

Synthesis of sodalite from Brazilian kaolin wastes

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ABSTRACT: Kaolin wastes from the Capim and Jari regions (Brazil) were used to produce sodalite under the same conditions used in the Bayer process, in order to control its formation when necessary. Of the two kaolin source materials, the kaolinite from the Jari region was more reactive in the synthesis of sodalite, which is attributed to the low degree of structural order of this clay mineral which increased its reactivity. At a temperature of 150°C and with a Na/Al ratio of 2, although the kaolinite did not react completely, sodalite was the primary reaction product. An increase in the temperature to 200°C provoked the complete reaction of the kaolinite only for the products in which carbonate and sulfate were used. With a Na/Al ratio >2 and for both of the temperatures, the kaolinite reacted completely to form sodalite.

KEYWORDS: kaolin waste, kaolinite, sodalite.

Sodalite and cancrinite are crystalline compounds formed as byproducts in the Bayer process. The Bayer process involves the extraction of alumina from bauxite using concentrated NaOH solutions at 150–240°C. Kaolinite is present as a mineral impurity in bauxites, and, in hot caustic solutions, it forms desilication products consisting mainly of sodalite. Anions such as OH⁻, Cl⁻, CO₃²⁻ and SO₄²⁻, from different sources that are also present in the liquor as impurities, have a negative effect on the efficiency of the process. It is possible to remove these ions, however, by incorporating them in the structures of sodalite and cancrinite (Buhl, 1997; Whittington *et al.*, 1998; Barnes *et al.*, 1999; Armstrong & Dann, 2000).

Partial transformation of sodalite to cancrinite in a caustic aluminate solution supersaturated with respect

to SiO₂ appears to occur more rapidly at 160°C than at 90°C (Zheng *et al.*, 1997).

Thus, knowledge of the conditions of the synthesis of sodalite from kaolinite becomes a very important tool in the Bayer Process, although the formation of sodalite has a positive effect on the capture of reactive silica and other inorganic impurities that are harmful to the process. Sodium and aluminum are also captured, however, thereby increasing the cost of the process.

Since the study of Borchet and Keidel in 1947, the hydrothermal transformation of kaolinite in concentrated NaOH solutions has become the most widely used method for synthesis of members of the sodalite group, though other methods do exist (Buhl *et al.*, 1997). This synthesis process has been studied widely in order to obtain information about its use during the Bayer Process (Gerson & Zheng, 1997; Whittington *et al.*, 1998; Barnes *et al.*, 1999) or simply to learn more about it (Breck, 1974; Barrer, 1978; Buhl, 1996;

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Engelhardt *et al.*, 1992; Benharats *et al.*, 2003; Heller-Kallai & Lapides, 2007).

Kaolin wastes from the Amazon area, Brazil, more specifically those from the Capim and Jari regions, are used widely in ceramics, cement and zeolites because they consist primarily of kaolinite (Flores & Neves, 1997; Angélica, 2006; Maia *et al.*, 2007, 2008, 2011, 2014, 2015; Paz *et al.*, 2010; Barata & Angélica, 2012; Hildebrando *et al.*, 2012). The mining companies operating in the state of Pará generate these wastes, and the initiative to use the wastes instead of natural materials has contributed to the economy of the processes and to environmental protection.

Kaolinite is a 1:1 (T-O) layer silicate, with a unit cell composed of six octahedra and four tetrahedra (Bergaya *et al.*, 2006). The structure of sodalite consists of a framework made of Si and Al tetrahedra. This framework consists of a perfectly periodic arrangement of polyhedra [4⁸, 6⁶] and the β cage (the sodalite cage) that fills the space, with a unit-cell content of [SiAlO₄]₆⁶⁻, which corresponds to two β cages. In addition to the cations, M⁺, which compensate for the negative charge of the framework, the β cages may contain a variety of encapsulated salts, *i.e.* M⁺, A⁻ and hydroxide M⁺ OH⁻, and/or molecules of water. The structure of sodalite is cubic and belongs to the space group P43n, with the following stoichiometry: Na_{6+X} [AlSiO₄]₆2X.nH₂O, with X=OH⁻, Cl⁻, ½CO₃²⁻, ½SO₄²⁻ or NH₃ (Engelhardt *et al.*, 1992).

Generally, in the synthesis of zeolites from kaolin, the kaolin is first transformed to metakaolin by heating. The reaction of kaolin is as quick as the reaction of metakaolin, however, and the formation of hydroxy-sodalite occurs more rapidly from kaolin, showing that it is not the formation of an amorphous precursor gel that is important, but the structural reorganization in a crystalline product, which in this case, is the hydroxy-sodalite (Benharats *et al.*, 2003).

The present study thus aimed to synthesize sodalite under conditions similar to those used in the Bayer process to understand and control its formation if required for this process. Another objective of this study was to utilize kaolin wastes from the Amazon in the Jari and the Capim regions as a source of Si and Al, in order to find inexpensive raw materials and reduce cost in these types of processes in addition to considering the environmental issues.

EXPERIMENTAL PROCEDURES

The waste from kaolin processing for the paper-coatings industry in the region of Capim (KC) and the

River Jari (KJ) was used as a source of Si and Al in the synthesis of sodalite. The kaolin waste was collected from the centrifugation stage of the process of two companies which operate in mines located in the state of Pará, Amazon Region. This waste was the only source of Si and Al, because the sodalite has a Si/Al ratio equal to that of the kaolinite. A 5 M NaOH solution was used as the source of sodium. To incorporate anions into the structure of sodalite, 1 M NaCl, Na₂CO₃ and Na₂SO₄ solutions were used.

