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Study of the influence of the basicity and chromate-chloride anionic composition in the synthesis of the cancrinite–sodalite system

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Abstract The influence of basicity and anionic composition (CrO_4^{2-} and Cl^-) was studied in the synthesis of chromate-cancrinite and chlorosodalite zeolites. Zeolite X was used as starting material by using different NaOH concentrations (3, 8 and 16 M) and variable weight ratio (NaCl/(NaCl + K_2CrO_4)) equal to: 0.00, 0.25, 0.50, 0.75, and 1.00 in such a way that the total grams were 1.5 g. The syntheses were carried out at 80 °C and autogenous pressure during 40 h. The crystals obtained were characterized by powder X-ray diffraction (XRD), FT-IR spectroscopy, and scanning electron microscopy (SEM) coupled with an energy-disperse X-ray detector (EDX). Depending on the basicity employed and anionic composition (CrO_4^{2-} and Cl^-), the chromate-cancrinite or chlorosodalite zeolite was obtained. Owing to a low 3 M NaOH concentration and 100% Cl^-, chlorosodalite mixed with zeolite X was observed in the XRD pattern. Owing to another Cl^-–CrO_4^{2-} proportions, inclusive to 100% CrO_4^{2}, the starting material were not transformed (3 M NaOH). Pure chromate-cancrinite was produced when 8 and 16 M NaOH and 0% Cl^- concentrations were used. Chloride anions showed a strong structure directing effect for sodalite framework structure in comparison with chromate anions which favoring the cancrinite structure. Therefore, we determined pure chlorosodalite, when it was used until 75%Cl^- (8 M NaOH) and 25% (16 M NaOH). Results showed that cancrinite or sodalite zeolites are separately formed.

Introduction

Cancrinites and sodalites are naturally occurring minerals that belong to both the feldespathoid group, as well the zeolite family. Both zeolites are comprised of the six ring stacking sequences: ABCABC to sodalite and ABAB to cancrinite. These zeolites can contain diverse anion into framework, which balancing the positive charge generated by structural cations [1]. Due to the structural similarity between both zeolites, they can be synthesized under similar reaction conditions. The formation of cancrinite or sodalite depend on present anion and the basicity of reaction medium during the synthesis process. Anions with threefold rotation axis, such as chromate or carbonate, generally direct the formation of the hexagonal cancrinite structure, while simple monoatomic ions, e.g., Cl^-, Br^-, and those with lower symmetry, e.g., NO_2^- generate sodalite framework [2]. Likewise, the concentration of NaOH in reaction gel plays an important role in the synthesis of these zeolites: high concentrations (16 M NaOH) preferably produce sodalite, while medium NaOH concentrations (4 or 8 M) produce cancrinite [3].

Additionally, studies of entrapped chromate anion inside cancrinite structure could be very interesting for environmental applications [4], while the chloride anions are commonly founded in the reaction gels. Barrer et al. [1] studied the synthesis of chromate cancrinite using standard condition reactions, such as: kaolinite and a large excess of

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Table 1 Weight or mol proportions of NaCl or K_2CrO_4 used in the chromate cancrinite–chloride sodalite synthesis

K_2CrO_4 (g)	NaCl (g)	NaCl/(NaCl + K_2CrO_4)	K_2CrO_4 Mol	NaCl Mol	K_2CrO_4 molarity (mol/L)	NaCl molarity (mol/L)
1.500	0.000	0.00	0.0077	0.0000	0.7724	0.0000
1.125	0.375	0.25	0.0057	0.0064	0.5793	0.6416
0.750	0.750	0.50	0.0038	0.0128	0.3862	1.2833
0.375	1.125	0.75	0.0019	0.0192	0.1931	1.9250
0.000	1.500	1.00	0.0000	0.0256	0.0000	2.5667

aqueous 4 M-NaOH saturated with Na_2CrO_4 at 80 °C to obtain chromate cancrinite. However, mixture of these anions (Cl^- and CrO_4^{2-}) using different basicity and anionic composition have been a little reported by the literature.

This article represents a contribution to the knowledge over the cancrinite–sodalite synthesis, using a combination of anions (chromate and chloride anions) at three different NaOH concentrations (3, 8, and 16 M). The results showed that the formation of zeolite chlorosodalite was preferentially produced at medium NaOH concentrations (8 M) and high (100%) and medium (50 and 75%) chloride concentrations. The formation of chromate-cancrinite was favored at high NaOH concentration (16 M) and low (25%) or null chloride concentrations. At 3 M NaOH, the starting material was not dissolved and any pure zeolite was produced.

