Chemical Activation of a Kaolinite under Acid and Alkaline Conditions

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Four metakaolins were prepared by calcination of a natural Spanish kaolin (Navalacruz deposit, Zamora province) at 600, 700, 800, and 900 °C. These four metakaolins, more reactive than the parent kaolin, were submitted to acid and alkaline activations. Acid activation was carried out with 6 M HCl at room temperature and at 90 °C under reflux conditions, with times of treatment of 6 and 24 h. Treatment at room temperature did not produce any alteration in the structure or in the properties of the metakaolins. Treatment under reflux conditions for 6 h led to the removal of most of the octahedral Al^{3+} cations, and the formation of an amorphous silica phase, with surface area up to 219 m²/g, because of a high development of both the internal and the external surface of the solids. Acid treatment under stronger conditions (reflux, 24 h) also removed the octahedral cations, but provoked an amorphization of the silica obtained ($S \approx 23$ m²/g). The metakaolin prepared by calcination at 900 °C showed a lower reactivity than those synthesized at the other temperatures considered. The alkaline treatments were carried out with 1 M and 5 M KOH solutions, the treatments with the concentrated solution, both at room temperature and, especially, under reflux, led to the dissolution of the metakaolins and to the formation of well-crystallized K–F zeolite. The solids obtained by acid treatments are promising as adsorbents and catalyst supports, while treatment in alkaline conditions may be a good method for preparing K–F zeolite.

1. Introduction

Kaolin is one of the clay materials most widely used by humanity since antiquity. Kaolinite is the major mineral component of kaolin, which may contain impurities such as quartz, illites, smectites, and feldspars. Today, millions of tons of kaolin are used each year in the world for a large variety of applications, such as ceramics, paper coating, paper filling, paint extender, rubber filler, plastic filler, cracking catalysts, or cements.[1,2]

However, the improvement of the properties of kaolin by chemical methods is difficult because of the high passivity of this material. Thus, it is not significantly affected by acid or alkaline treatments, even under strong conditions (concentrated solutions and/or high temperatures).[3–9] Metakaolinite, a metastable phase

obtained by calcination of kaolinite, has been reported to be more reactive under chemical treatments. Metakaolins are obtained by calcination of kaolins at temperatures between ≈550–950 °C;[10] this transformation occurs with the loss of structural water with a reorganization of the structure; only a small part of AlO_6 octahedra is maintained, while the rest are transformed into much more reactive tetra- and pentacoordinated units.[11] The conditions of the kaolin calcination strongly influence the reactivity of the solids obtained; the best conditions for obtaining very reactive metakaolins have been discussed by different authors who reported values between 600 and 800 °C.[3–9] Calcination at higher temperatures leads to the formation of mullite and cristobalite.[10]

Acid activation has been widely studied as a chemical treatment for the improvement of the surface and catalytic properties of fibrous clays (sepiolite and palygorskite) and smectitic clays (saponite and montmorillonite). It consists of the leaching of the clays with inorganic acids, causing disaggregation of clay particles, elimination of mineral impurities, and dissolution of the external layers, thus altering the chemical composition and the structure of the clays. This produces an increase in the surface area, the porosity, and the number of acid centers with respect to the parent clays, depending on the intensity of the treatment. The treated solids are

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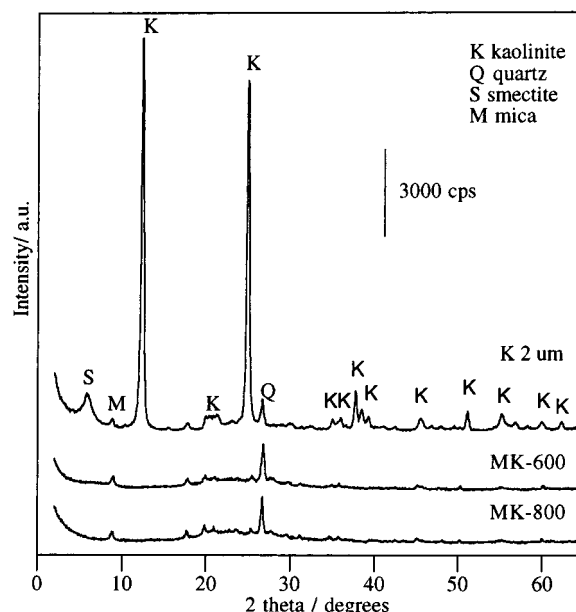
composed of a mixture of nonattacked clay layers and a hydrous, amorphous, and partially protonated silica phase.[12−19] These high surface area silica gels are competitive in different industrial uses and very promising as sorbents or as catalyst supports. By contrast, the acid activation of metakaolins has been dealt with in only a few articles.[3,6,20,21]

