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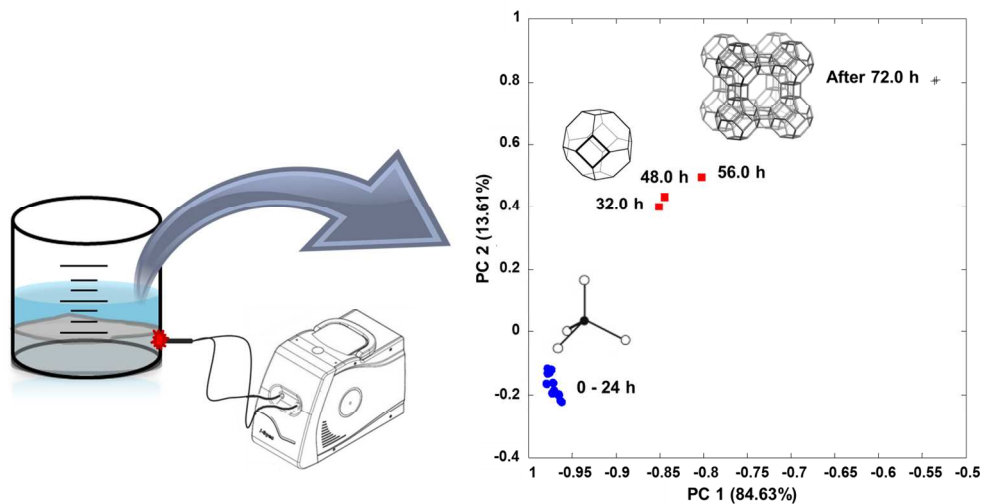


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The synthesis of zeolite LTA was monitored using Raman spectroscopy. The PCA shows 3 stages of the reaction: amorphous reactants, nucleation process and crystallization.
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ARTICLE

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

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LTA zeolite is used both in industry as well as in laboratories, because of its spatial-specific structure which is useful in gas adsorption and in the ion exchange separation. At-line reaction monitoring and multivariate analysis of data, such as Principal Component Analysis (PCA), are fundamentals of the Process Analytical Technology (PAT), which consists of the use of analyzers with rapid detection and low sample preparation for analysis during the process stream. In this work, an optimization of zeolite LTA synthesis was performed aiming to obtain nanocrystals and the synthesis was monitored using Raman spectroscopy and PCA. It was used a reaction mixture of 6.2 Na₂O : Al₂O₃ : 2 SiO₂ : 128 H₂O and it was possible to obtain small particle size and high crystallinity after 72 h of synthesis at 25 °C. The synthesis was monitored at-line, using Raman spectroscopy in both liquid and solid phases. The extension of the reaction could be clearly observed by the PCA scores. As expected, the liquid phase presented changes over time, but the solid phase presented three specific stationary conditions at 0 – 24 h, 32 – 56 h and 72 – 80, related to the beginning of the reaction, the nucleation process, and the crystal formation, respectively. In addition, it was possible to identify the intermediates of reaction and with the aid of PCA to monitor the reaction close to the real time.

Introduction

Zeolites are microporous crystalline aluminosilicates formed by tridimensional networks of SiO₄ and AlO₄ tetrahedrons[1]. These materials are usually synthesized under hydrothermal conditions in basic medium, containing aluminosilicate gel precursor. Changes in the reaction mixture composition and synthesis conditions may lead to different zeolite structures, for example, FAU, LTA, GIS and MOR [2].

Zeolite A (LTA) is used for many different applications, such as, water treatment, adsorption of molecules, ionic exchange and selective gas separation. The largest application of Zeolite A is in detergent builders and water softener compositions. In Europe, the zeolites correspond to 30 % of the powdered detergents, aiming at the softening of hard waters, replacing the phosphates that are harmful to the environment [3]. Lately, zeolites formed by nanocrystals have been used in the construction of porous materials hierarchically structured [4] for catalysis applications, membranes and thin films with low dielectric constant [5]. Interest in nanocrystalline materials is mainly due to high external area values, low diffusional limitations and porosity control that can be achieved in some synthesis procedures.

