3 = 3.2, 3.7, 4.2, 4.7, 5.2, 5.7, 6.2 and 6.7. The reaction mixtures were left for 4h at 100º C in an autoclave. X-ray diffraction showed that the increase of the alkalinity preferentially leads to the SOD structure, instead of the LTA structure. Pure LTA was obtained using a Na_2O/Al_2O_3 ratio from 3.2 to 5.2 and pure SOD was obtained using 6.7 Na_2O/Al_2O_3 ratios. The ratios 5.2 to 6.2 presented a mixture of SOD and LTA. For the conditions where only pure LTA was obtained, it was evidenced that the higher the alkalinity, the lower is the size of the synthesized LTA crystals. The diffractograms and MEV analyses are presented in the Figures 1SM and 2SM, respectively.

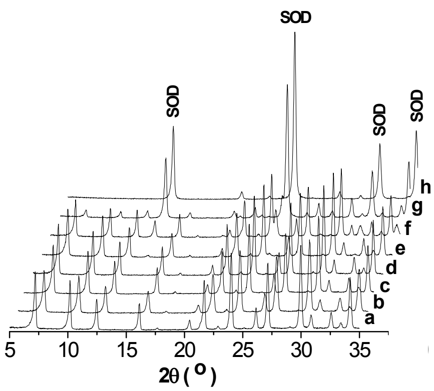

Figure 1SM. X-ray diffractograms for samples with different Na_2O/Al_2O_3 ratios: 3.2 (a), 3.7 (b), 4.2 (c), 4.7 (d), 5.2 (e), 5.7 (f). 6.2 (g) e 6.7 (h). Four hours of hydrothermal treatment at 100 C°.

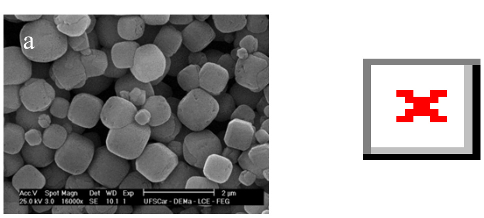

Figure 2SM. Micrograph of samples with different Na_2O/Al_2O_3 ratios: 3.2 (a) e 5.2 (b).

Effect of the crystallization time. In order to evaluate the effect of the crystallization time, a reaction mixture using 3.2 Na_2O/Al_2O_3 was left at 100°C in an autoclave and the hydrothermal syntheses ranged from 2 h up to 168 h. Between 2 h and 48 h of hydrothermal treatment is was possible to obtain a pure LTA phase, which presented just a small variation of the diffraction intensities. Reaction times higher than 72 h presented higher SOD presence. The diffractograms are presented in the Figure 3SM. Due to the alkalinity and crystallization time effects, the 5.2 Na_2O/Al_2O_3 ratio was chosen, using a short hydrothermal treatment time, in order to obtain pure zeolite LTA nanoparticles. In addition, due to the fast formation of the zeolite LTA (and slow formation of zeolite SOD), as evidenced by crystallization time and alkalinity effects, a lower temperature for the hydrothermal synthesis was studied.

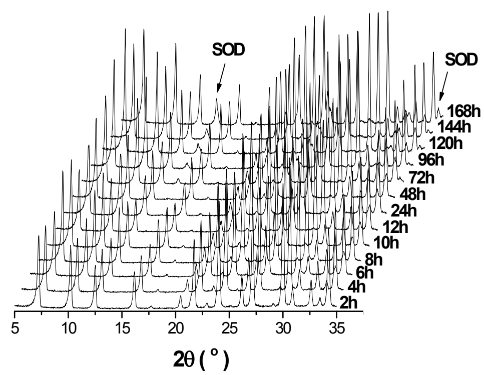

Figure 3SM. X-ray diffractograms for synthesized samples with different times of hydrothermal treatment at 100°C.

Effect of the temperature. Syntheses were performed using the reaction mixture 5.2 Na_2O : Al_2O_3 : 2 SiO_2 : 128 H_2O using hydrothermal treatment at 60ºC for 1h, 2h, 3h and 4h. For an hour of reaction, the product presented amorphous characteristics. After 2h of hydrothermal treatment, some characteristic peaks for LTA start to rise. The crystallization process stabilizes after 3 h, and it was not possible to note a difference (both in intensity and profile) between the diffractograms for 3h and 4h of hydrothermal treatment. Compared with the synthesis using 100ºC (*Effect of the alkalinity*) and the same reaction mixture, the product presented similar characteristics regarding the crystal size. The diffractograms of this study are presented in the Figure 4SM.