Experimental

Synthesis of cancrinite–sodalite type zeolite system

The used methodology for the synthesis of cancrinite or sodalite was carried out according to the procedure

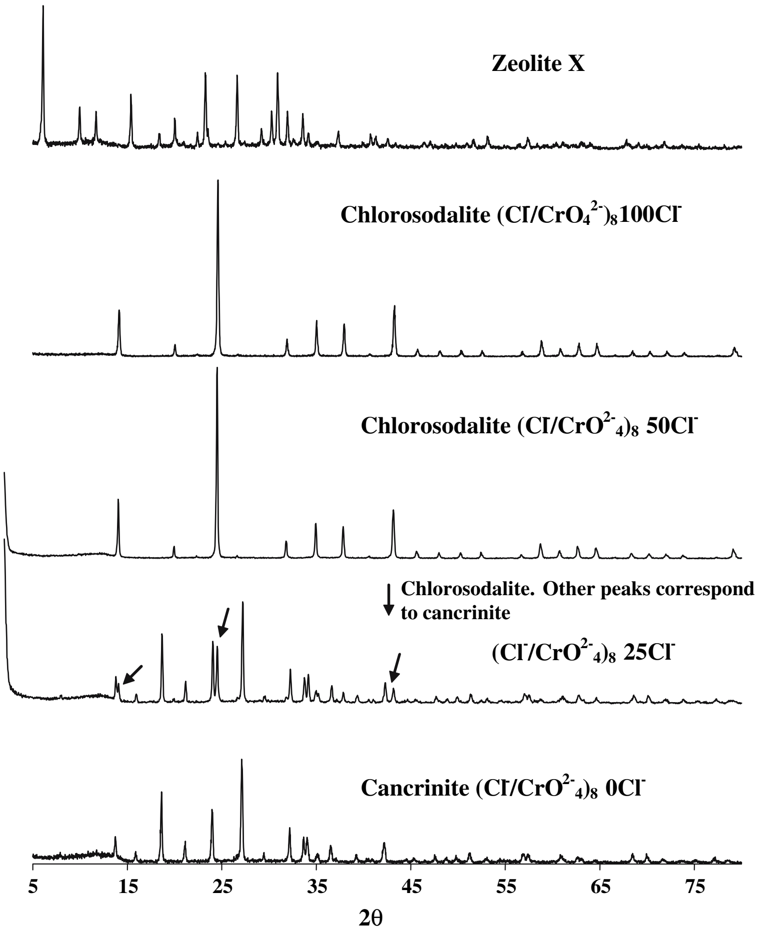


Fig. 1 XRD spectra of samples synthesized at 8 M NaOH solution and different CrO_4^{2-}/Cl^- concentrations