Several authors have reported that, changes in the alkalinity of the reaction mixture have modified the morphology and crystal size distribution of different zeolites structures, such as, BEA, FAU, MFI and LTA [6-10]. High alkalinity values tend to increase the solubility of the precursors and form a larger number of smaller crystals [8, 10]. For the LTA structure, the synthesis conducted under high alkalinity leads to formation of irregular

particles with spherical form. This occurs due the attack of the hydroxyls, presented in greater quantities, on the crystal surface [10,11].

Due to a widespread application in laboratory and industry, studies on zeolite synthesis continue to be carried out. The research on crystallization pathways allows the understanding of the structure formation and allows higher control over the properties of the synthesized material. Thus, the in situ characterization experiments are quite interesting, because they monitor all synthesis stages in real time. Among the most widely used techniques for monitoring of LTA synthesis DLS, SAXS and Raman spectroscopy stand out [12-15].

The in situ reaction monitoring is one of the foundations of the process analytical technology (PAT), which consists of the use of analyzers with rapid detection and low sample preparation for chemical and physical analysis during the process stream [16-18]. The implementation of PAT tools provides several advantages to the crystallization process, such as: understanding the mechanism involved in the process and to decrease its failure chances; finding the end point of the reaction and to decrease the batching time, thus increasing the process efficiency; controlling the particle size of product with high precision; knowing, in real-time, the reaction progress in order to correct or stop the batch if the process is out of control. There are four ways to perform this monitoring: in-line invasive, in-line non-invasive, on-line and at-line. The best way to perform real-time analysis is using in-line procedures. However, sometimes it is convenient to perform on-line analyses using a continuous flow system for sampling, due to the extreme experimental conditions inside the reactor.

Sometimes we need to perform techniques where in-line or on-line analyses are not possible to be performed, such as X-Ray Diffraction, Scanning Electron Microscopy and others. Then, a sample is collected in a fixed time interval, in order to perform an at-line analysis. PAT uses many chemometric tools to process the obtained data. To classify the status of the process, Principal Component Analysis (PCA) is the main tool. To quantify the analytes during the process, Partial Least Square (PLS) and spectrometric techniques such as Near Infrared and Raman spectroscopy are employed.

As such, the objectives of this work were to study the synthesis of LTA zeolite at room temperature, to monitor the crystallization process by Raman spectroscopy and PCA analyzing liquid and solid phases, identifying the beginning and the end of crystallization process and reaction intermediates.

Experimental

Reagents

Fumed silica (Aerosil 380 Degussa), sodium aluminate (Riedel de Haën – 54% Al₂O₃ : 41% Na₂O : 5% H₂O), sodium hydroxide (Quimis – 99%) and distilled water were used. For the synthesis of Zeolite LTA it was used the initial reaction mixture 3.2 Na₂O : 1.0 Al₂O₃ : 2 SiO₂ : 128 H₂O, 4 h of hydrothermal treatment at 100 °C, without aging time, which is described in Verified Synthesis of Zeolitic Materials [19]. Some changes were made in the initial composition in order to produce Zeolite LTA nanocrystals.

Syntheses

Sodium hydroxide and water were added under magnetic stirring until complete dissolution. After that, sodium aluminate was added. After complete solubilization of the sodium aluminate, Aerosil was slowly added and the magnetic stirring was turned off after fifteen minutes. The reaction media was put in an autoclave and left in an oven during a specific time and temperature. After the hydrothermal syntheses, the products were recovered by centrifugation, washed (pH < 8) and dried in oven at 60°C. The concentration of the reactants, the autoclave temperature and the reaction time were varied in order to perform an investigation on the influence of the alkalinity, crystallization time, crystallization temperature and aging time. The aim of this optimization was to find an ideal synthesis condition to obtain small-sized zeolite LTA crystals.

