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SYNTHESIS OF ZEOLITES AND ZEOTYPES BY HIDROTHERMAL
TRANSFORMATION OF KAOLINITE AND METAKAOLINITE

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Synthesis of Zeolites and Zeotypes by Hydrothermal Transformation of Kaolinite and Metakaolinite

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ABSTRACT
The synthesis of zeolitic materials by hydrothermal transformation of kaolinite and metakaolinite in NaOH solutions of various concentrations was investigated between 100 and 200°C, over different reaction times, using in some cases precipitated SiO2 or organic templates. Materials were obtained, including clathrasils: cancrinite (CAN), sodalite (SOD), and Linde Type A (LTA), faujasite (FAU), Na-P1 (GIS), analcime (ANA) and nepheline hydrate I (JBW) zeolites. In general, co-crystallization of CAN and SOD, likely via an unstable LTA zeolite intermediate, was observed after dissolution of kaolinite at low temperature; although the feldspathoids tend to be unstable at high temperature. LTA zeolite was synthesized after metakaolinite reaction, with minor amount of FAU zeolite, ANA and SOD. Solids were characterized by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA).

KEY WORDS:
Synthesis, kaolinite, metakaolinite, cancrinite, sodalite, LTA zeolite, FTIR, SEM, XRD.

RESUMEN
La síntesis de materiales zeolíticos a partir de la transformación hidrotermal de caolinita y metacaolinita en soluciones de NaOH se investigó entre 100 y 200°C, durante diferentes tiempos de reacción, usando en algunos casos SiO2, precipitada o templantes orgánicos. Los materiales obtenidos incluyen cancrinita (CÂN), sodalita (SOD), y Linde Type A (LTA), faujasita (FAU), Na-P1 (GIS), analcima (ANA) y nefelina hydratada I (JBW). En general, se observó la co-cristalización de CAN y SOD, posiblemente vía zeolita LTA, una fase metastable intermedia, a partir de la disolución de la caolinita. Zeolita LTA fue sintetizada a partir de la reacción de la metacaolinita, con menor cantidad de zeolita FAU, ANA y SOD. Los sólidos fueron caracterizados por difracción de rayos X, espectroscopia infrarroja transformada de Fourier, microscopio electrónico de barrido, y análisis termogravimétrico.

PALABRAS CLAVES
Síntesis, caolinita, metacaolinita, cancrinita, sodalita, zeolita LTA
INTRODUCTION
Zeolites are crystalline, microporous, hydrated aluminosilicates of alkaline or alkaline earth metals. The frameworks are composed of \([\text{SiO}_4]^{4-}\) and \([\text{AlO}_4]^{5-}\) tetrahedra, which corner-share to form different open structures. The negative charge on the lattice is neutralised by the positive charge of cations located within the material’s pores. In the basic zeolites these are usually univalent and bivalent metals or a combination. The metal cations may be replaced by acidic protons via ion-exchange to ammonium and subsequent calcination. By reason of electrostatic forces it is not possible to make an Al-O-Al bond. They are made up of «T-atoms» which are tetrahedrally bonded to each other with oxygen bridges. Other “T-atoms” such as P, Ga, Ge, B, Be, etc. can exist in the framework as well.

The synthesis of zeolites in forms suitable for industrial applications is of great importance. The first natural zeolite was discovered by Cronstedt in 1756, and the first synthesis was attempted by St. Claire-Deville in 1862. Barrer’s pioneering work in 1940s demonstrated that a wide range of zeolites could be synthesized from aluminosilicate gels. The discovery that quaternary ammonium salts could act as structure directing agents (SDAs), sometimes called “templates”, has resulted in the preparation of nearly 100 different silicate frameworks (International Zeolite Association, www.iza-structure.org). The mode of action of the SDA has been extensively investigated by Davies and Zones and this has led to some empirical rules, if not the absolute ability to design new solids (Lobo et al., 1995). Use of fluoride as a mineraliser in zeolite synthesis was developed by Flanigen in the 1970s and has resulted in zeolites being prepared with fewer defect sites and higher silica contents.