The synthesis process was performed in stainless steel autoclaves with an internal Teflon cup which has a volume of ~50 mL. Two synthesis temperatures were tested, 150 and 200°C, similar to those in the Bayer process. The quantity of the starting materials was calculated stoichiometrically, according to the following structural formula of sodalite: Na_{6+X} [AlSiO₄]₆A_X.nH₂O, with A=Cl⁻, ½CO₃²⁻ or ½SO₄²⁻. X=6 was considered, to give a Na/Al ratio of 2 and a Na/anion ratio of 2 for Cl⁻ and 4 for CO₃²⁻ and for SO₄²⁻ over the entire sodalite series. Once the products were characterized, the new values of the Na/Al ratio were determined to explore the conditions under which complete or partial reaction of kaolinite was possible. In all reaction products, kaolinite was detected in both the KC and KJ samples. In the second stage, the amount of sodium in the reaction medium increased during synthesis to yield Na/Al ratios >2, *i.e.* 2.25 (chloride), 2.22 (carbonate) and 2.30 (sulfate). The amount of each anion was held constant in the reaction mixture, however. Note that in addition to comparing the reactivities of the kaolinites from the Capim and Jari regions, which are related to differences in the crystal order, the reactivity of each kaolinite source with the different anions in the synthesis process was also addressed. When using the expression “there was a complete reaction of kaolinite”, this reflects the disappearance of the main peak of this mineral in the X-ray diffraction (XRD) patterns, indicating that practically all of the kaolinite had been consumed/converted into the synthesis product.

All tests were performed in duplicate in autoclaves in which a stoichiometric kaolinite mass reacted with the source solutions of Na and the anion and 15 mL of water. The autoclaves were transferred to the oven at 150 and 200°C. The synthesis products were washed and filtered until the filtrate had neutral pH. After washing, the synthesis products were dried at 100°C for 6 h, and characterized subsequently by XRD and infrared (IR) spectroscopy.

The XRD analyses were performed using an X'Pert Pro MPD (PW 3040/60) PANalytical diffractometer,

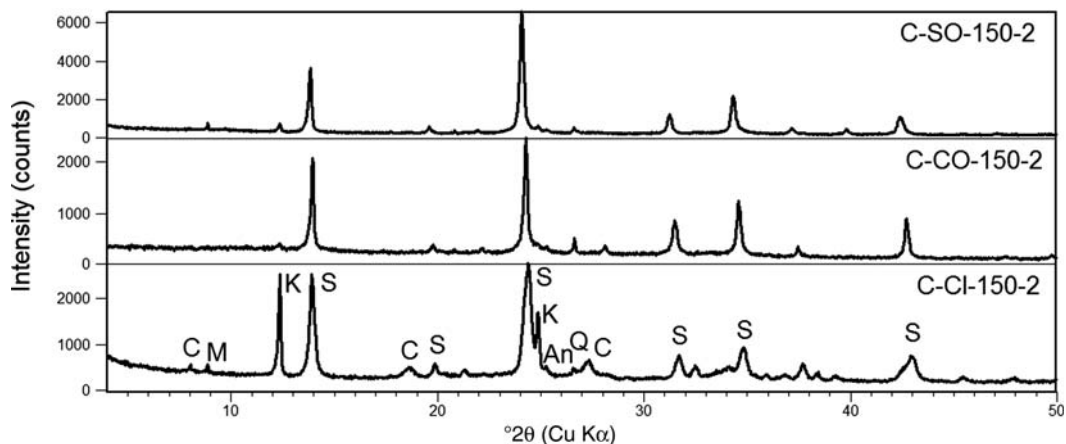


FIG. 1. XRD patterns of the products synthesized from the KC source at 150°C and with Na/Al ratio = 2. S: sodalite, C: cancrinite, K: kaolinite, M: muscovite, An: anatase, Q: quartz.

with a PW3050/60 (theta/theta) goniometer using a ceramic X-ray tube with a Cu anode ($K\alpha_1 = 1.540598 \text{ \AA}$) (model PW3373/00), a long fine focus, a Ni $K\beta$ filter, and an X'Celerator RTMS (Real Time Multiple Scanning) detector in the scanning mode and with an active length of 2.122° . The following instrumental conditions were maintained: scanning range from 5 to $75^\circ 2\theta$, 40 kV, 40 mA, $0.02^\circ 2\theta$ step size and 5 s/step, $\frac{1}{2}^\circ$ divergent slit and 1° anti-scatter slit, 10-mm mask, and spinning rotation of the sample at 1 rps. The data acquisition was performed using the X'Pert Data Collector v. 2.1a software, and the data treatment was performed using X'Pert HighScore v. 2.1b software.

Fourier transform infrared (FTIR) spectroscopy was performed using a Perkin Elmer FTIR 1760X spectrometer in the region $4000\text{--}400 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} and using KBr pellets. The XRD and IR analyses were performed at the Institute of Geosciences, Martin-Luther Universität, Halle-Wittenberg, Germany.

The synthesis products were named using letters or numbers according to the synthesis conditions: (1) C or J, to indicate the source of kaolin that was used (Capim or Jari); (2) the letters of the anion to be inserted into the structure of the sodalite (SO, CO, or Cl); (3) the synthesis temperature; and (4) the value of the Na/Al

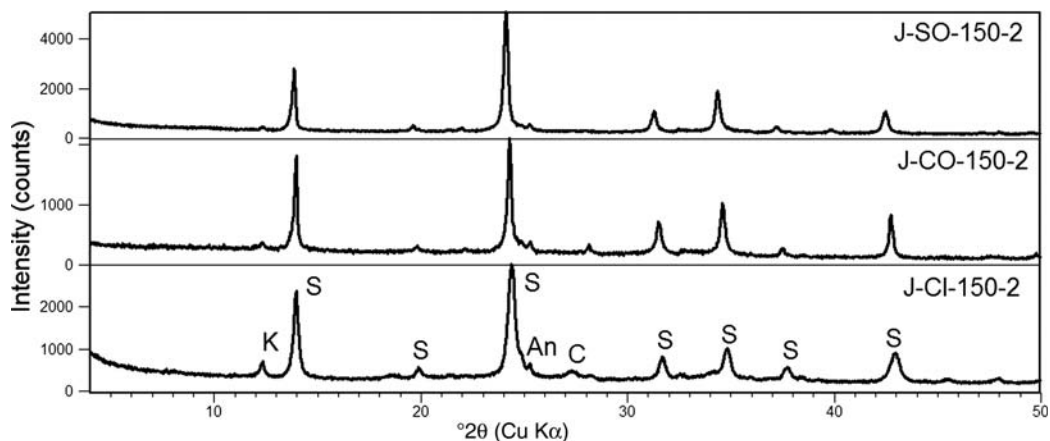


FIG. 2. XRD patterns of the products synthesized from the KJ source at 150°C and with Na/Al ratio = 2. S: sodalite, C: cancrinite, K: kaolinite, An: anatase.