The alkaline treatment of clays has been much less studied. A priori, the progressive leaching of aluminic and silicic layers may be predicted, both elements being soluble in alkaline conditions as aluminates and silicates. The alkaline treatment of fibrous or smectitic clays has received little attention,[22,23] but the modifications of metakaolins have been widely studied.[4,5,7−9,24−26] Usually, the transformation into zeolites has been reported, although the selective leaching of the Si sheets, leading to γ-alumina with interesting properties, has recently been reported.[24−26]

Despite the studies described above, a systematic analysis of the chemical activation of kaolin, with a wide characterization of the obtained solids and a complete discussion of the phenomena governing this process, lacks in the literature. The increasing interest in looking for new applications of clays, natural, quiet common, and very cheap materials, justifies such a systematic study of this process. By this reason, our target in this work is to study the behavior, under acid and alkaline treatment, of metakaolins obtained by calcination of a Spanish kaolin. Metakaolins were prepared by calcination at four different temperatures between 600 and 900 °C; these metakaolins were submitted to treatments with HCl and KOH of different concentrations, employing different times and temperatures of reaction.

2. Experimental Section

2.1. Materials. The kaolin used came from the deposit of Navalacruz, Zamora province, west of Spain. The origin of this kaolinitic deposit is the weathering alteration of the feldspars of a granite. The raw sample is composed of about 93% phyllosilicates and 7% quartz (estimated from the XRD pattern by the "Reflectance power" method, using the values reported by Martín Pozas[27]). The separation by aqueous decantation of

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Figure 1. XRD patterns of the parent kaolin and of the metakaolins prepared by calcination at 600 and 800 °C.

the ≤ 2-μm fraction was very effective, only small amounts of quartz, smectite, and mica being detected in this fraction (Figure 1). The estimation of the composition of this fraction, made by applying the "Reflectance power" method to an oriented film after ethyleneglycol swelling, was kaolinite, 94%, smectite (montmorillonite), 3%, and mica, 3%. The chemical weight percent composition of this fraction was as follows: SiO_2, 46.97; Al_2O_3, 33.57; Fe_2O_3, 2.08; MgO, 0.44; TiO_2, 0.31; MnO, 0.004; CaO, 0.20; Na_2O, 0.08; K_2O, 0.64; and loss by ignition, 15.27 wt %. The following chemical formula may be calculated for this fraction: $Si_{2.0}Al_{1.906}Fe_{0.010}Mg_{0.038}K_{0.060}O_{7.2}$. This formula is very close to the theoretical formula of kaolinite, $Si_2Al_2O_5(OH)_4$, the differences being due to the small amounts of impurities in the solid: Mg and K must be in the composition of the mica and of the montmorillonite, and the presence of these two impurities makes the Si/Al ratio higher than the theoretical value in a kaolinite. This sample has a BET surface area of 18 m²/g (12 m²/g for the raw material, before aqueous decantation).

The ≤ 2-μm fraction (from now on, the parent clay) was submitted to calcination at 600, 700, 800, and 900 °C to give the corresponding metakaolins. Calcination was carried out under an air atmosphere in a programmable furnace, with a heating rate from room temperature to the calcination temperature of 10 °C min⁻¹ and 10 h at the calcination temperature. The metakaolins obtained are named MK-*T*, *T* being the calcination temperature. One part of these solids was kept for characterization and the rest was submitted to activation treatments.

Acid treatments were carried out with 6 M HCl solutions, at room temperature and 90 °C with reflux conditions, and for each temperature, times of treatment of 6 and 24 h were employed; 6.0 g of the metakaolin were mixed with 180 mL of the acid solutions and stirred during the times indicated above. After this, the suspensions were centrifuged and the solids were washed with distilled water until no chloride anions could be detected (Ag⁺ test) and dried at 50 °C. The samples are designated as follows: MK-*T*-HCl-C-*T′*-*t*, *T′* (RT or 90) denotes the treatment temperature, and *t* (6 or 24) denotes the time of treatment.