At present, synthetic zeolites are used commercially more often than natural zeolites due to the purity of crystalline products and the uniformity of particle sizes (Breck, 1974). However, the preparation of synthetic zeolites from chemical sources of silica and alumina is expensive. Such costs may be reduced by the use of clay minerals, volcanic glasses (perlite and pumice), rice husks, diatoms, fly ash or paper sludge ash as starting materials. Zeolite synthesis has been also developed by the transformation of one zeolite type into other zeotypes.

Previous work has shown that kaolinite is not stable under highly alkaline conditions and different zeolitic materials can form, and that kaolinite is usually used after calcination to obtain a more reactive phase (metakaolinite). After dehydration (endothermic dehydroxylation), kaolinite is transformed into amorphous metakaolinite. Raw kaolinite and metakaolinite have been used as the Al and Si sources for synthesis of zeolites Linde Type A, X, Y, P, 4A, Na-A, KI, cancrinite, sodalite, hydroxysodalite, faujasite, phillipsite, chabazite and several other types of zeolites (e.g., Dudzik and Kowalak, 1974; Buhl, 1991; Rees & Chandrasekhar, 1993; Alberti et al., 1994; Buhl & Loens, 1996; Gualtieri et al., 1997; Akolekar et al., 1997; Bauer & Berger, 1998; Bauer et al., 1998; Sanhueza et al., 1999; Saavedra et al., 2000; Barnes et al., 2004; Mon, et al., 2005; Covarrubias et al., 2006).

In this paper we investigate the hydrothermal reaction of kaolinite or metakaolinite in alkaline solutions. Moreover, we adjust the SiO\(_2\)/Al\(_2\)O\(_3\) ratio at selected compositions with precipitated or fly ash and introduce organic structure directing agents. In this way we explore the influence of reaction time, NaOH and Al concentrations in the hydrothermal treatments.

MATERIALS AND METHODS
Materials were synthesized hydrothermally by treating kaolinite (Supreme Powder, ECC International, UK) or metakaolinite with solutions of sodium hydroxide (99 %, Aldrich). Kaolinite (composition 46.44 % SiO\(_2\), 38.80 % Al\(_2\)O\(_3\), 0.03 % TiO\(_2\), 0.52 % Fe\(_2\)O\(_3\), 0.08 % MgO, 0.33 % Na\(_2\)O and 0.69 % K\(_2\)O) was used without further purification. Metakaolinite was
prepared by calcining kaolinite at either 600, 950 or 1000 °C in air for 2 hours. All solid starting materials were first ground and particles of less than 75 μm selected by sieving, before gels were prepared by mixing with aqueous NaOH. The resulting mixtures were transferred to either 65 cm³ polytetrafluoroethylene (PTFE)-bottles (Cowie Technology) or 20 cm³ PTFE-lined stainless steel autoclaves and heated under static conditions at 100 or 200°C for different reaction times. On removal from the oven they were quenched in cold water and the product recovered by vacuum filtration, washed with distilled water and dried at 80°C overnight.

To examine the effect of modifying the SiO₂/Al₂O₃ ratio experiments were preformed in which this was adjusted by the addition SiO₂, either as precipitated silica (98 %, BDH). Furthermore, in selected preparations, tetrapropylammonium bromide (98 %, Aldrich) or triethanolamine, (AnalaR, BDH) were added as structure directing agents (SDAs). Further details of the gel compositions and synthesis conditions are given in Table 1.

RESULTS

X-ray diffraction

XRD patterns of unheated and activated (600, 950 and 1000°C) kaolinite are shown in Figure 1. Kaolinite is identified by its characteristic X-ray diffraction peaks at 12.34° and 24.64° 2θ as has been reported in previous studies (Zhao et al., 2004). After thermal treatment, the XRD patterns exhibit a significant change in comparison to the pattern of untreated kaolinite, which is characterized by the disappearance of the diffraction peaks of kaolinite, accompanied by the appearance of an amorphous aluminosilicate (see the broad hump at 2θ = 13-33°), which persists between 600 and 950°C, with relicts of the original kaolinite. However, this amorphous material contains mullite as the main crystalline phase at 1000°C. Therefore, the activation of kaolinite produces structural changes of this mineral, promoting its reactivity to synthesize zeolitic materials.