After the evaluation of the reaction parameters, the experiment using 6.2 Na₂O : 1.0 Al₂O₃ : 2 SiO₂ : 128 H₂O at 25 °C presented the best conditions to obtain zeolite LTA nanocrystals. This synthesis was performed in a beaker, using a thermostatic bath for temperature control, and it was at-line monitored for 80 h using Raman spectroscopy.

Characterization

To characterize the products, a Rigaku Diffractometer was used (Cu K α , Ni filter, 40 kV and 30 mA), using 2° min⁻¹, 5 up to 35° 2 θ and resolution 0.02°. The morphology and crystal size were examined by scanning electronic microscopy (SEM) and transmission electronic microscopy (TEM), using a Phillips XL 30 FEG and a Phillips CM 120 equipment, respectively. For the at-line monitoring of the best synthesis condition, a Raman spectrometer from B&W Tek, model i-Raman BWS 415-785H (785 nm laser and spectral resolution 3.5 cm⁻¹) was used. An optical microscopy with 20 x objective lens was used to focus the laser on the sample. The acquisition time for each spectrum was 120 seconds, the laser power was 320 mW and the spectral

range of 464 – 1557 cm⁻¹. Aliquots were taken from the liquid and solid phases of the reaction and the monitoring was performed for the two phases.

Principal Component Analysis

The raw data obtained by Raman spectroscopy were organized in a matrix with 17 samples (reaction times) and 691 variables (Raman shifts, cm⁻¹). The spectra were pretreated with an adjustment on the baseline and moving average smoothing. To perform PCA, the singular value decomposition (SVD) function was used, present on the Matlab 2011a (Mathworks, Natick, MA, USA). PCA is a tool for exploratory analysis and can be implemented in the crystallization process control to understand the end point reaction, based on the similarity (or dissimilarities) [20] of the first and second principal component (or in some cases the third). These similarities (or dissimilarities) can represent a presence of interference presented in the process [21] or the end of the reaction [22]. Using a score plot from PCA, it is possible to determine a group with substrates (first hours of reaction), and a group of samples with products (last hours of reaction). In some cases, it is also possible to observe a dispersed group that can represent the reaction intermediaries.

Results and discussion

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 results of these investigations are presented as Supplementary Material. The crystallization at 25°C using the reaction mixture 6.2 Na₂O : Al₂O₃ : 2 SiO₂ : 128 H₂O 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.

At-line monitoring

During the reaction time, samples were collected for at-line Raman analysis of the solid and liquid phase. These analyses were performed without any sample preparation, in order to obtain information about what was happening inside the reaction media. At-line was used instead of in-line monitoring due to the formation of two phases in the mixture reaction and to obtain spectra of better quality. Apart from at-line analyses, for the reaction times 24, 48, 72 and 80 hours the obtained solids were collected, washed several times and dried at 60°C. These samples were characterized using Raman spectroscopy and X-Ray diffraction, in order to correlate the solid obtained in these reaction times with the Raman spectra obtained in the at-line analyses. For the final solid product obtained from seventy two hours of reaction, Transmission Electron Microscopy and electron diffraction analysis were performed.

Liquid phase. Figure 1 shows the Raman spectra (without pretreatment in Figure 1a and baseline correction and normalization in Figure 1b) of the liquid phase obtained during the reaction. The intensity of Raman scattering can change even when the same sample is analyzed. The main reasons for that are the variations of the laser focal point and turbidity of (or bubbles in) the sample, which hinder the scattering radiation reaches the detector. So, it is highly recommended to evaluate both the untreated and the normalized Raman spectra.