Effect of the aging time. A study of the aging time effect from 1 up to 5 days at 25ºC was performed using the reaction media 5.2 Na_2O : Al_2O_3 : 2 SiO_2 : 128 H_2O. After the aging time, the reaction mixtures were put in

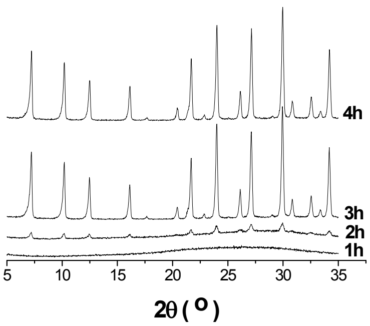

Figure 4SM – X-ray diffractograms for synthesized samples with different times of hydrothermal treatment at 60°C. Composition: 5.2 Na_2O : Al_2O_3 : 2 SiO_2 : 128 H_2O.

autoclaves at 100ºC for 1h or 2h. The diffractograms and MEV analyses of this study are presented in the Figures 5SM and 6SM, respectively. Results showed that the increasing of the aging time led to a reduction of LTA particle size, when aging time varied from 1 to 3 days. However, crystalline products (LTA) were observed after 4 days of aging time at 25 ºC, without any hydrothermal treatment. Since higher alkalinity produce smaller particles was verified in a previous study, the crystallization at 25 ºC was studied using the reaction mixture 6.2 Na_2O : Al_2O_3 : 2 SiO_2 : 128 H_2O, in order to decrease the time necessary to obtain crystalline products and small particles. The diffractograms of this study are presented in the Figure 7SM. As can be seen in the study of the alkalinity effect, the reaction mixture 6.2 Na_2O : Al_2O_3 : 2 SiO_2 : 128 H_2O yields a mixture of SOD and LTA zeolites when a hydrothermal treatment at 100ºC was used, however, through the study of crystallization time, it could be seen that the zeolite LTA production kinetics are higher than for the zeolite SOD. Thus, at 25ºC it is easy to control the synthesis in order to obtain only LTA zeolite even using a 6.2 Na_2O/Al_2O_3 molar ratio.

Some samples were characterized by N_2 physisorption and the results are presented in the Figure 8SM. The results were compared with a sample obtained using the standard condition of synthesis: 3.2 Na_2O : 1.0 Al_2O_3 : 2 SiO_2 : 128 H_2O, 4 h of hydrothermal treatment at 100 °C, without aging time [17] (Figure 1SMa). The sample of the standard condition of synthesis presented a low adsorption capacity and external area. To evaluate a possible effect of the adsorption kinetics, the isothermal equilibration time was modified to the sample which was not aged. The results show that the increasing of the adsorption time (15 s to 60 s) did not lead to an increase in the volume adsorbed at low pressures. The increasing of the alkalinity and aging time (5.2 and 6.2 Na_2O/Al_2O_3, 3 days of aging time and 2 h of hydrothermal treatment 100 °C) resulted in an increasing of the external area and adsorption capacity. It can be observed that at low pressures the amount adsorbed increases very pronounced, this is a behavior of microporous materials. This shows that the increasing of the alkalinity favored the increasing of the external area and micropores availability for the adsorbate.

The crystallization at 25ºC using the reaction mixture 6.2 Na_2O : Al_2O_3 : 2 SiO_2 : 128 H_2O was the condition which presented the best LTA zeolite. Raman spectroscopy was then used to evaluate what occurred in the reaction media of this synthesis close to the real time.