Alkaline treatments were carried out with 1 and 5 M KOH solutions. The same conditions used for the acid treatments were employed, room temperature and 90 °C with reflux

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conditions were considered and times of treatment of 6 and 24 h; 6.0 g of the metakaolin were mixed with 180 mL of the alkali solutions and stirred during the times indicated. Then, the suspensions were centrifuged and the solids were washed with distilled water until neutral pH and dried at 50 °C. The samples are designated as follows: MK-*T*-KOH-*C*-*T'*-*t*, *C* (1 or 5) denotes the KOH concentration, *T'* (RT or 90) denotes the treatment temperature, and *t* (6 or 24) denotes the time of treatment.

2.2. Techniques. Elemental analyses of the solids were carried out by Activation Laboratories Ltd., Ancaster, Ontario, Canada, using inductively coupled plasma spectroscopy (ICPS) and atomic absorption spectroscopy (AAS).

X-ray powder diffraction patterns were obtained by using a Siemens D-500 diffractometer, at 40 kV and 30 mA (1200 W), and employing Cu Kα filtered radiation. The equipment was connected to a DACO-MP microprocessor and used Diffract-AT software.

Thermal analyses were performed on Perkin-Elmer analyzers, TGA7 and DTA7 for gravimetric and differential thermal analyses, respectively; both were connected to TAC 7/DX data stations and used TGA 7HT and DTA7 software, respectively. All measurements were carried out at a heating rate of 10 °C min^{-1} under a flow of air of 20 mL min^{-1}. Al$_2$O$_3$ was used as reference for the DTA measurements.

FT-IR spectra were recorded in the region 4000−350 cm^{-1} in a Perkin-Elmer 1730 infrared Fourier transform spectrometer, using the KBr pellet technique (about 1 mg of sample and 300 mg of KBr were used in the preparation of the pellets).

Textural analyses were carried out from the corresponding nitrogen adsorption−desorption isotherms at 77 K, obtained from a static volumetric apparatus (Micromeritics ASAP 2010 adsorption analyzer). The samples were degassed 1 h at room temperature and then degassed up to $P \leq 50$ μmHg. The nitrogen adsorption data were obtained using 0.2 g of sample; for the low relative pressure range successive doses of nitrogen of 4 cm^3 STP/g were added, equilibrating for 1.5 h. This method was used up to $P/P_0 = 0.1$. Subsequently, the isotherm was obtained following a previously fixed 40-points P/P_0 table. For some samples with low structure changes and for which low surface area was expected, the surface area was estimated by measuring four adsorption points using a Micromeritics Gemini apparatus.

The concentration of Brönsted acid centers has been calculated from the amount of cyclohexylamine retained by the solids. The solids were situated in a desiccator and exposed to cyclohexylamine vapor for 24 h and then transferred into the above cited thermogravimetric balance and heated at 10 °C min^{-1} under a flow of nitrogen of 20 cm^3 min^{-1}. The number of acid centers is calculated from the amount of cyclohexylamine desorbed between 240 and 420 °C and normalized to the weight of solid remaining at 240 °C.