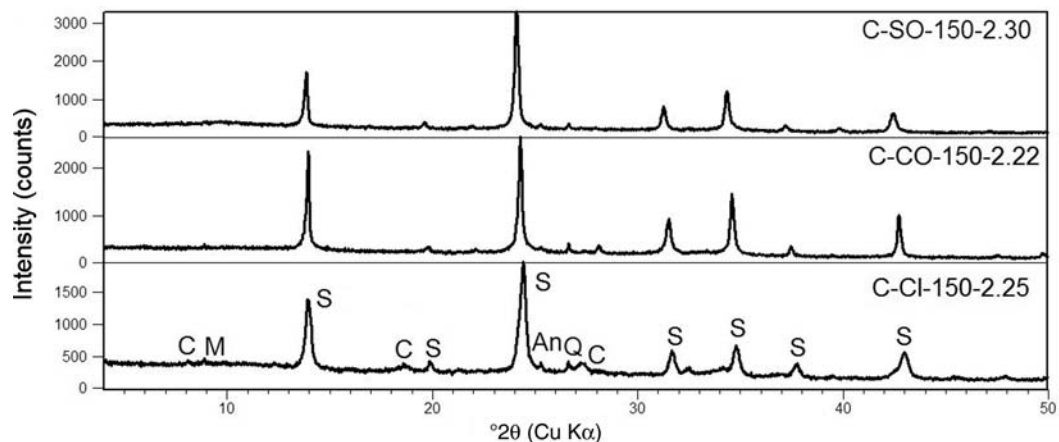


FIG. 3. XRD traces of the products synthesized from the KC source at 150°C and with Na/Al ratio > 2. S: sodalite, C: cancrinite, M: muscovite, An: anatase, Q: quartz.

ratio in the reaction mixture. Hence, product C-SO-150-2 was synthesized from waste kaolin from the Capim, with the anion SO_4^{2-} present in the reaction mixture, at a temperature of 150°C and a Na/Al ratio of 2.

RESULTS AND DISCUSSION

Characterization of the starting materials

The kaolin wastes from the Capim (KC) and the Jari (KJ) regions consist mainly of kaolinite and trace anatase in the KC and KJ and muscovite and quartz in the KC (Maia *et al.*, 2007, 2008, 2011, 2014). The KC kaolinite has a greater degree of structural order than that of KJ. According to the chemical composition, KJ

contains 1.72% Fe_2O_3 whereas KC contains only 0.69% Fe (Maia *et al.*, 2008, 2011, 2014). The large Fe_2O_3 content in the KJ is related to the replacement of Al by Fe in the kaolinite structure which was confirmed by IR spectroscopy and by Nuclear Magnetic Resonance spectroscopy (Maia *et al.*, 2014). This replacement may, therefore, be one of the reasons for the lower degree of structural order of the kaolinite of the KJ (Mestdagh *et al.*, 1980; Brindley, 1986; Petit & Decarreau, 1990; Fysh *et al.*, 1993).

Characterization of the synthesis products

Products synthesized at 150°C: Influence of the amount of Na in the reaction medium. The XRD

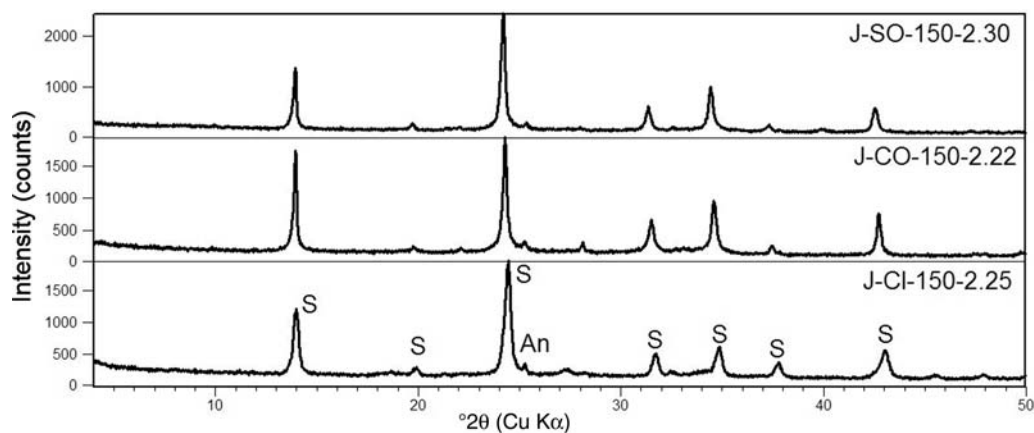


FIG. 4. XRD traces of the products synthesized from the KJ source at 150°C and with Na/Al ratio > 2. S: sodalite, C: cancrinite, An: anatase