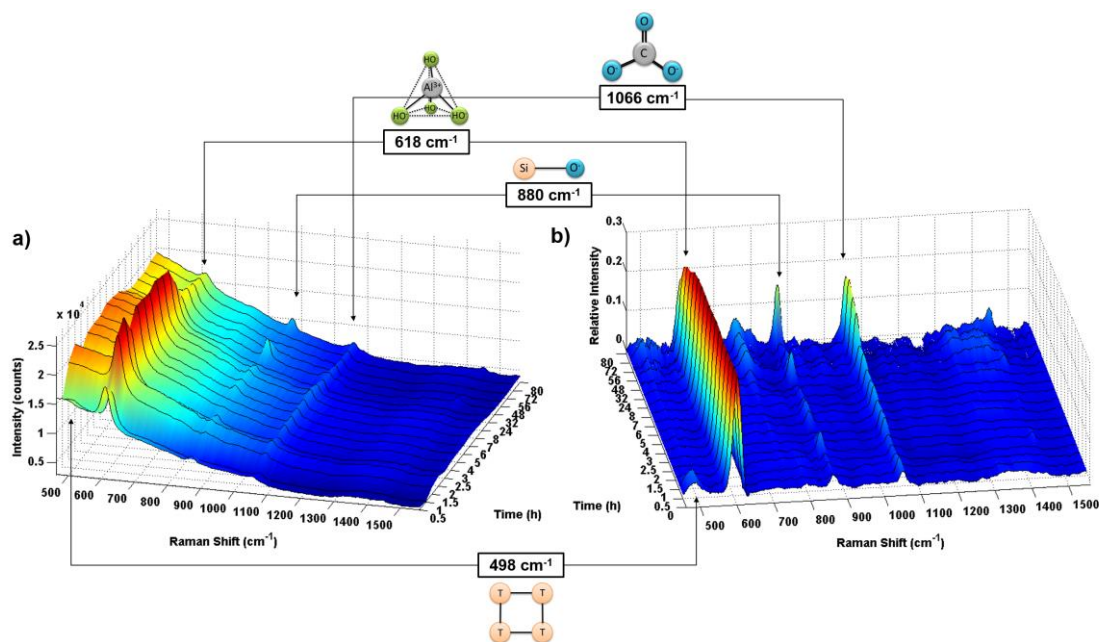


Figure 1. Raman spectra of the liquid phase of the reaction media for zeolite LTA synthesis. a) without pretreatments; b) baseline correction and normalization.

The main vibrations found in Raman spectra of liquid phase, come from the aluminate complex at 618 cm^{-1} , carbonate species at 1066 cm^{-1} (which are produced due to the incorporation of atmospheric carbon dioxide into the alkaline solution and are correlated with the peak around 750 cm^{-1}) and from amorphous aluminosilicates containing mainly 4 membered-rings around 498 cm^{-1} [14, 23, 24]. The signal at 880 cm^{-1} comes from amorphous silicate species, as the peak around the wavenumber 1450 cm^{-1} , which presents high correlation with the peak at 880 cm^{-1} [23, 25, 26]. Figure 1 shows that aluminate complex concentration decreases mainly after 24 hours due its consumption to yield zeolite crystals; the silicon-oxygen signal at 880 cm^{-1} varies over the time, probably due to the transition of silicon-oxygen species which can present more or less activity in the Raman spectroscopy and [25, 26]; carbonate species seem to increase over time.

Using the normalized data, a principal component analysis was performed in order to investigate if the at-line Raman analysis will be capable of monitoring the reaction by the direct analysis of the liquid phase. Figure 2a presents PC1xPC2 scores from PCA analysis. The results show that there were significant changes only after twenty four hours. After that there were some changes in the reaction media until 80h hours of reaction time. Based on this observation, it would be possible to develop a model for monitoring the reaction progress only by analyzing the liquid phase of the mixture reaction.

Figure 2b presents the loadings of the PCA for the liquid phase data where, over time, there is a decrease of the aluminate concentration. This conclusion can be reached due to the negative loading for PC1 at 618 cm^{-1} and negative scores which are increasing for PC1, in Figure 2a. PC2 presents less influence on aluminate concentration and more influence for carbonate species (that can be notice by the high value of loadings at 1066 cm^{-1} and around 750 cm^{-1} for PC2 if compared with PC1). In that case, there is an increase of carbonate species, since the loading at 1066 cm^{-1} for PC 2 is highly positive and the scores at PC2 present positive values (after 24 hours) which are

increasing. The peak related to amorphous silicate species around 880 cm^{-1} presents a tendency of increase, but Figure 1 shows the high variability of this signal.