3. Results and Discussion

3.1. Preparation of the Metakaolins. The preparation of the metakaolins was carried out by calcination of kaolin at four different temperatures. The XRD patterns of the calcined products showed amorphous patterns, the peaks of kaolinite disappeared and also the 001 reflection of the smectite present as impurity, while the peak of mica remained (Figure 1). The patterns of the calcined products are similar to those reported for metakaolins,[5] and no significant differences were observed between the four metakaolins. The surface area decreased during calcination; surfaces of 9−11 m^2/g were observed for the metakaolins. The IR spectra were also similar for the four metakaolins. So, from these data, no apparent differences between these four metakaolins may be deduced, and calcination at these four different temperatures seemed to lead to very similar solids.
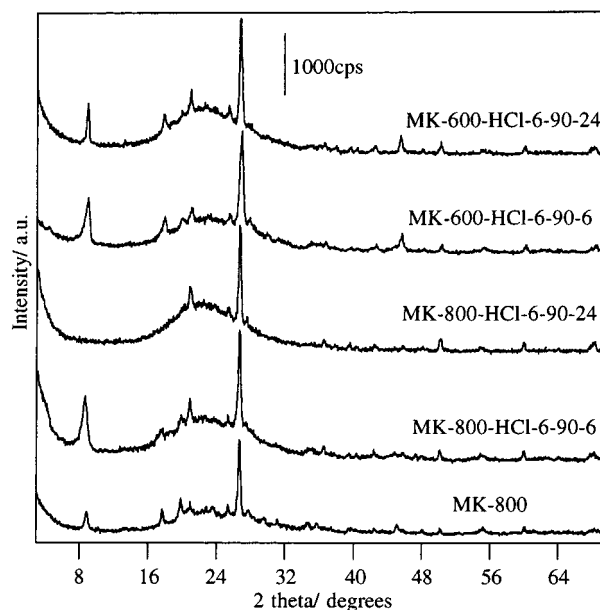
Figure 2. XRD patterns of some acid-activated solids.

3.2. Acid Treatments. Activation with HCl was first explored with a 1 M solution, but no modifications were observed in the structure or in the properties of the solids neither when 6 or 24 h of treatment were employed. Thus, 6 M solutions were used for further treatments. Even with this concentration, the XRD patterns of the solids treated at room temperature did not show significant variations with respect to the metakaolins, while treatment under reflux conditions showed a clear increase in the amount of amorphous silica in the solids, by the presence of the characteristic wide band of this species between $2\theta = 20-40°$ (Figure 2), clearly different from the band of the metakaolins in this region. No other differences were observed in the XRD patterns, all of them showing the presence of this amorphous phase, with peaks of variable intensity corresponding to quartz and mica, which remained in the solids due to their high resistance under acid conditions.

The acid treatments produced a partial dissolution of Al^{3+} cations from the octahedral sheet, which provoked a relative increase in the percentage of silica in the activated solids, reaching values up to 85% (Table 1). Thus, treatment of MK-600, MK-700, and MK-800 for 6 h made the content in Al$_2$O$_3$ decrease from 34.02 to 4−6% (≈90% of the cations removed), while treatment for 24 h made this content decrease to 1−2% (more than 95% of the cations removed). It may be considered here that the content of water changed from one solid to the others (vide infra), and the oxide contents may be more exact if normalized to water-free samples; we prefer to show the water content in the solids to better illustrate their properties.

In contrast to MK-600, MK-700, and MK-800, the metakaolin MK-900 was almost not altered by the acid treatment, although it was treated for 6 or 24 h. The intensity of the silica band in the XRD patterns was low; the content of silica in these solids was 61−67% and the content of alumina was 23−28%, that is, with the elimination of about only 30% of Al^{3+} cations. This suggested that calcination at 900 °C had a negative effect with respect to calcination at 600, 700, and 800 °C for the later acid activation of the prepared metaka-

Table 1. Chemical Composition, in wt %, of the Natural Kaolin and of the Acid- and Alkaline-Treated Solids