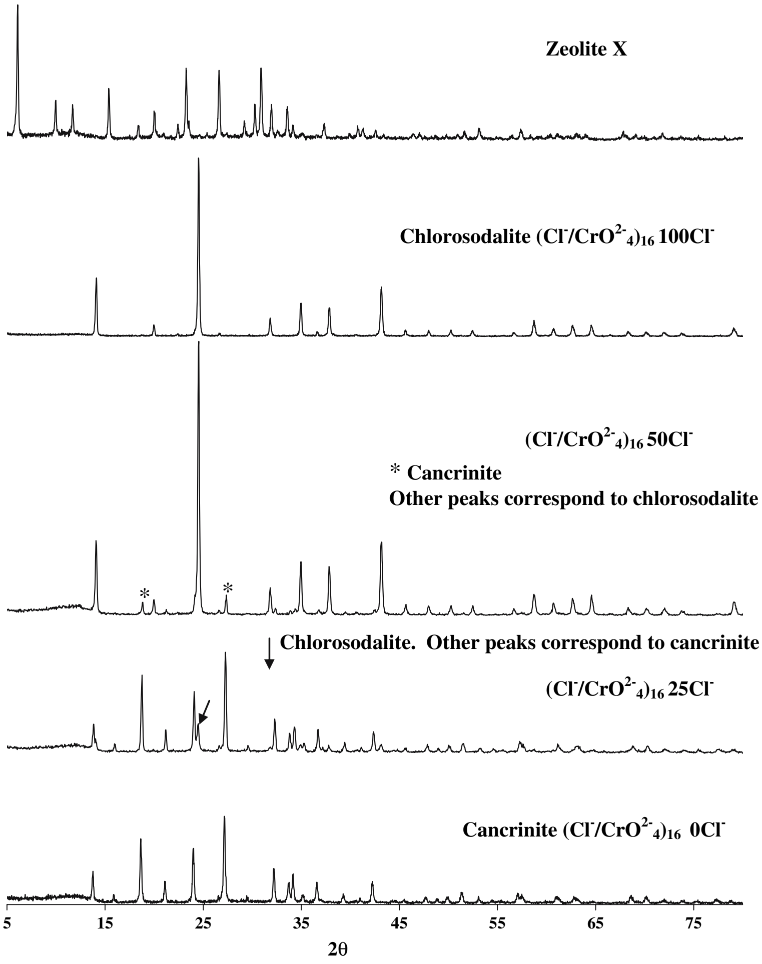


Fig. 2 XRD spectra of samples synthesized at 16 M NaOH solution and different $\mathrm{CrO}_4^{2-}/\mathrm{Cl}^-$ concentrations

previously reported [5]. A zeolite X, previously characterized (ZX, Strem Chemicals, Si/Al = 1.3) was used as silicon and aluminum source. Subsequently, 3, 8, and 16 M NaOH (Labqg reagents) solutions were prepared. These solutions contained also previously mixed chromate and chloride anions (K_2CrO_4 from Golf Chemical CO Reagent A.C.S and NaCl from Riedel-de Haën) in with a weight ratio (NaCl/(NaCl + K_2CrO_4)) equal to: 0.00, 0.25, 0.50, 0.75, and 1.00 in such a way that total grams were 1.5 g (Table 1). One gram of zeolite X (8.458×10^{-5} mol) was impregnated with 10 mL of previously mentioned NaOH solutions in Teflon reactors and placed them in a convection oven at 80 °C for 40 h without agitation. After that, the solids were washed with abundant distilled water until pH $\cong 7$ and dried at 80 °C for 18 h. The following nomenclature was used for the sample identification:

$$(\mathrm{Cl}^-/\mathrm{Cro}_4^-/)_x \cdot \mathrm{YCl}^-$$

where x, represents the NaOH molar concentration; Y, represents the Cl^- weight percentage as NaCl

Characterization

Solids were characterized by XRD, FT-IR spectroscopy and scanning electron microscopy (SEM) coupled with energy-disperse X-ray detector (EDX). XRD studies were carried out by using a Siemens D500S diffractometer with a CuKα radiation (1.542 Å) for crystalline phase detection between 5° and 80° (2θ). The presence of functional groups and purity evaluation of the solids was achieved by FTIR; spectra were recorded in a Perkin-Elmer 283 spectrometer in the 4000–400 cm^{-1} range. Samples were prepared by mixing the solids with KBr. Then, solids were analyzed by SEM using 20 kV of accelerating voltage; samples were previously covered with gold for morphology studies and covered with carbon to its analysis by EDX.

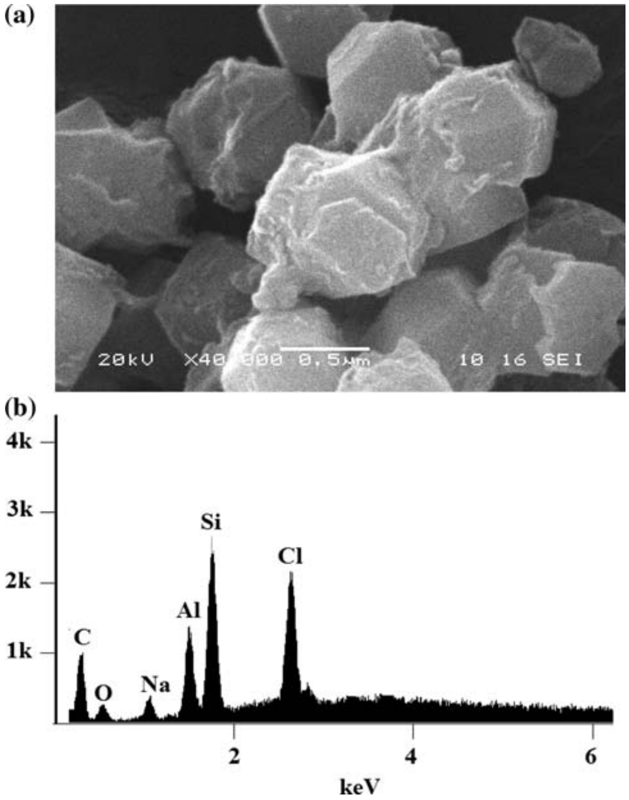


Fig. 3 Sample synthesized at 16 M NaOH and 100%Cl$^-$ (chlorosodalite): (**a**) SEM image, (**b**) EDX analysis