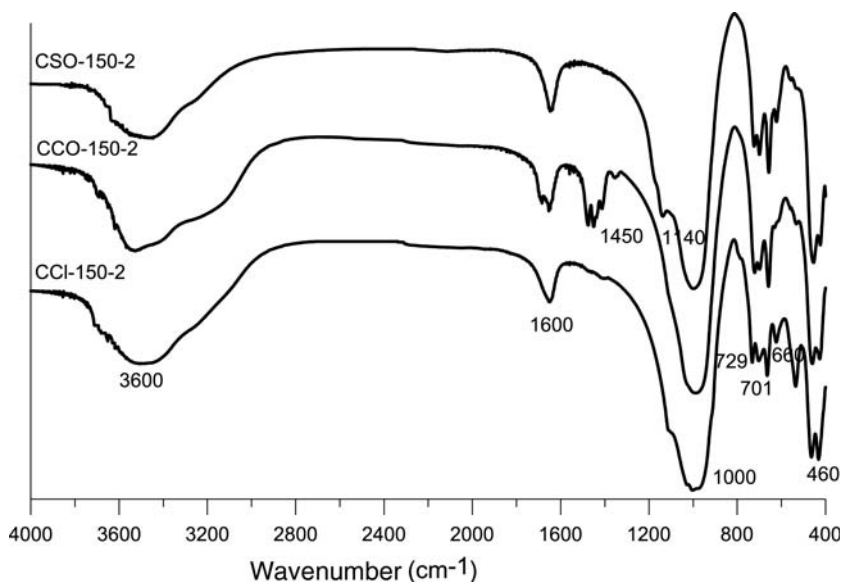


FIG. 5. IR spectra of the products synthesized from the KC source at 150°C and with Na/Al ratio = 2.

traces of the products synthesized from the kaolin waste from the Capim (KC) and the Jari (KJ) regions, respectively, using chloride, sulfate and carbonate anions and a Na/Al ratio of 2 in the reaction mixture are shown in Figs 1 and 2, respectively. Sodalite was formed in all reaction products but the kaolinite did not react completely under these experimental conditions.

Characteristic diffraction maxima for cancrinite were also observed for the products formed from chloride from both starting materials, but with significantly lower intensities than those of the sodalite. By comparing the two sources of kaolinite, KJ is more reactive in the synthesis of sodalite because the main peak of kaolinite shows less intensity in the reaction

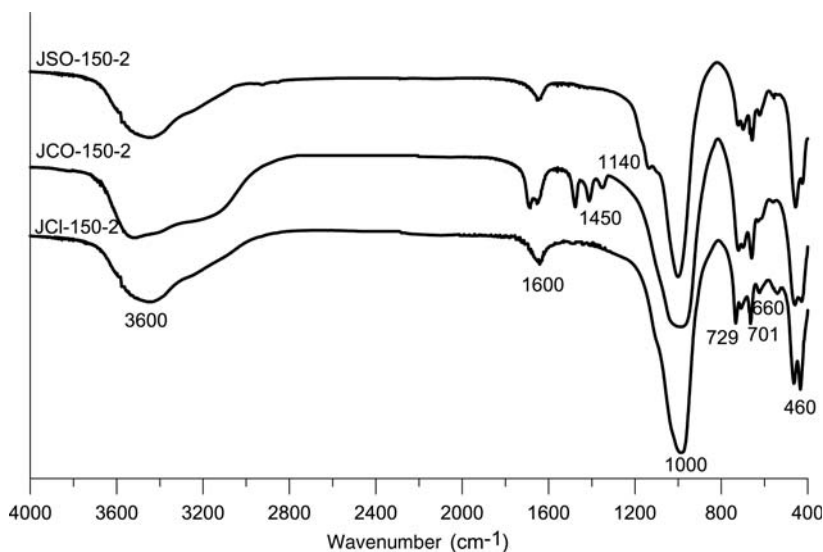


FIG. 6. IR spectra of the products synthesized from the KJ source at 150°C and with Na/Al ratio = 2.

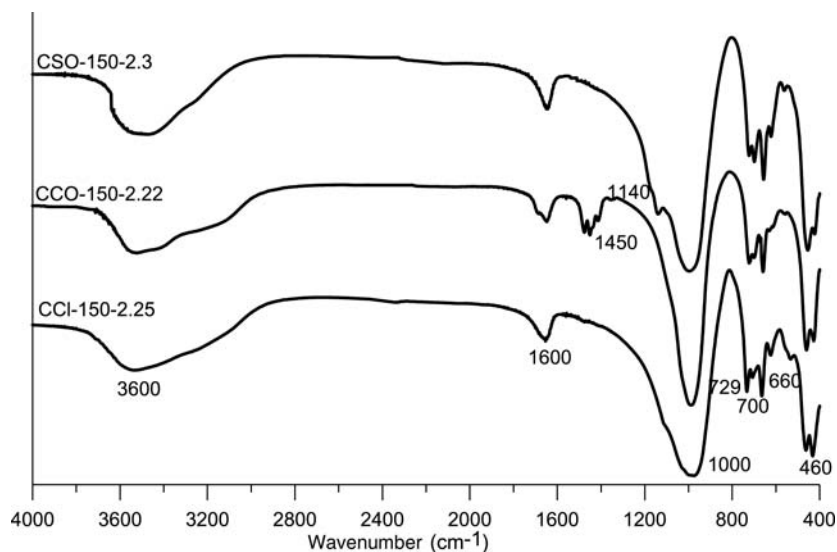


FIG. 7. IR spectra of the products synthesized from the KC source at 150°C and with Na/Al ratio > 2.

products than that of KC. This result was expected because the KC kaolinite has a greater degree of structural order than its counterpart KJ kaolinite with low degree of structural order, and therefore, is less reactive. Among the anions, chloride was less reactive, as can be observed from the intensity of the main kaolinite peak in the products in which this anion was

used in the reaction mixture. In the synthesis of sodalite from kaolin, the presence of carbonate accelerates its rate of crystallization (Buhl *et al.*, 1997). In the present study, this behaviour was observed not only with carbonate but also with sulfate.