The X-diffraction patterns of unreacted and reacted kaolinite treated with alkaline solutions are presented in Figure 2. The most distinct changes in the XRD patterns are the reduction in intensity of the kaolinite peaks and the appearance of new crystalline phases. The hydrothermal treatment of kaolinite in low NaOH solutions resulted in the crystallization of CAN and SOD, along with metastable LTA zeolite (Figures 2-1a and 2-1b). When precipitated SiO₂ was used a high Si/Al ratio LTA, FAU and GIS zeolites with minor amount of CAN and SOD was formed (Figures 2-2a and 2-2b), which is reflected in strong peaks for these zeolites and relatively weak peaks for the feldspathoids, compared with what is observed in Figures 2-1a and 2-1b. No interesting changes were observed using tetrapropylammonium bromide (Figures 3-1a and 3-1b). In general, at low reaction times (Figures 2-1a, 2-2a and 2-3a) the raw kaolinite is dominant respect to the as-synthesized products, which display low intensity peaks compared with those in Figures 2-1b, 2-2b and 2-3c, respectively. Higher NaOH solutions produced a faster dissolution of the original
kaolinite accompanied by more crystalline zeolitic materials. The relative height of the diffraction peaks of CAN and SOD, as well as LTA zeolite increased as shown in Figures 2-4a and 2-4b (compared with Figures 2-1a and 2-1b). A reaction at higher temperature promoted an increase in intensity of the LTA zeolite, as well as the appearance of JBW, ANA and FAU zeolites (Figures 2-5a and 2-5b). When triethanolamine was used CAN and SOD were the main dominant crystalline phases at low reaction time (Figure 2-6a), whereas LTA, ANA and FAU zeolites (Figure 2-6b) crystallized with weak diffraction peaks for CAN and SOD at high reaction time.

In Figure 3 the XRD patterns of metakaolinite and the resulting as-synthesized products after its hydrothermal reaction with alkaline solutions are illustrated. The most important change observed in the XRD patterns is the appearance of the characteristic peaks of LTA, FAU and ANA zeolites. The as-synthesized LTA zeolite has several common peaks located at 7.14°, 10.10°, 12.38°, 16.20°, 21.58°, 23.92°, 27.00°, 29.82° and 34.08° 2θ on its XRD pattern (Figures 3-7a and 3-7b). When precipitated SiO₂ was used, the as-synthesized product show intensity peaks of LTA zeolite at low reaction time (Figure 3-8a), which however disappear with reaction time to produce an amorphous aluminosilicate material (Figure 3-8b). Using tetrapropylammonium bromide a reduction in the intensity of the peaks of LTA zeolite was observed (Figures 3-9a and 3-9b). However, at higher NaOH concentration and temperature, using precipitated SiO₂, a mixture of LTA, FAU and ANA zeolites were obtained (Figures 3-10a and 3-10b).

**FTIR spectroscopy**

The FTIR spectra of the original kaolinite and as-synthesized products obtained after its hydrothermal treatment with alkaline solutions are shown in Figure 4a, and the assignment of their spectral frequencies are given in Table 2. We recognize the characteristic OH-stretching vibrations of kaolinite at 3687 cm⁻¹ (surface OH stretching) and 3619 cm⁻¹ (inner OH stretching), as well as the peaks at 1115, 1030, 1007, 937 (surface OH bending), 912 (inner OH bending), 800, 792 and 751 cm⁻¹, which disappeared after hydrothermal reaction. However, the peaks at 689, 647 and 535 cm⁻¹ were shifted to higher frequencies, and the vibration bands at 466 and 430 cm⁻¹ were shifted to lower frequencies. Coincident with the disappearance of kaolinite, characteristic zeolite bands appeared on the spectra, including the asymmetric Al-O stretch located in the region of 950-1250 cm⁻¹, and their symmetric Al-O stretch located in the region of 660-770 cm⁻¹. The bands in the region of 500-650 cm⁻¹ are related to the presence of the double rings (D4R and D6R) in the framework structures of the zeolitic materials. The bands in the region of 420-500 cm⁻¹ are related to internal tetrahedron vibrations of Si-O and Al-O of the synthetic zeolites. The bands in the region of 400-420 cm⁻¹ are related to the pore opening or motion of the tetrahedra rings, which form the pore opening of zeolites (Breck, 1974).