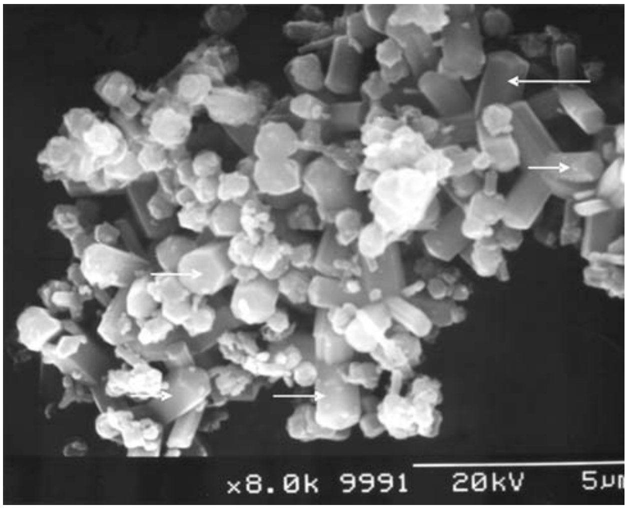


Fig. 4 SEM image of sample synthesized at 16 M NaOH and 0%Cl$^-$ (chromate-cancrinite). Arrows show the typical crystals

Results and discussion

All the synthesized samples were previously analyzed by powder X-ray diffraction (XRD). When the zeolite X was impregnated with a 3 M NaOH solution and 100% Cl$^-$ chlorosodalite was formed (spectra not shown); however, many peaks of zeolite X were observed which indicates that the transformation of zeolite X to chlorosodalite was not completed. When the sodium chloride concentration in the reaction gel was diminished (75 until 0% Cl$^-$), the transformation to chlorosodalite or other sodalite was not observed. Both factors: the NaOH and Cl$^-$ concentration (or chromate concentration) are decisive to produce chlorosodalite. A low NaOH concentration in the gel does not allow the dissolution of zeolite X, and the reactive species (silicates and aluminates) were not produced. On the other hand, chlorosodalite was not produced when a low Cl$^-$ concentration in the reaction gel was used. Likewise, the chromate anion concentration did not have any influence for these reaction conditions. In this experience, the NaOH concentration was more important than Cl$^-$ or CrO_4^{2-} concentration, due to the fact that the dissolution of starting material (zeolite X) is an important key for the formation of cancrinite or sodalite zeolite [6].