sample	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	K$_2$O	TiO$_2$	CaO	Na$_2$O	H$_2$O
K 2 μm	46.97	33.57	2.08	0.44	0.64	0.310	0.20	0.08	15.27
MK-600-HCl-6-RT-6	53.36	37.30	2.07	0.40	1.39	0.533	0.16	0.10	4.66
MK-900-HCl-6-RT-6	54.56	38.61	2.12	0.42	1.60	0.543	0.19	0.10	1.81
MK-600-HCl-6-90-6	75.98	6.70	0.30	0.29	1.17	0.742	0.06	0.05	14.25
MK-700-HCl-6-90-6	69.20	4.01	0.24	0.15	0.60	0.664	0.03	0.03	25.07
MK-800-HCl-6-90-6	72.86	5.46	0.41	0.12	0.67	0.711	0.05	0.04	19.66
MK-900-HCl-6-90-6	61.56	28.46	1.68	0.33	0.96	0.617	0.14	0.06	6.15
MK-600-HCl-6-90-12	84.89	3.01	0.20	0.20	0.80	0.777	0.15	0.08	9.85
MK-600-HCl-6-90-18	84.05	2.48	0.14	0.14	0.70	0.731	0.09	0.06	11.57
MK-600-HCl-6-90-24	79.16	2.67	0.10	0.10	0.71	0.694	0.02	0.04	16.48
MK-700-HCl-6-90-24	84.86	1.54	0.10	0.08	0.31	0.732	0.01	0.02	12.32
MK-800-HCl-6-90-24	82.98	1.23	0.11	0.05	0.23	0.743	0.01	0.01	14.61
MK-900-HCl-6-90-24	67.10	23.04	1.37	0.30	0.51	0.603	0.12	0.04	6.8
MK-600-KOH-1-RT-6	53.50	37.17	2.06	0.42	3.18	0.526	0.21	0.13	2.76
MK-900-KOH-1-RT-6	53.11	37.83	2.07	0.41	3.28	0.538	0.22	0.10	2.33
MK-600-KOH-1-90-6	52.54	35.57	2.10	0.43	5.39	0.565	0.23	0.23	2.90
MK-700-KOH-1-90-6	52.72	35.96	2.12	0.43	5.54	0.555	0.23	0.20	2.19
MK-800-KOH-1-90-6	52.60	35.62	2.19	0.44	5.45	0.563	0.23	0.17	2.65
MK-900-KOH-1-90-6	48.25	32.70	1.95	0.40	8.87	0.511	0.23	0.17	6.83
MK-600-KOH-5-RT-6	49.47	34.28	1.94	0.41	7.23	0.531	0.21	0.14	5.75
MK-900-KOH-5-RT-6	50.29	35.75	2.00	0.40	6.14	0.507	0.21	0.12	4.52
MK-600-KOH-5-90-6	32.33	23.19	1.27	0.28	28.94	0.355	0.14	0.18	13.28
MK-700-KOH-5-90-6	30.25	21.94	1.22	0.27	31.67	0.342	0.14	0.18	13.96
MK-800-KOH-5-90-6	28.97	21.39	1.16	0.26	29.03	0.332	0.13	0.17	18.52
MK-900-KOH-5-90-6	28.06	28.12	1.53	0.32	25.68	0.416	0.17	0.16	15.5
MK-600-KOH-5-90-24	33.77	24.81	1.31	0.28	25.02	0.383	0.14	0.13	15.88
MK-700-KOH-5-90-24	31.82	24.05	1.26	0.27	28.19	0.345	0.15	0.13	13.74
MK-800-KOH-5-90-24	27.22	20.45	1.05	0.23	34.83	0.316	0.11	0.18	15.60
MK-900-KOH-5-90-24	25.96	20.38	1.08	0.23	30.19	0.346	0.12	0.15	20.51

olins, the reactivity of the solid calcined at the higher temperature being lower. This may be related to the beginning of sintering of kaolinite particles at 900 °C and perhaps to the beginning of the transformation from kaolinite to mullite, although this process is usually reported to occur at higher temperatures, about 980 °C. The permanence of the solid 10 h in the furnace at 900 °C and the fact that the transformation from montmorillonite to mullite has been reported at about 900 °C may induce the formation of mullite from kaolinite at lower temperatures, thus provoking a higher passivity of MK-900 metakaolin, although no clear peaks of mullite were found in the XRD pattern of this solid. In contrast, calcination at 600, 700, and 800 °C gave much more reactive solids; this reactivity has been reported to be related to the formation of tetra- and pentacoordinated Al units from the initial AlO$_6$ units in the octahedral sheet of the kaolinite.[3,5,7,21]

The water content showed a higher variation between the different solids; the loss of weight for some solids in different intervals is shown in Table 1. The parent clay contained 15% of water, very close to the ideal mass loss of kaolinite, 13.96%.[28] A small amount of water may be physically adsorbed on the surface of the kaolinite particles and also associated to the smectite, thus explaining the slightly higher amount of water retained. The metakaolins did not show any weight loss due to the elimination of water during the calcination step. The acid-activated solids showed water contents between 2 and 25%, depending on the treatment conditions. Thus, when mild conditions were used for treatment, as in

samples MK-600-HCl-6-RT-6 or MK-900-HCl-6-RT-6, the water content was only 2−4%. The solids prepared by treatment of MK-600, MK-700, and MK-800 under reflux showed water contents between 15 and 25%, while in the solid prepared from MK-900 in the same conditions, the water content was only 7%.