The decrease of aluminum species and the increase of carbonate species in the liquid phase of the reaction mixture were obviously expected. However, using the PCA, we can see (and study) the extension of the reaction. In another words, it is possible to predict the end of the reaction, the time of crystallization after the rising of the first crystals and then to extend the study to the control of the particle size distribution of the final product.

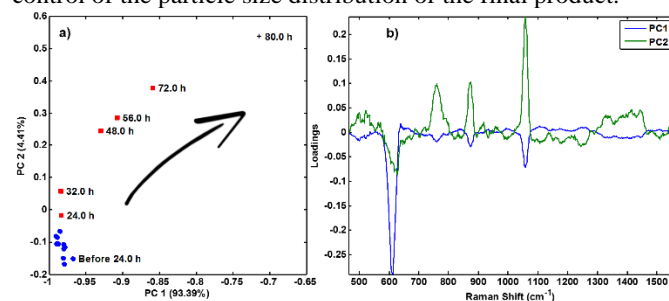


Figure 2. PCA of liquid phase dataset. (a) scores and (b) loadings for PC1 and PC2.

Solid phase. Figure 3 shows the Raman spectra of the solid precipitated during the reaction (without pretreatment in Figure 3a and baseline correction and normalization in Figure 3b). Note that for the at-line analysis, the samples were not washed or dried. The main peaks for the solid phase were around 489, 498, 618 and 1066 cm^{-1} .

The peak at 489 cm^{-1} is related to the breathing vibration mode of the four-membered ring in the crystalline framework of zeolite LTA and could be a good reaction progress indicator. During the reaction, the peak at 498 cm^{-1} (easily observed in Figure 3b) presented a shift to 489 cm^{-1} and an increase in its relative intensity. The increase of the symmetry due to the crystallization makes this peak sharper when compared with amorphous

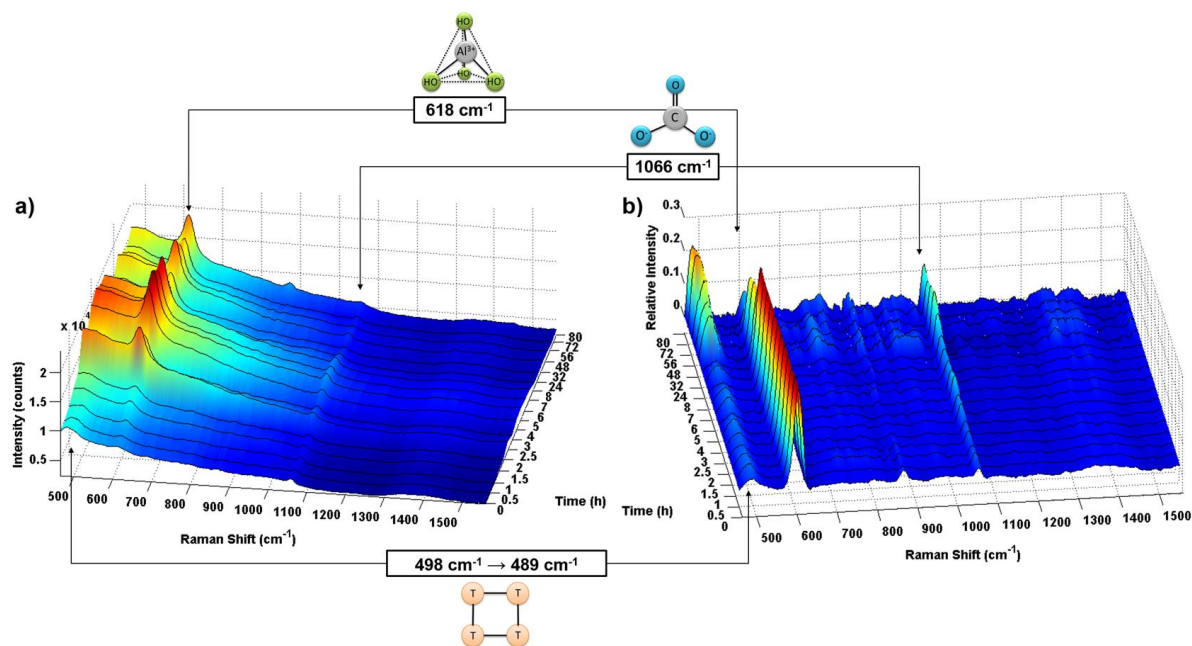


Figure 3. Raman spectra of the solid phase of the reaction media for zeolite LTA synthesis. a) without pretreatments; b) baseline correction and normalization.