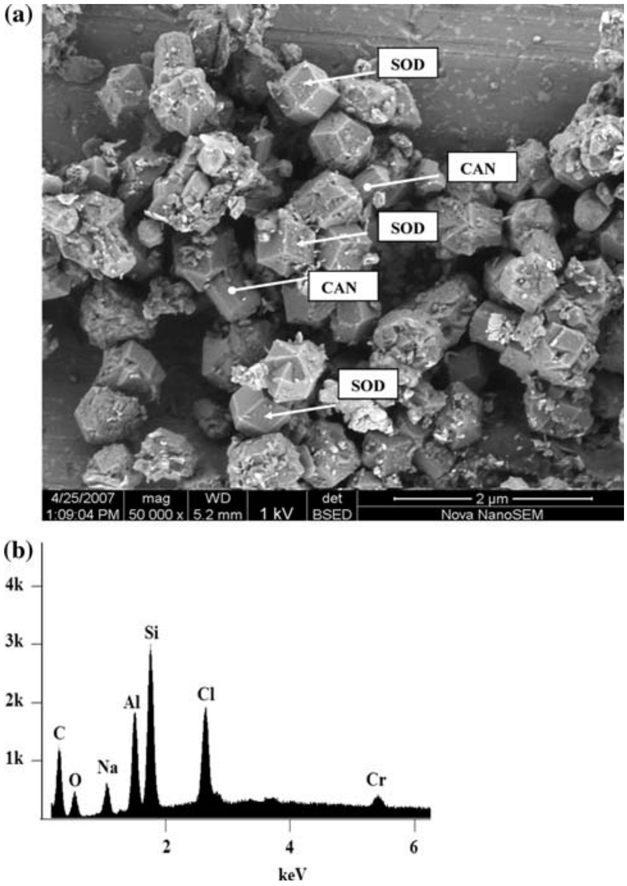
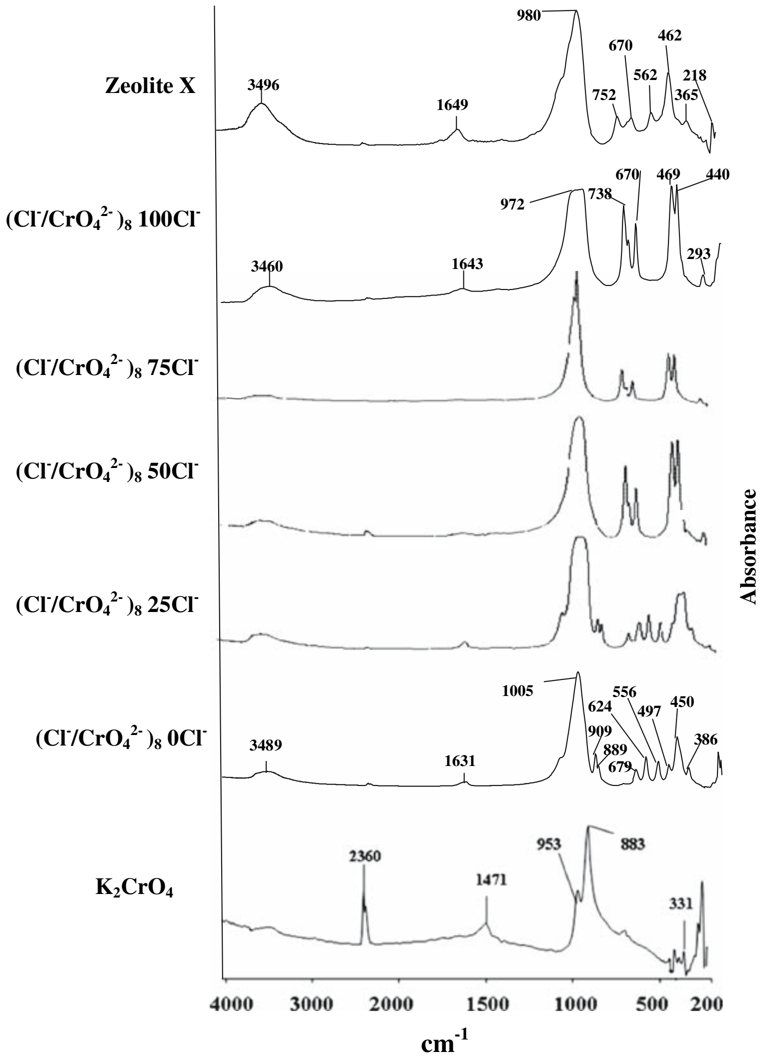


Fig. 5 Sample synthesized at 16 M NaOH and 50%Cl$^-$: (**a**) SEM image: SOD: chlorosodalite, CAN: chromo-cancrinite; (**b**) EDX analysis

When the NaOH concentration was increased (8 and 16 M), the XRD spectra of reaction products were modified in comparison to those obtained at 3 M NaOH concentration (Figs. 1, 2). At 100% Cl$^-$ (8 and 16 M NaOH), chlorosodalite was formed without other collateral

Fig. 6 FT-IR spectra of the samples synthesized at 8 M NaOH solution and different CrO_4^{2-}/Cl^- concentrations



phases as zeolite X. Cubic crystals determined by SEM confirmed the presence of pure chlorosodalite (Fig. 3a) [7]. Moreover, the EDX analyses (Fig. 3b) determined only the presence of Cl^- anions. At 0% Cl^- and, 8 and 16 M NaOH, the pure chromate-cancrinite phase was observed. The typical SEM image of needle-type hexagonal crystals was obtained in the process of the phase transformation (Fig. 4) [7]. Additionally, the EDX analyses confirmed the presence of chromium in the analyzed samples (spectra not shown).