The thermogravimetric analyses of the parent kaolin showed the loss of the water molecules as two effects, the first one between room temperature and about 200 °C, with the loss of ≈1.5% of the weight of the solids, and the second one as a strong weight loss, centered at 510 °C, with a decrease of 13 wt % (Figure 3). At the same time, the differential thermal analyses showed in the region of low temperature three small endothermal effects centered at 70, 175, and 285 °C, assigned to the removal of the water adsorbed on the surface of the kaolinite particles and on the surface of the smectite impurity. The central region was dominated by a very strong endothermal effect at 560 °C, assigned to the loss of the structural water of the kaolinite. In the high-temperature region, an endothermal effect centered at 930 °C was observed, followed by an exothermal peak at 965 °C. These effects have been assigned to the endothermal loss of the last structural hydroxyl groups of the clay, followed by the exothermal phase change to form Al$_2$O$_3$−mullite and SiO$_2$−cristobalite. (The first one has also been assigned to a small entrophy change due to the change in oxygen packing from metakaolinite to mullite.)[10]

The calcination of the kaolin to form the metakaolins produced the loss of the water content in the solids and, as expected, in the thermal curves of the metakaolins only the phase change effects at high temperature were observed. Thus, the effects observed in the activated

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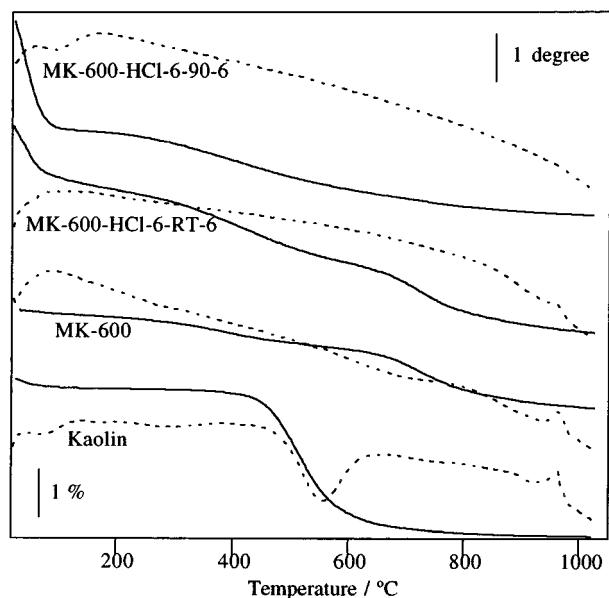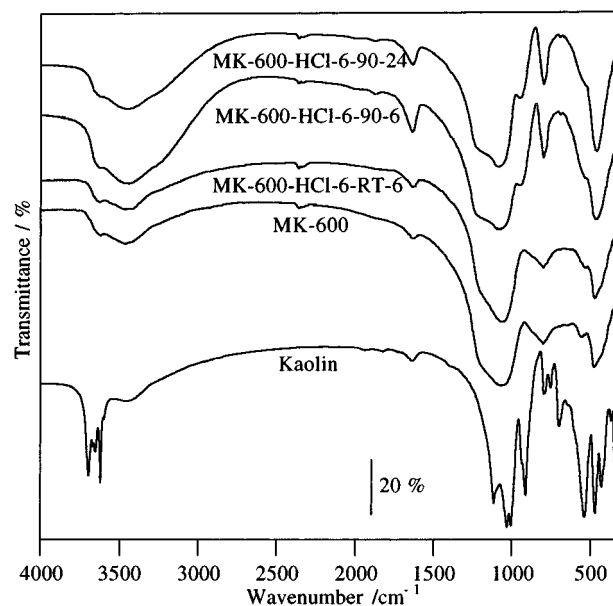
Figure 3. Thermal curves of the parent kaolin, a metakaolin, and the indicated acid-treated solids.

Figure 4. FT-IR spectra of the parent kaolin, a metakaolin, and the indicated acid-treated solids.

solids were due to the modifications introduced by the treatments. When the treatments were carried out in acid media and at room temperature, the weight loss in the treated solids was about 3–4%, distributed in three different processes, centered at about 60, 400, and 700 °C. These effects did not appear at the same temperatures as in the parent kaolin, so there was no "reconstruction" of the kaolinite structure. The first effect was clearly associated with the removal of water molecules adsorbed on the surface of the metakaolins, while the other two effects were assigned to the removal of hydroxyl groups or water molecules fixed on different sites of the structure of the metakaolinites. The high temperatures at which these effects were observed indicated that these molecules may be strongly fixed in active sites of the structure, perhaps to coordinatively unsaturated Al sites.