Figure 4b illustrates the FTIR spectra of the unreacted and reacted metakaolinite in alkaline solutions, whereas the assignment of their spectral frequencies is presented in Table 2. The transformation of kaolinite to metakaolinite can be observed, by comparing Figures 5a and 5b, showing the loss of Al-OH bands (937 and 912 cm⁻¹), changes in the Si-O stretching bands, and the disappearance of Al-O-Si bands at 788 and 751 cm⁻¹. These changes are similar to those reported in other studies (Akolekar et al., 1997; Zhao et al., 2004; Covarrubias et al., 2006). The characteristic bands observed in the metakaolinite were 1043, 796, 562 and 422 cm⁻¹. Three broad bands are centered at 1043, 796 and 422 cm⁻¹. A significant shift of the Si-O vibration bands at 1030 and 1007 cm⁻¹ in kaolinite to a higher frequency band at 1043 cm⁻¹ in metakaolinite was observed, which has been assigned to amorphous SiO₂ as reported by Sinha et al. (1995) and Valcke et al. (1997). The band located at 796 cm⁻¹ was not observed in the zeolitic products, whereas the band at 1043 cm⁻¹ was shifted to the bands at 970, 974, 964 and 972 cm⁻¹. The low intensity band at 562 cm⁻¹ was shifted to low frequency bands (538, 527, 532 and 527 cm⁻¹).
The band at 455 cm\(^{-1}\) is close to the band at 456 cm\(^{-1}\) (bending vibrations of the TO4) of FAU zeolite. The bands at 557, 684 and 970 cm\(^{-1}\) are close to the bands at 560, 686 and 971 cm\(^{-1}\), which corresponds to the 6-membered double-ring vibration, to the symmetric stretching and to the asymmetric stretching, respectively, of FAU zeolite. The band at 557 cm\(^{-1}\) could represent the beginning of the crystallization of a zeolite with double rings (Alkan et al., 2005). The bands at 463 and 671 or 672 cm\(^{-1}\) are close to the bands at 462 and 668 cm\(^{-1}\) assigned to the internal linkage vibrations of the TO4 (T = Si or Al) tetrahedra and to the asymmetric stretching, respectively, of LTA zeolite. However, the band at 463 cm\(^{-1}\) is close to the band at 461 cm\(^{-1}\), which indicates the presence of hydroxysodalite. The band at 600 cm\(^{-1}\) corresponds to the double-ring vibration of GIS zeolite, whereas the bands at 671 or 672 cm\(^{-1}\) are close to the band at 670 cm\(^{-1}\) (symmetric stretching) of this zeolite. The band at 621 cm\(^{-1}\) is close to the band at 618 cm\(^{-1}\) assigned to the 6-membered double-ring vibration of CAN. The band at 663 cm\(^{-1}\) (corresponds to the symmetric stretching) is close to the band at 660 cm\(^{-1}\), which was also observed, of this zeolite-like material.

**Scanning electron microscopy**

SEM micrographs (Figures 5 and 6) of the as-synthesized products after hydrothermal treatment of kaolinite and metakaolinite show a marked change in the morphology of the starting materials. Kaolinite can be recognized by its platy morphology and hexagonal outlines (Figure 5a). A predominantly lephispheric morphology is typically observed in the zeolitic products obtained after hydrothermal reaction of kaolinite in 1.33M NaOH solutions at 100°C for 120 hours with spheroidal «ball of yarn» morphologies for CAN and rod-shaped structures for SOD (Figure 5b).