Similarly, pure chlorodalite was also produced at 8 M NaOH when the Cl^- concentration was diminished to 50% Cl^- (Fig. 1). When, the Cl^- concentration was reduced to 25%, a new phase identified as chromate-cancrinite-type zeolite was obtained. This last zeolite was found in less proportion that chlorosodalite zeolite (Fig. 1). Now, if the NaOH concentration is increased (16 M), the cancrinite structure is also increased while the chlorosodalite structure is descended; inclusive, the few peaks observed by XRD of the cancrinite zeolite at 8 M NaOH and 25% Cl^- are more abundant at 16 M NaOH and 25% Cl^-. These results show that chromate anion can act as template agent in presence the chloride anions if the NaOH concentration is higher. At 16 M NaOH and 50% Cl, we also determined the cancrinite phase by XRD (Fig. 2), SEM (Fig. 5a) and EDX (Fig. 5b). XRD show a spectrum combined of cancrinite and sodalite zeolite with a major presence of the last one. On the other hand, isolated needle-type hexagonal crystals typical of cancrinite zeolite were identified together to cubic crystals of sodalite. All these results indicate that the formation of cancrinite and sodalite are individually produced in presence of mixed chloride or chromate anions. A general analysis by EDX determined the presence of chromium and chloride species in this sample (Fig. 5b); but was not possible to associate a specific chemical composition to each observed crystal. The co-crystallization of these zeolites, according to the SEM images, does not seem to be possible; while the

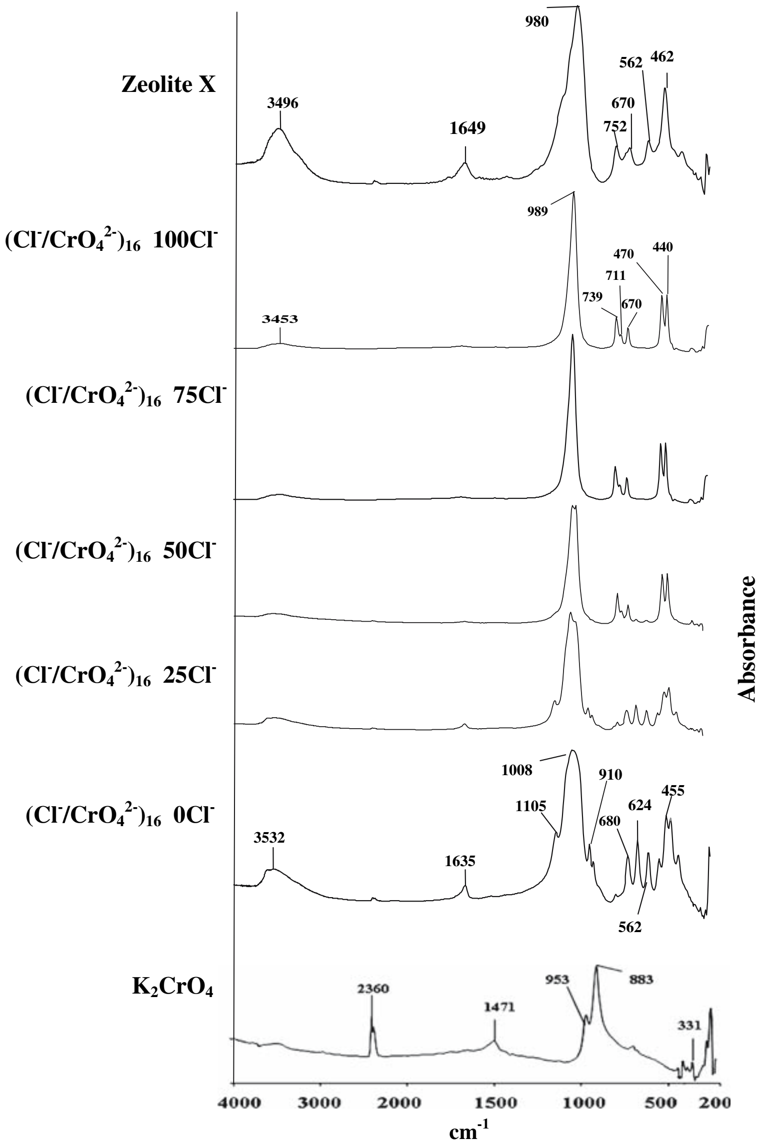


Fig. 7 FT-IR spectra of the samples synthesized at 16 M NaOH solution and different CrO_4^{2-}/Cl^- concentrations

XRD analysis does not show the possibility of formation of intermediate phases between these zeolites.