aluminosilicates with four-membered rings. After 32h it was possible to observe a better definition of the peak at 489 cm^{-1} in the spectra.

The peak at 618 cm^{-1} decreases in Figure 3b due to the consumption of the aluminate complex and formation of zeolite crystals (these spectra are normalized by area) and the peak at 1066 cm^{-1} increases, due to the incorporation of atmospheric carbon dioxide. It is worth noting that the aluminate complex and most of carbonate species are not present in the solid phase, but in the reaction mixture which is present in the analyzed solid phase because it was not washed or dried before the at-line analyses. This analytical procedure was performed intentionally to verify if it was possible to monitor the reaction as close as possible to the real time, which is an important criterion to employ the technique as a tool in the Process Analytical Technology for zeolite synthesis.

A PCA was performed using the Raman spectra from the solid phase of the reaction media, with normalization and baseline correction. The scores and loadings of PC1 x PC2 are presented in Figure 4a and 4b, respectively. Figure 4a clearly shows the formation of three clusters: 0 h - 24 h; 32 h - 56 h and; 72 h - 80 h.

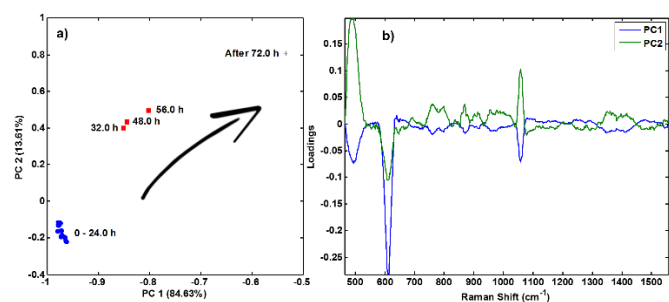


Figure 4. PCA of solid phase dataset. (a) scores and (b) loadings for PC1 and PC2.

Figure 4a shows that before 24 h of reaction there is no significant change in the solids of the reaction media, which present only amorphous aluminosilicates, since a significant signal in 489 cm^{-1} is not observed and there are no differences between the initial time and 24 h. Between 32 and 56 h, probably the nucleation process is occurring, that can be inferred due to the increasing and sharpening of the signal around 489 cm^{-1} . This occurs due to the increase of the symmetry in the structure where the four-membered rings are present. However, a crystalline structure is not presented yet, since with 48 h of reaction no diffraction patterns are observed, as will be observed in the Figure 5. The solids obtained from 72 and 80 h of reaction did not present significant differences. These two analyses presented better definition of the peak at 489 cm^{-1} , as observed in Figure 3, and after 72 h of synthesis a characteristic diffraction pattern for zeolite LTA was observed, as will be observed in Figure 5.

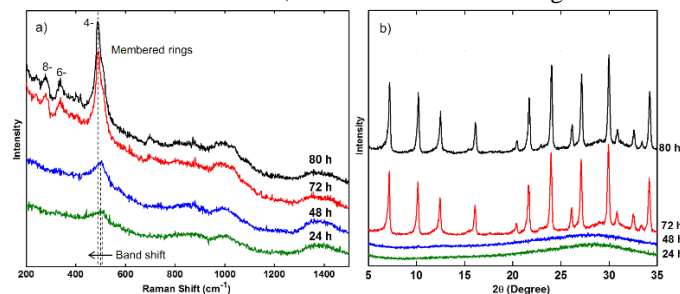


Figure 5. Raman spectra and diffractograms of the products obtained after 24 h, 48 h, 72 h and 80 h which were isolated, washed and dried.