The XRD traces of the end products from the kaolin wastes of the Capim and the Jari regions at 150°C

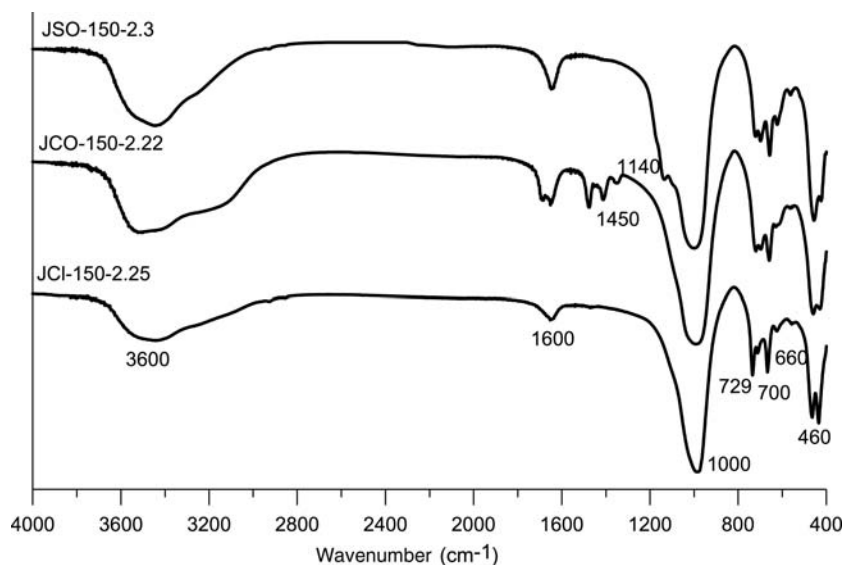


FIG. 8. IR spectra of the products synthesized from the KJ source at 150°C and with Na/Al ratio > 2.

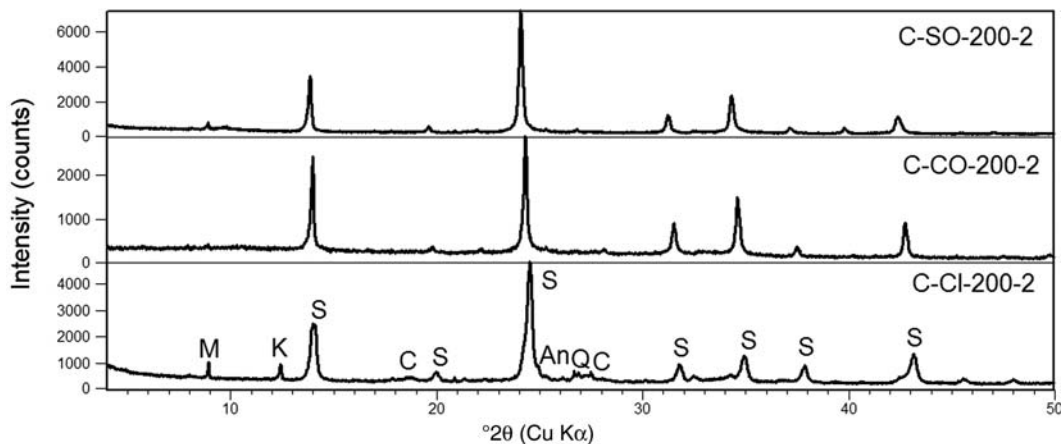


FIG. 9. XRD patterns of the products synthesized from the KC source at 200°C and with Na/Al ratio = 2. S: sodalite, C: cancrinite, K: kaolinite, M: muscovite, An: anatase, Q: quartz.

using chloride, sulfate and carbonate, with a Na/Al ratio >2 are shown in Figs 3 and 4, respectively. An increase in the quantity of Na in the reaction medium resulted in complete reaction of the kaolinite and the formation of sodalite for all products in which chloride, sulfate and carbonate were used. Furthermore, in these products, a sharp increase in the intensity of the main peak of sodalite was not observed. This indicates that under the present experimental conditions, an increase in Na content in the reaction medium did not contribute to an increase in the degree of structural order of the sodalite. In the case of chloride, the characteristic peaks of cancrinite were also observed, for both

products, though sodalite is the main phase, similar to the experiments at the Na/Al ratio = 2.

The FTIR spectra of the products synthesized from KC and KJ with different anions at 150°C are shown in Figs 5, 6, 7 and 8. The bands at $\sim 3600\text{ cm}^{-1}$ and 1600 cm^{-1} are related to zeolitic water (Mead & Weller, 1995; Buhl, 1996; Buhl *et al.*, 1997). The bands attributed to the bending mode in the tetrahedra ($\sim 460\text{ cm}^{-1}$) and to the symmetric stretching mode ($\sim 660\text{ cm}^{-1}$) and the anti-symmetric Si–O–Al bonds in the TO_4 (~ 1000 and 990 cm^{-1}) are characteristic of sodalite (Breck, 1974). The bands close to 729, 701, 660, 461 and 432 cm^{-1} which were observed in all

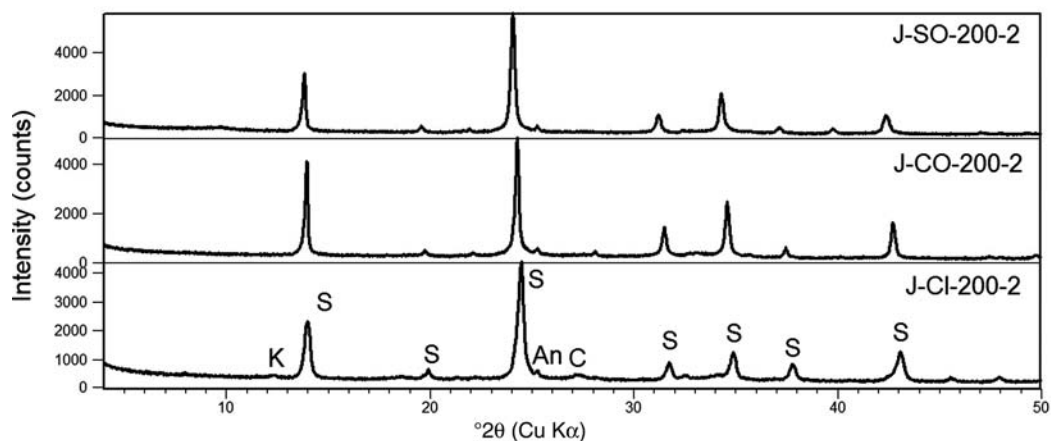


FIG. 10. XRD patterns of the products synthesized from the KJ source at 200°C and with Na/Al ratio = 2. S: sodalite, K: kaolinite, C: cancrinite, An: anatase.