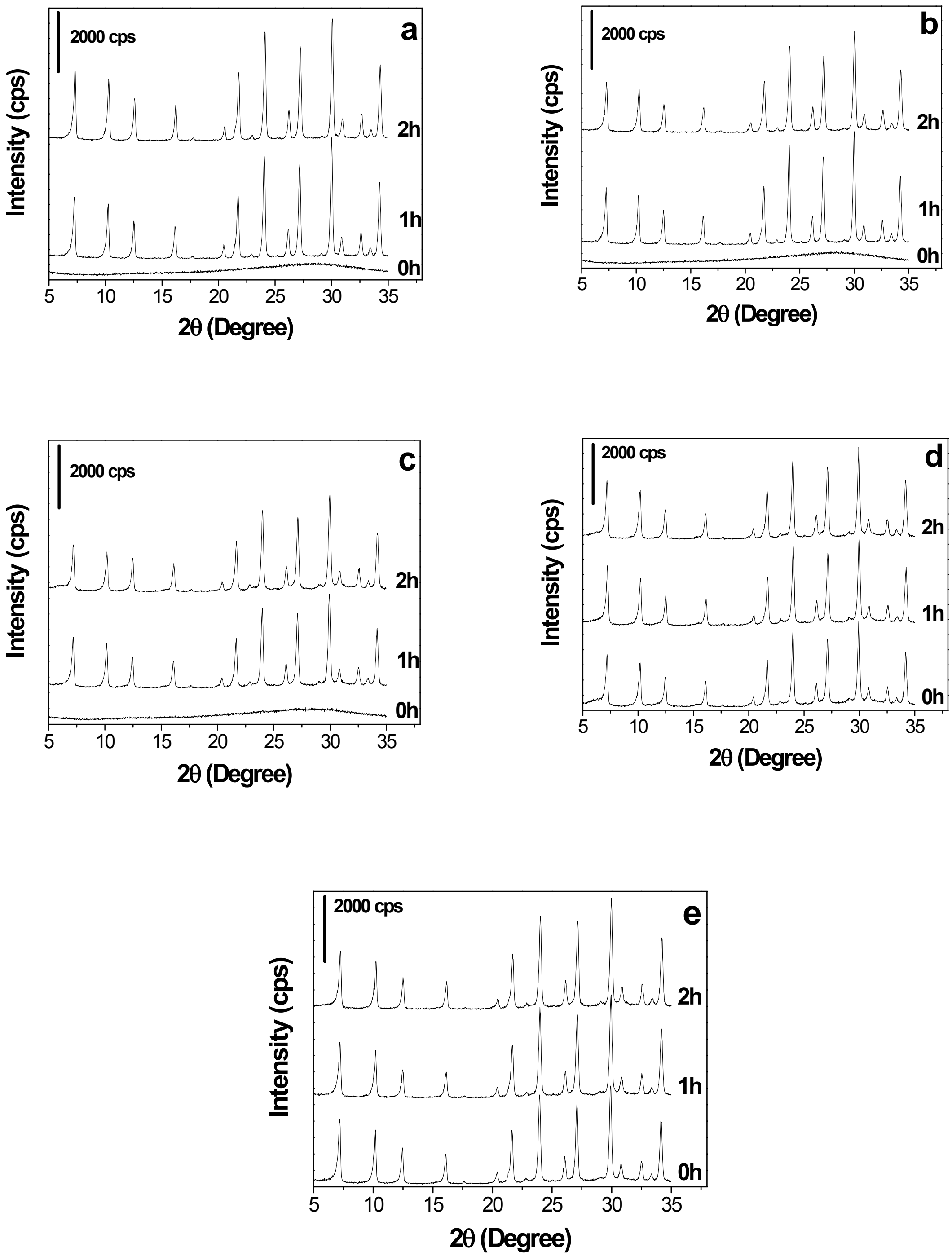

Figure 5SM. X-ray diffractograms for synthesized samples with aging times of 1 (a), 2 (b), 3 (c), 4 (d) e 5 (e) days at 25 °C, followed by 1, 2 and 3 hours of hydrothermal treatment at 100 °C. Composition: 5.2 Na_2O : Al_2O_3 : 2 SiO_2 : 128 H_2O.