The loadings of the PCA for the solid phase, presented in Figure 4b, shows that the peak at 489 cm^{-1} is explained mainly by the PC2, and the peak at 618 cm^{-1} is explained mainly by PC1. As was expected, the PC2 loadings show an increasing of the peak at 498 cm^{-1} , relative to the zeolite LTA formation, since this loading present a positive signal in the PC2 and the scores of the

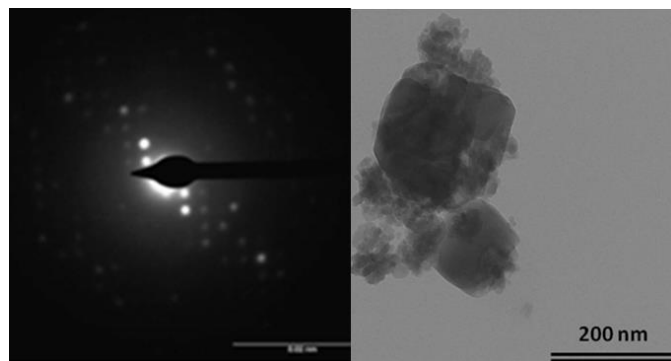
PC2 (Figure 4a) increase as function of the reaction time. In the same way, there is a decrease in the signal presence from the aluminum hydroxide complex, since the loadings of PC1 for 618 cm^{-1} are negative and the PC1 scores are increasing as function of the reaction time.

It is worth to note, again, that the increase of the presence of zeolite LTA crystals were expected, however, using the PCA, it is possible to monitor the synthesis close to the real time, which makes it easier to control the properties of the final product, such as the particle size distribution.

Characterization of solid phase. In order to characterize the solids yield during the synthesis, the products obtained after 24 h, 48 h, 72 h and 80 h were isolated, washed, dried and analyzed by Raman spectroscopy and PXRD. These spectra and diffractograms are presented in Figure 5.

Figure 5a shows that even Raman spectra showing the presence of four-membered rings in the final solids (Raman signal around 500 cm^{-1}), the peak relative to the zeolite LTA only appears after 72 h. It was a band shift and a better definition of the peak related to four-membered rings over the time, due to the incorporation of these rings into organized structures, giving rise to LTA zeolite crystals. Two new peaks can be observed in the Raman spectra after 72 h, around to 340 cm^{-1} and 275 cm^{-1} , which are related to the breathing vibration mode of the six and eight-membered rings, respectively, from the crystalline framework of zeolite LTA [9].

The diffractograms of these solids, in Figure 5b, indicate the same occurrence observed by the Raman spectra; there are crystalline products only after 72 h of reaction time. Figure 6 shows the result of a transmission electron microscopy analysis of the sample collected after 72 h of reaction, which shows small particles (smaller than 200 nm) and the presence of aggregates. The electron diffraction indicated that the obtained particles present high crystallinity.



Conclusions

Nanocrystalline zeolite LTA was successfully synthesized at near room temperature through an optimization process. The increase of the alkalinity yielded small zeolite LTA crystals without the need of hydrothermal treatment, using 6.2 $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 2 \text{SiO}_2 : 128 \text{H}_2\text{O}$ ratio and 72 h of reaction time. The at-line analysis of the best synthesis condition showed that both liquid and solid phase could be used to monitor the synthesis progress using Raman spectroscopy and PCA. The liquid phase could be used to monitor the progress of the reaction since this phase present a constant change, while the solid phase presents a stationary condition, with a probable increase of crystallinity

after 72 h of reaction. It was possible to identify the intermediates in the reaction mixture: amorphous aluminosilicates containing mainly 4 membered-rings; amorphous silicate species; and the aluminum hydroxide complex. The characterization of the final solids using 24, 48, 72 and 80 h of reaction time were in agreement with the results obtained by at-line Raman analysis and PCA, since when the solid phase was analyzed without washing or drying, it was observed that the samples of 72 and 80 h (which are crystalline, in fact) presented different characteristics compared with samples of 32 to 56 h, as observed in Figure 4a.

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