To both experiences (8 and 16 M NaOH), the starting material is dissolved. Therefore, the synthesis of cancrinite–sodalite system is established by the basicity and anionic concentration of director agent in the gel reaction. It is well-known that sodalite zeolite is preferentially formed at high NaOH concentrations, but in presence of other anions, such as chromate anion, a competitive reaction between these anions is presented, and the formation of cancrinite or sodalite will depend on the capacity of the anion as template agent. Likewise, our result reveled that chloride anions have a strong structure directing effect for sodalite framework in comparison to chromate anions which produce cancrinite structure.

The IR spectroscopy has also been applied for these zeolite structures analyzed. The products of carried out hydrothermal synthesis (cancrinite and sodalite), as well as zeolite X could be identified by comparing the IR spectra according to the characteristic absorption bands of the framework building units, given by Flaningen et al. [8], Farmer [9] or Hackbarth et al. [10]. In the obtained FT-IR spectra (spectra not shown) using 3 M NaOH solutions in the reaction gel, one can see that there were no differences between the different spectra, and the intensity and location of the bands were similar to those obtained to zeolite X. Using a 3 M NaOH concentration, the starting material was not dissolved, and the sodalite or cancrinite production was not observed. Similar results have been obtained by Hackbarth et al. [10]. By XRD a mixture of zeolite X and chlorosodalite was observed when a 3 M NaOH and 100% Cl$^-$ concentration was used in the gel reaction; while by IR spectroscopy any differences between these spectra and the zeolite X spectrum was observed. The proximity between bands (location and intensity) corresponding to zeolite X, sodalite, cancrinite or its intermediate phase does not allow a clear distinction between these tectosilicates when they are mixed. According to our results, the phase most intense (zeolite X in this case) eclipses the minority phase (sodalite structure), and this later phase cannot be determined by IR spectroscopy. From IR spectra (Figs. 6, 7) obtained at 8 M NaOH and different Cl^-–CrO_4^{2-} anionic composition, it was possible to observe that spectra corresponding to the reaction products are notably different to that showed by zeolite X.

The 100, 75, and 50% Cl^- spectra show two splitting band pairs placed at 738 and 670 cm^{-1} (the first one) and 470 and 440 cm^{-1} (the second one) which are characteristics for the chlorosodalite zeolite. At 25 and 0% Cl^- composition, the same bands placed in the fingerprint region, appear as three symmetric bands placed at 679, 624 and 556 cm^{-1} which are typical for the cancrinite zeolite. A little band at 909–889 cm^{-1} has been assigned as chromate anion inside the cancrinite zeolite framework [11]. To this NaOH concentration, the zeolite X can easily be dissolved and the Cl^- or chromate anions can template to produce chlorosodalite or chromate-cancrinite zeolite. The formation of a particular zeolite depends of the anionic composition in the reaction gel. Observing Fig. 7, (16 M NaOH), one can see that the reaction products are very similar to those obtained when an 8 M NaOH concentration is used. At 100, 75, and 50% Cl^- the spectra basically correspond to chlorosodalite zeolite, while at 25 and 0% Cl^-, the spectra are similar to cancrinite zeolite. As already mentioned, by using IR spectroscopy cannot be easy distinguished when these zeolites are mixed. Basically, one can display the majority formation of a particular zeolite in comparison with other minority zeolite. Best results are obtained when X-ray diffraction is used.

Conclusions

The chromate-cancrinite and chlorosodalite system was studied at different NaOH concentrations and variable Cl^-–CrO_4^{2-} anionic composition. The results showed that at 3 M NaOH concentration, the starting material (zeolite X) is not dissolved and the formation of cancrinite or sodalite is not produced. In this case, the alkalinity was a key factor. Higher NaOH concentrations conduct to dissolution of zeolite X and the chlorosodalite or chromate-cancrinite can be synthesized. Chlorosodalite was preferentially produced at high Cl^- concentrations and, 8 and 16 M NaOH concentrations; while the chromate-cancrinite is formed at low Cl^- concentrations (high CrO_4^{2-} concentration) and high NaOH concentration (16 M NaOH). Powder XRD spectroscopy was more effective for mixed phases identification than IR spectroscopy. These results represented a contribution to the systematic study of the synthesis of these especial zeolites.

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