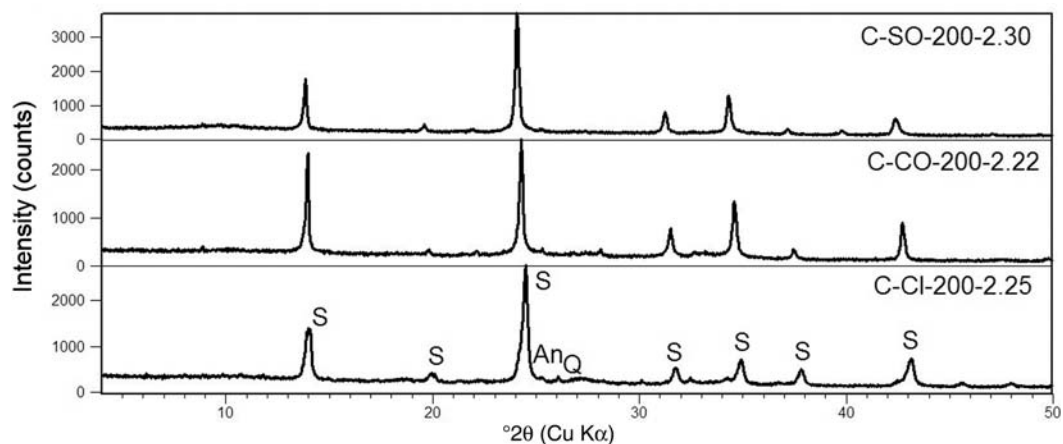


FIG. 11. XRD patterns of the products synthesized from the KC source at 200°C and with Na/Al ratio > 2. S: sodalite, K: kaolinite, An: anatase, Q: quartz.

reaction products are also characteristics of sodalite (Zheng *et al.*, 1997; Whittington *et al.*, 1998; Alkan *et al.*, 2005). The incorporation of the anions used in the reaction mixture was verified in the sodalite structure for each product synthesized from the KJ and KC at all Na/Al ratios, from the presence of characteristic bands, *i.e.* at $\sim 1140\text{ cm}^{-1}$ (sulfate), $\sim 1450\text{ cm}^{-1}$ (carbonate) and $\sim 659\text{ cm}^{-1}$ (chloride) (Mead & Weller, 1995; Buhl, 1996; Whittington *et al.*, 1998). The bands at 691, 629 and 565 cm^{-1} which are related to cancrinite (Zheng *et al.*, 1997) were not observed in the spectra of the products synthesized using chloride in the reaction mixture. According to the XRD data, cancrinite is present in those products, in

quantities which are significantly less than those of sodalite. Hence, the absence of these FTIR bands confirms the previous observation from the XRD analysis.

Products synthesized at 200°C: Influence of temperature at a Na/Al ratio = 2. The addition of chloride to the reaction mixture for KC and KJ starting materials yielded products consisting of sodalite, cancrinite and kaolinite at 200°C (Figs 9, 10). Even at the higher synthesis temperature of 200°C with a Na/Al ratio = 2, kaolinite did not react completely. The intensity of the main kaolinite peak was significantly less than that of the product which resulted at 150°C, however. Greater

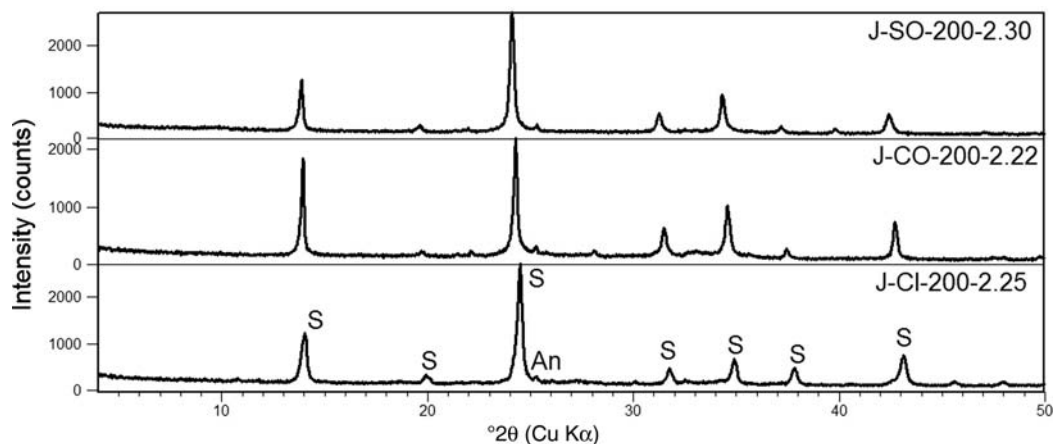


FIG. 12. XRD patterns of the products synthesized from the KJ source at 200°C and with Na/Al ratio > 2. S: sodalite, An: anatase.