Behavior was different when the acid treatments were carried out under reflux conditions, both for 6 and 24 h. In this case, the water content increased greatly, between 12 and 25 wt %, excluding the solids obtained from MK-900, in which the content is lower due to the low reactivity of this metakaolin. In the solids derived from MK-600, MK-700, and MK-800, the weight loss was clearly divided into two processes, a fast loss between room temperature and 100 °C, and a second one centered at 400 °C but really appearing as a continuous effect between 250 and 900 °C. The first effect was again clearly associated with adsorbed water, and the fact that the amount of amorphous silica increased in these solids made the amount of adsorbed water higher. The second effect was associated with the elimination of hydroxyl groups from $Si(OSi)_3OH$ groups, formed during the treatment[20] or with water molecules fixed on specific sites of the solids, again probably coordinated to the remaining Al cations.

The water content depended directly on the treatments to which the solids had been submitted. When carrying out the treatments at room temperature, the metakaolinite structures were not modified, so only small amounts of water were retained on the surface of the particles, and the water content was as low as 2–4%. In contrast, for samples prepared under reflux conditions, the water content increased to about 15–25% of the weight of the solids, the form of the thermogravimetric curves being similar to that reported for acid-treated smectites,[15,17] that is, characteristic of the adsorption of water molecules on the surface of silica. For sample MK-900-HCl-6-90-24, a lower water content, ≈7%, was found. The samples prepared from MK-600, MK-700, and MK-800 under these conditions contained large amounts of amorphous silica generated by the acid treatments and, as indicated, the water molecules were adsorbed on the surface of the silica. When the highly passive MK-900 was treated, its structure was slightly modified, thus making the amount of associated water low.

The FT-IR spectrum of the parent kaolin showed the typical bands of this material (Figure 4). Thus, a band assigned to water OH stretching is found at 3459 cm^{-1}, with the bands of the stretching of OH groups coordinated to the octahedral cations at 3696, 3668, 3653, and 3619 cm^{-1}. The water bending band is observed at 1633 cm^{-1}. In the region of low wavenumbers, there are up to 10 characteristic bands of this mineral: 1114, 1030, and 1006 (Si–O stretching modes), 912 (Al–Al–OH bonds), 795 (free silica and/or quartz admixtures, always present in natural samples), 754 (Si–O–Al), 698 (Si–O out-of-plane bending), 536 (Si–O–Al bending, Al octahedral), 468 (Si–O–Si in-plane bending), and 428 cm^{-1} (Si–O). The metakaolins showed very simple spectra, with the almost total disappearance of water and hydroxyl bands, the spectra being composed of three wide bands centered at 1100, 800, and 470 cm^{-1}. The first one corresponded to the vibrations of the tetrahedral sheet, clearly showing the distortion of this sheet during calcination. The second band corresponded to the free silica or quartz, not affected by calcination. Finally, the third band corresponded to the structural bending vibrations, the simplification of this region also showing the distortion of the structure from the kaolinite to the metakaolinites.[5,29,30]
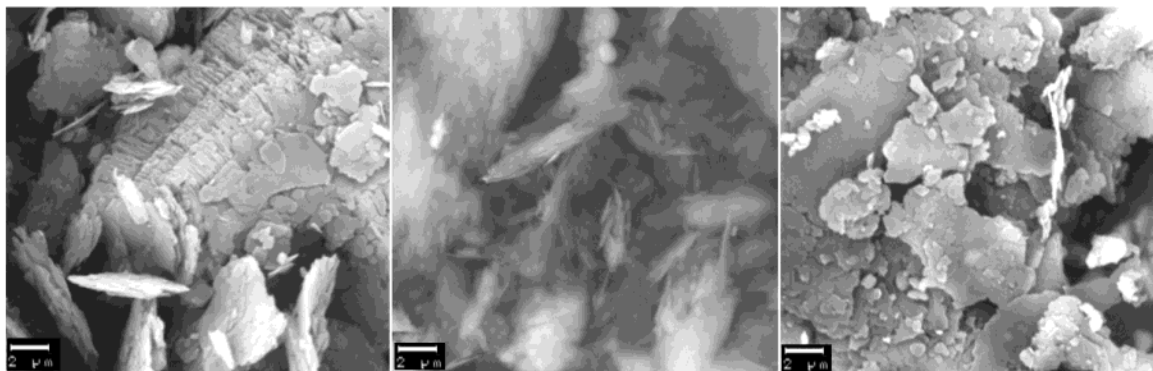
Figure 5. SEM micrographs of MK-600 metakaolin (left) and this solid treated with 6 M HCl under reflux conditions for 6 h (center) and 24 h (right).