LTA zeolite can be identified by its characteristic cubic morphology (Figure 5c); it probably formed before CAN and SOD, as shown by the occurrence of crystals of these feldspathoids growing at the surface of LTA zeolite. Figure 5d illustrates spheroidal aggregates of cubic crystals of LTA zeolite, showing penetrating twinning, which were obtained at 1.33M NaOH + precipitated SiO\(_2\) at 100°C for 96 hours. In some cases, an intergrowth of crystals of LTA and FAU zeolites are observed in these spheroidal morphologies (Figure 5e). Characteristic prismatic lath-like crystals of JBW zeolite (Figure 5f) were produced after hydrothermal treatment of kaolinite at 3.99M NaOH at 200°C for 168 hours. On the other hand, the hydrothermal treatment of metakaolinite reflects a common occurrence of cubic crystals of LTA zeolite. Lephaspheric morphologies corresponding to CAN and SOD grow at the surface of cubic crystals of LTA zeolite, which sometimes display interpenetrating twinning, (Figures 6a and 6b), at 1.33M NaOH solutions at 100°C for 52 hours. Some deformed pseudohexagonal platelets of the original kaolinite still remain after its activation. When precipitated SiO\(_2\) was added to the reaction gel, amorphous spheroidal morphologies, from which aggregates of very small cubic LTA zeolite crystals are growing (Figure 6c) were obtained at 1.33M + precipitated SiO\(_2\) at 100°C for 96 hours, whereas massive to clusters of radiating needlelike crystals of SOD (Figure 6d) crystallized at higher NaOH concentration and temperature.

**Thermogravimetric Analysis (TGA)**

TG/DTG curves of starting kaolinite and as-synthesized products are shown in Figure 7. The characteristic DTG peaks and weight loss percentages of zeolitic products and starting materials are presented in Table 1. The DTG curve of the kaolinite (Figure 7a) displays a strong peak at 517°C, which is due to dehydroxylation of kaolinite within the 450-600°C temperature range resulting in a weight loss of 15.34% and formation of metakaolinite. The peak on the DTG curve at approximately 980°C is an evidence of breakdown of the metakaolinite structure and the formation of mullite. The as-synthesized products show three or four dehydration steps. The position of these DTG peaks and the number of dehydration steps has been attributed to the different compensating cation-water binding energies as well as to the different energy associated with the diffusion of the desorbed water through the porous structure of the zeolitic materials; their weight loss percentages reflects the water loss from the zeolite structure, and the
DISCUSSION

Based on this study, the kaolinite \((\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4)\) experienced chemical transformation by dehydroxylation between 450 and 600°C, which results in the formation of metakaolinite \((\text{Al}_2\text{Si}_2\text{O}_7)\). The decomposition of metakaolinite at a temperature between 980 and 1000°C produces an amorphous material from which mullite crystallized, that is consistent with the results obtained by XRD.

There is evidence that \(\text{LTA}, \text{FAU}, \text{GIS}\) and \(\text{JBW}\) zeolites and feldspathoids (\(\text{CAN}, \text{SOD}\) and \(\text{ANA}\)) are present in the reaction products after hydrothermal treatment of raw materials in alkaline solutions. There were two major chemical processes involved in the reaction between kaolinite (or metakaolinite) and alkaline solutions: dissolution of kaolinite (or metakaolinite) followed by formation of zeolitic materials. The structural similarity between zeolites and feldspathoids explain why them can coexist in the as-synthesized products and the dominant crystalline phase depends on the conditions of formation.

The dissolution of kaolinite is favored at high NaOH concentrations, which is probably the reason why more kaolinite converted to zeolitic materials in alkaline solutions of 3.99M NaOH than solutions of lower concentration of NaOH. The main crystalline phases obtained at low NaOH solutions and temperatures were \(\text{CAN}\), \(\text{SOD}\) and \(\text{LTA}\) zeolite. \(\text{FAU}\) and \(\text{GIS}\) zeolites also crystallized at high \(\text{SiO}_2/\text{Al}_2\text{O}_3\) ratio solutions. On the other hand, at high NaOH solutions and temperatures, similar phases crystallized, except by the formation of \(\text{JBW}\) and \(\text{ANA}\). A high crystallinity \(\text{LTA}\) zeolite was obtained. We suppose that \(\text{CAN}\) appeared more stable than \(\text{SOD}\), and would be the final product, whereas amorphous material, \(\text{LTA}\) zeolite and \(\text{SOD}\) would be the transition phases at low NaOH concentrations and temperature, and that during the hydrothermal transformation of kaolinite an initial formation of \(\text{SOD}\) occurred with subsequent transformation to \(\text{CAN}\) as has been reported in other studies (e.g., Barnes et al., 1999a; Choi et al., 2005b). However, different zeolites crystallized at high NaOH concentrations and temperature, with minor amount of \(\text{CAN}\) or \(\text{SOD}\).