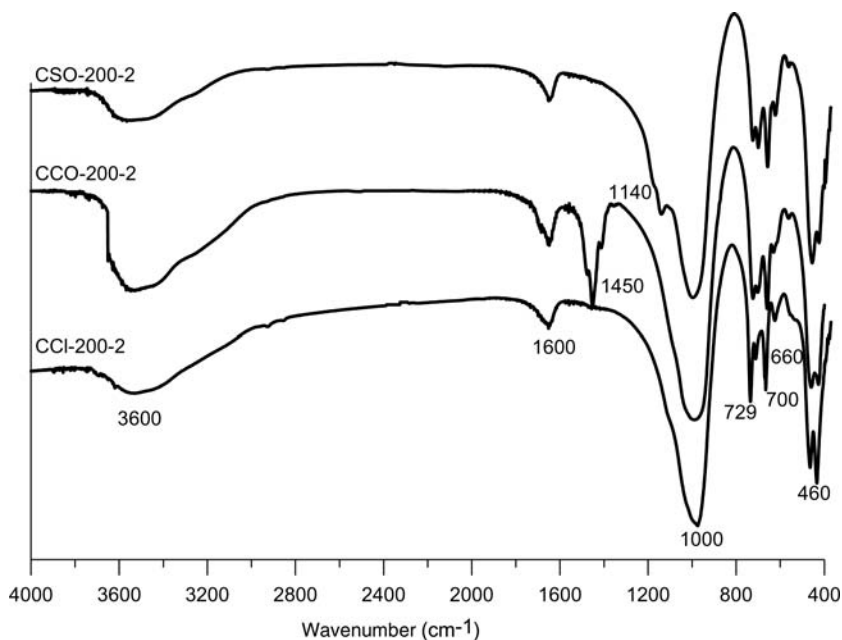


FIG. 13. IR spectra of the products synthesized from the KC source at 200°C and with Na/Al ratio = 2.

intensities of the main peaks of sodalite and kaolinite were observed in CCI-200-2 compared with JCI-200-2. In KJ, the kaolinite probably reacts more quickly to form sodalite which, after a few hours, transforms into cancrinite. According to the Ostwald step rule, the least thermodynamically stable phase may be kinetically

inclined to precipitate first, before the more stable phase (Breck, 1974). In this case, sodalite forms first, followed by cancrinite, the most stable phase, and both phases may coexist depending on the synthesis conditions. Therefore, because the kaolinite in KC has a high degree of structural order, this transformation may occur over

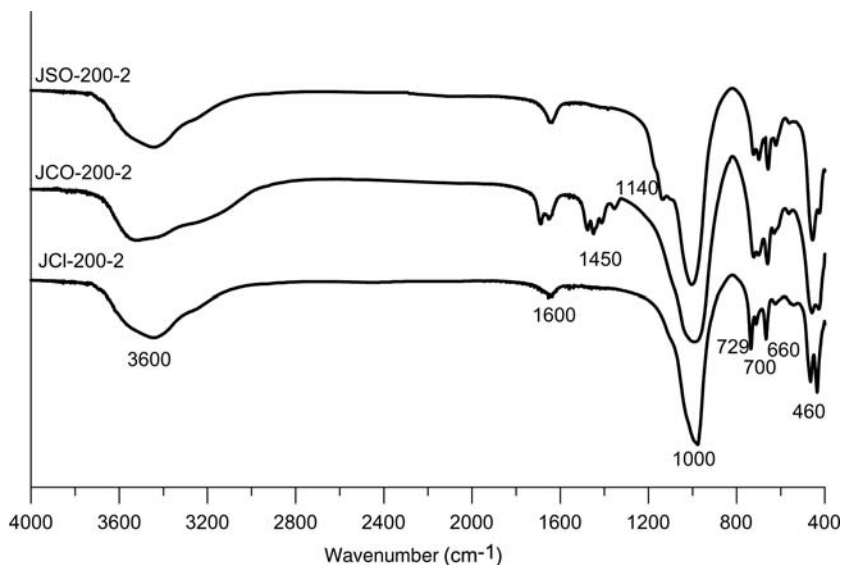


FIG. 14. IR spectra of the products synthesized from the KJ source at 200°C and with Na/Al ratio = 2.

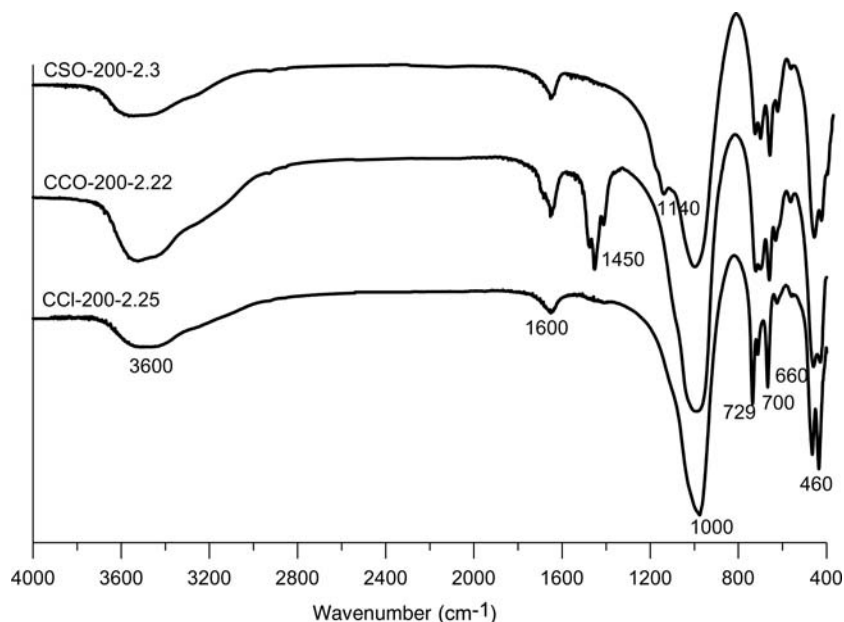


FIG. 15. IR spectra of the products synthesized from the KC source at 200°C and with Na/Al ratio > 2.

longer periods. However, the kaolinite from the KJ may be more reactive and its 001 peak in the synthesis product (JCI-200-2) less intense than that of the other product (CCI-200-2). Therefore, starting from a more reactive material, the formation of sodalite occurs more quickly, and after a certain time, it dissolves to form cancrinite.