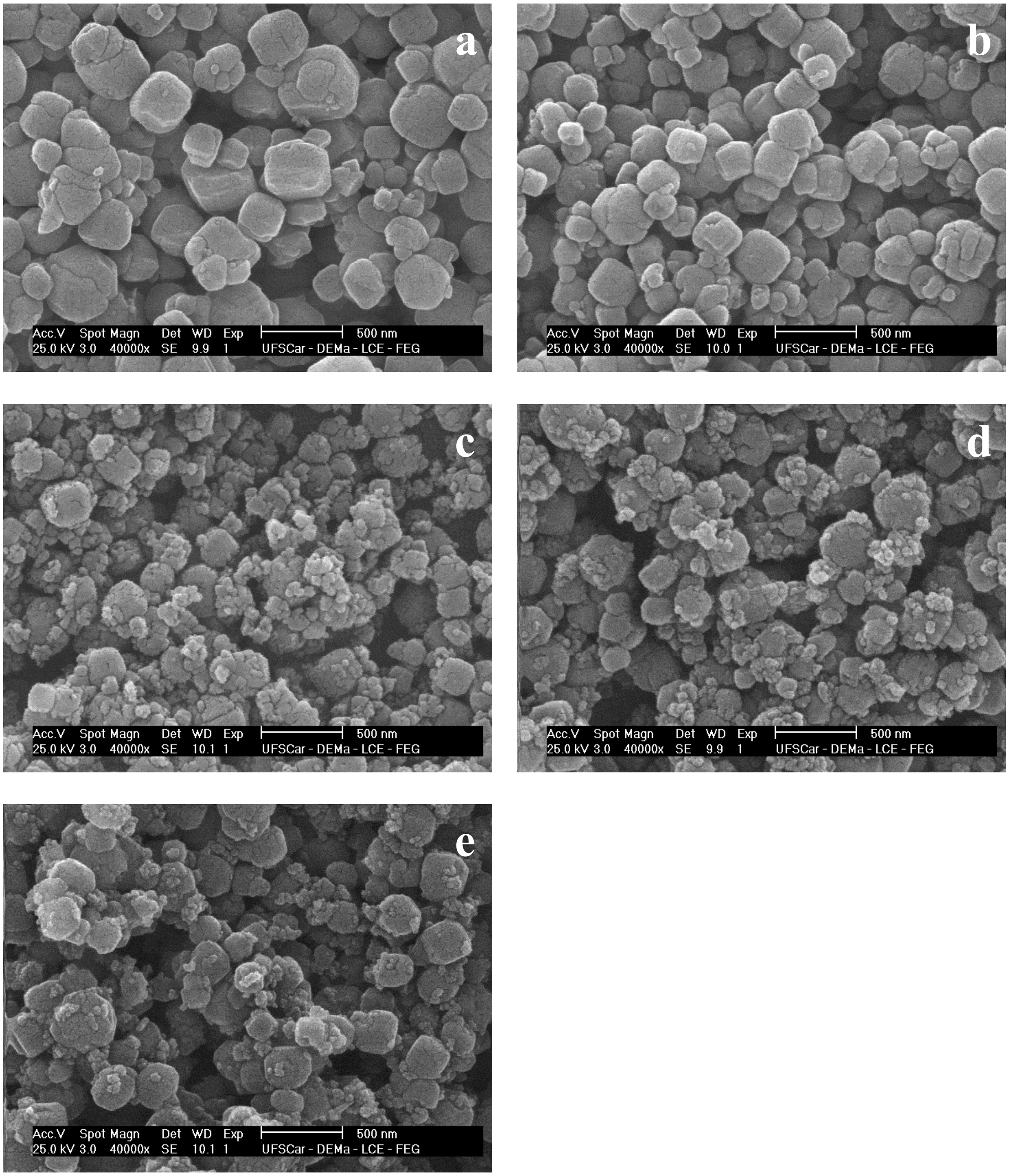

Figure 6SM. Micrograph of the synthesized samples using 5.2 Na_2O/Al_2O_3, aging time of 1 (a), 2 (b), 3 (c), 4 (d) e 5 (e) days at 25 °C and 2 hours of hydrothermal treatment at 100 °C.

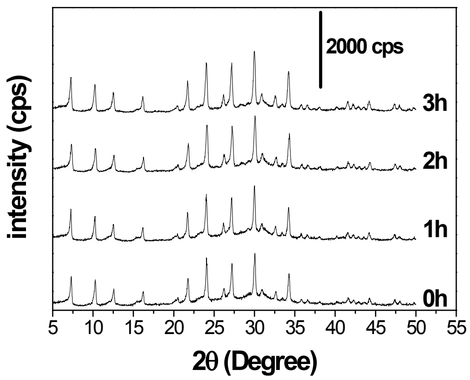

Figure 7SM. X-ray diffractograms for synthesized samples with aging time of 3 days at 25 °C, followed by 1, 2 and 3 hours of hydrothermal treatment at 100 °C. Composition: 6.2 Na_2O : Al_2O_3 : 2 SiO_2 : 128 H_2O.

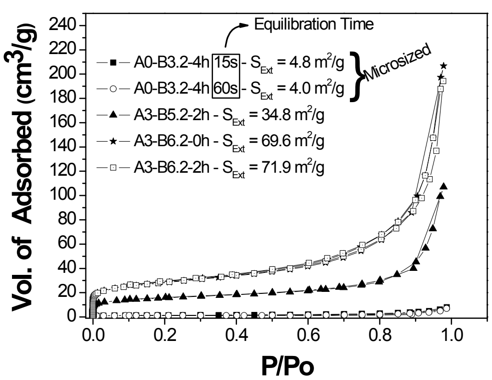

Figure 8SM. N_2 adsorption of samples synthesized at different conditions: aging time at 25ºC (A, in days); Na_2O/Al_2O_3 ratio and crystallization time at 100 °C (B).