\(\text{LTA}\) zeolite was the most important zeolitic material that crystallized after hydrothermal treatment of activated metakaolinite. When precipitated \(\text{SiO}_2\) was used at low NaOH concentrations and temperature, an amorphous aluminosilicate phases was obtained, but when this silica source was used at high NaOH concentrations and temperature, high crystallinity...
phases such as LTA and FAU, along with ANA were obtained. The use of organic templates produced LTA zeolite with a low crystallinity compared with that obtained without using it.

The production of microporous materials by the reaction of kaolinite or metakaolinite with NaOH solutions at 100°C or 200°C and different reaction times does not represent a new synthesis, but provides valuable scientific knowledge on their transformation on the nucleation and growth of aluminosilicates, with dissolution dominating initially and precipitation dominating in the later stages.

Only LTA and JBW zeolites were produced as nearly pure crystalline phases from hydrothermal reaction of metakaolinite and kaolinite, respectively.

For a future research we are going to evaluate the efficiency of such zeolitic materials in selective cation exchange as a potential remediation alternative for purification of waste waters, analyzing the incorporation and diffusion of contaminant cations (e.g., Cs or Sr) in their structures, similar to what have been reported in previous studies (e.g., Serne et al., 1998; Flury et al., 2002; Chorover et al., 2003; Liu et al., 2003; Mashal, 2003; Zhao et al., 2004; Mon et al., 2005; Choi et al., 2005a, 2005b).

Different hybrid organic–inorganic zeolitic materials could be synthesized containing into their frameworks organic groups. However, the introduction of organic linkers requires very long synthesis times because the hydrolysis and polycondensation of organic groups covalently bonded to inorganic matrix retard the crystallization process. The zeolite framework is a very important parameter to introduce higher or lower amount of organic groups inside of its networks.

ACKNOWLEDGMENTS
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Table 1
Synthesis conditions for hydrothermal treatment of kaolinite and metakaolinite and DTG peaks and weights loss for starting materials and zeolitic products.

<table>
<thead>
<tr>
<th>Batch composition of the reaction gel</th>
<th>[NaOH] (M)</th>
<th>SDA</th>
<th>Temperature (°C)</th>
<th>Time (hour)</th>
<th>As-synthesized products</th>
<th>DTG peaks (°C)</th>
<th>Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KLAO</td>
<td></td>
<td>1.33</td>
<td>100</td>
<td>6</td>
<td>1a c, s, A</td>
<td>76</td>
<td>517</td>
</tr>
<tr>
<td>LTAO</td>
<td>2SiO:2H₂O</td>
<td>1.33</td>
<td>100</td>
<td>24</td>
<td>2a c, s, A, P, F, P</td>
<td>96</td>
<td>107, 162, 264, 483</td>
</tr>
<tr>
<td>NAO</td>
<td>AIO:2SiO:0.5(CH₃)NBr</td>
<td>3.33</td>
<td>(CH₃CH₂OH)(H₂O)</td>
<td>120</td>
<td>3b c, s, A</td>
<td>86</td>
<td>128, 223, 487</td>
</tr>
<tr>
<td>FAU</td>
<td>2SiO:8H₂O</td>
<td>3.99</td>
<td>100</td>
<td>120</td>
<td>4b c, s, A, P</td>
<td>86</td>
<td>54, 123, 155, 216</td>
</tr>
<tr>
<td>SIO</td>
<td>2SiO:8H₂O</td>
<td>3.99</td>
<td>200</td>
<td>24</td>
<td>5a c, s, A, P, N, F</td>
<td>95</td>
<td>127, 230</td>
</tr>
<tr>
<td>NAO</td>
<td>AIO:2SiO:0.5(CH₃CH₂OH)(H₂O)</td>
<td>3.99</td>
<td>(CH₃CH₂OH)₂</td>
<td>200</td>
<td>6a c, s, A</td>
<td>86</td>
<td>107, 162, 264, 483</td>
</tr>
</tbody>
</table>