In experiments with sulfate and carbonate, at 200°C sodalite is the only microporous material found for both the KC and KJ samples. Thus, the increase in temperature contributed to the complete reaction of kaolinite. Moreover, the increase in temperature to 200°C contributed to the increase in the reaction rate of the hydroxyborate sodalite and basic sodalite (hydroxy-sodalite) (Buhl *et al.*, 1997).

When chloride, sulfate and carbonate were used in the reaction mixture, in KC and KJ, the main diffraction maximum of sodalite was more intense than when the temperature increased from 150 to 200°C. The increase in temperature, therefore, also increased the degree of structural order of the sodalite, in accordance with Buhl *et al.* (1997).

Influence of temperature and the amount of Na in the reaction medium

Sodalite was the only mineral which was synthesized when chloride, sulfate and carbonate were added to the KC and KJ samples with a Na/Al ratio >2 in the

reaction mixture (Figs 11, 12). In the case of chloride, the increase in the quantity of Na in the reaction medium contributed to the complete reaction of kaolinite.

When the synthesis temperature increased, the intensity of the main peak of sodalite increased only in the products containing chloride. At 150°C, those products consisted of cancrinite and sodalite, whereas at 200°C, only sodalite was detected.

For larger amounts of Na in the reaction medium, the main diffraction peak of the sodalite synthesized from the KC sample was more intense. The increase in the Na in the reaction medium therefore favoured the formation of sodalite with a greater degree of structural order starting from a source of Si and Al which also showed a high degree of structural order. At high temperature, the material with a low degree of structural order (KJ) and more Fe than KC, was less reactive than KC. The Fe content in the impurities, which is released into the solution during the hydrothermal process, controls the kinetics of crystallization of the zeolites (Murat *et al.*, 1992). Alternatively, the decrease in the reactivity of the KJ might be explained by the fact that the Fe replaces the Al in the kaolinite structure, which in turn, has a lower tetrahedral Al content for the formation of the zeolites.

The FTIR spectra of the products synthesized from the KC and KJ with different anions at all Na/Al ratios

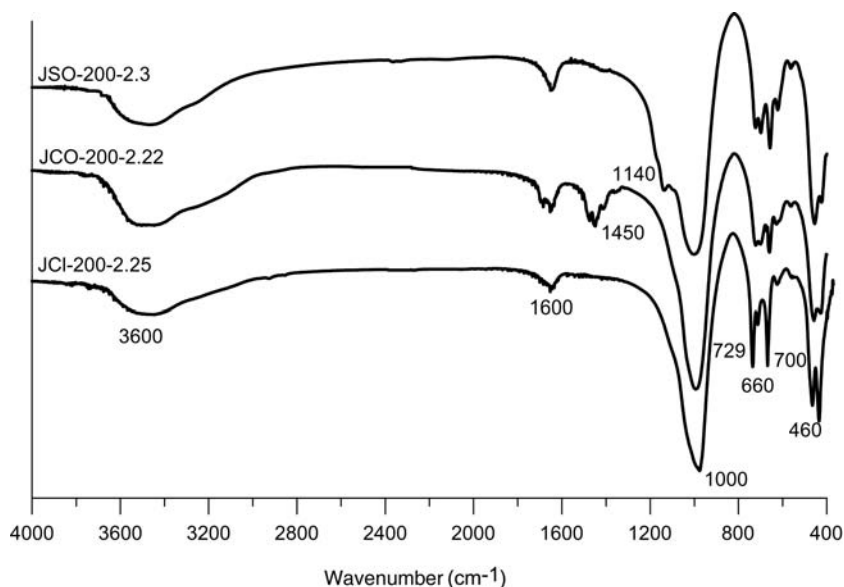


FIG. 16. IR spectra of the products synthesized from the KJ source at 200°C and with Na/Al ratio > 2.

and at 200°C are presented in Figs 13–16. In those spectra, no notable changes compared with those of the samples synthesized at 150°C were observed. At 200°C, in the product synthesized from the KJ and KC samples at Na/Al ratios = 2 and >2, the inclusion of specific anions used in the reaction mixture in the sodalite structure was confirmed by the presence of characteristic bands in the spectra: *i.e.* ~1140 cm⁻¹ (sulfate), ~1450 cm⁻¹ (carbonate) and ~659 cm⁻¹ (chloride) (Mead & Weller, 1995; Buhl, 1996; Whittington *et al.*, 1998). Even though bands that might be related to cancrinite were not observed in the products synthesized using chloride in the reaction mixture and a Na/Al ratio of 2, cancrinite is present in small amounts in these samples, as observed in the XRD traces.

CONCLUSIONS

The kaolinite in the kaolin waste from the Jari region was more reactive in the synthesis of sodalite because its structure has a low degree of structural order.

Under all of the experimental conditions, the chloride, sulfate and carbonate anions used in the reaction mixture were inserted into the sodalite structure.

At a synthesis temperature of 150°C, with a Na/Al ratio = 2 and using carbonate, sulfate and chloride in the reaction mixture, the kaolinite did not react

completely, although sodalite was the main end product. For a Na/Al ratio > 2, the kaolinite reacted completely, and the formation of sodalite occurred when using chloride, carbonate and sulfate from both the KC and the KJ source. For a Na/Al ratio = 2, therefore, sodalite is formed to a small extent only, which does not consume all the Al. In the case of the Bayer process, the limited amount of sodalite formed may contribute to the elimination of impurities that exist in the liquor.

At 200°C and using a reaction mixture with Na/Al ratio = 2 and with chloride, the kaolinite still did not react completely in both cases. The complete reaction of the kaolinite occurred only when the Na/Al ratio was increased to >2. In the case of carbonate and sulfate, the total transformation of kaolinite and the formation of sodalite occurred for both Na/Al ratios.

The present study showed that it is possible to use kaolin wastes from the Amazon to study the synthesis process of sodalite, providing an incentive to use the wastes.

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