**Note:**
- * activated kaolinite at 600°C; ** activated kaolinite at 950°C; * precipitated SiO₂ : (CH₃CH₂OH)(H₂O)NBr, tetrapropylammonium bromide; CH₃CH₂OH+N₃, triethanolamine.
- c, CAN; s, SOD; a, ANA; A, LTA zeolite; F, FAU zeolite; P, GS zeolite; N, JBW zeolite.
Table 2
Fourier transformed infrared assignments of raw materials and as-synthesized products.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Raw Kaolinite</th>
<th>Zeolitic products</th>
<th>Metakaolinite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asymmetric T-O stretching vibrations</td>
<td>1115 1117 1116 1115</td>
<td>1110 1114 1117</td>
<td>1054</td>
</tr>
<tr>
<td>1103 1101 1103</td>
<td>1106 1101 1103</td>
<td>1106 1101 1103</td>
<td>1006</td>
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<tr>
<td>1097 1097 1097</td>
<td>1094 1094 1094</td>
<td>1094 1094 1094</td>
<td>1084</td>
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<td>Symmetric T-O stretching vibrations</td>
<td>T31 720 720 724</td>
<td>719 719 719</td>
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<td>619 619 619</td>
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<td>617 617 617</td>
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<tr>
<td>4- or 6-membered double rings</td>
<td>621 621 621</td>
<td>621 621 621</td>
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<td>617 617 617</td>
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<tr>
<td>Bending vibrations of T-O</td>
<td>609 609 609</td>
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<td>592 592 592</td>
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Figure 1. X-ray diffraction patterns of uncalcined and calcined kaolinite at different temperatures. i, illite; k, kaolinite; m, muscovite; h, halloysite; M, mullite.

Figure 3. X-ray diffraction patterns of unreacted (upper part) and reacted metakaolinite treated with alkaline solutions. The numbers indicating XRD patterns correspond to the as-synthesized products column in Table 1. i, illite; q, quartz; A, LTA zeolite; F, FAU zeolite; a, ANA; c, CAN; s, SOD.
Figure 2. X-diffraction patterns of unreacted (upper part) and reacted kaolinite treated with alkaline solutions. The numbers indicating XRD patterns correspond to the as-synthesized products column in Table 1. k, kaolinite; i, illite; m, muscovite; h, halloysite; c, CAN; s, SOD; A, LTA zeolite; F, FAU zeolite; P, GIS zeolite; N, JBW zeolite.

Figure 4. FTIR spectra of unreacted and reacted (a) kaolinite and (b) metakaolinite treated with alkaline. The numbers indicating FTIR spectra correspond to the as-synthesized products column in Table 1.
Figure 5. Scanning electron microscopy images of (a) hexagonal platy crystals of unreacted kaolinite, (b) crystals of CAN and SOD growing at the surface of a cubic crystal of LTA zeolite, (c) lephispheric morphology of aggregates of CAN and SOD and relict kaolinite, (d) spheroidal aggregates of cubic crystals of LTA zeolite, showing penetrating twinning, (e) detail of a lephispheric morphology showing an intergrowth of crystals of LTA and FAU zeolites, (f) long prismatic lath-like crystals of JBW.

Figure 6. Scanning electron microscopy images of (a) lephispheric morphology of CAN or SOD associated to a cubic crystal of LTA zeolite, with crystals of the feldspathoids growing at the surface of LTA zeolite; observe some deformed pseudohexagonal platelets of the original kaolinite, (b) cubic LTA zeolite, displaying interpenetrating twinning, (c) amorphous spheroidal morphology from which aggregates of cubic LTA zeolite crystals are growing, (d) massive to clusters of radiating needlelike crystals of SOD.

Figure 7. (a) TG/DTG curves from 25 to 1000°C of raw kaolinite. (b) and (c) DTG curves from 25 to 700°C of zeolitic phases obtained after hydrothermal treatment of kaolinite and metakaolinite, respectively, with alkaline solutions. The numbers indicating DTG curves correspond to the as-synthesized products column in Table 1.
REFERENCES