The solids treated with concentrated HCl under reflux conditions showed different spectra, similar to those reported for amorphous silica, both for silica prepared by acid treatment of smectitic clays or silica prepared by other methods, thus confirming the formation of this species as the main component of the solids treated under these conditions. (The spectra of solids treated under milder conditions resembled those of metakaolins.) Thus, in the solids obtained under strong conditions, a wide band was found at 3460 cm^{-1}, assigned to the high amount of water physisorbed on the surface of the silica generated.[29] The bending band of these water molecules was found at 1636 cm^{-1}. Between 1200 and 400 cm^{-1}, bands corresponding to silica could be observed. Thus, the Si$-$O$-$Si stretching band appeared at 1088$-$1093 cm^{-1}, a position characteristic of this vibration for silica. Vicente et al.[29] have reported a shift of this band under acid treatment of magnesic clays from ≈1000 cm^{-1} in the natural clays to ≈1100 cm^{-1} in strongly activated solids, corresponding to a progressive transformation of Si$-$O$-$Mg$-$O$-$Si bonds in the silicate to the more rigid Si$-$O$-$Si$-$O$-$Si bonds in amorphous silica when the octahedral cations were removed.[19,29] A second band was observed at 800 cm^{-1}, corresponding to the unaltered free silica and/or quartz present in the sample, and the last band, at 460$-$465 cm^{-1}, corresponded to Si$-$O$-$Si and Si$-$O$-$Al bending bonds.

The nitrogen adsorption$-$desorption isotherm of the parent kaolin corresponded to type II of the IUPAC classification, being almost reversible. The surface area of this solid was 18 m^2/g. Both the form of the isotherm and the surface area were typical of natural kaolinites, as reported by Rouquerol et al.[31] These authors have indicated that the reversibility of kaolinite isotherms is due to particle rigidity and to a house-of-cards packing, resulting in the formation of macroporous aggregates. In this sense, the form and size of our kaolinite particles are typical for this material, showing a mixture of large plates and stacks. The metakaolinites maintained a similar habit, although showing a slight disorder in the plates, and the appearance of some particles with fiber or needle shapes, as can be observed in the SEM micrographs given in Figure 5.

Calcination of the parent kaolin to give the metakaolins produced a decrease in the surface area due to the aggregation of particles when the structural water molecules were removed, the surface area of the metakaolins being 9$-$11 m^2/g (Table 3). The surface area of the acid-activated solids also directly depended on the intensity of the treatment and on the reactivity of the metakaolins. When activation was carried out at room temperature, the activated solids had surface areas between 7 and 13 m^2/g. In contrast, high surfaces areas of 171$-$219 m^2/g were obtained when treating MK-600, MK-700, and MK-800 under reflux conditions for 6 h, whereas the solid obtained from MK-900 under the same conditions had a surface area of only 59 m^2/g. When the solids were treated under reflux conditions for 24 h, the surface area of the activated solids was, in all of them, close to 22 m^2/g.

The surface areas of the solids activated at room temperature were equivalent, within the error margin, to those of the metakaolins. This agreed with the absence of modifications of the clay structure during this treatment, as discussed before. When treating the solids under reflux conditions, the amorphous silica phase formed was responsible for the high surface area values obtained for samples MK-600-HCl-6-90-6, MK-700-HCl-6-90-6, and MK-800-HCl-6-90-6. The solids synthesized by reflux treatment for 24 h were also composed of silica; unaltered metakaolinite did not remain in them, so their low surface area may be somewhat surprising. However, for the acid treatment of fibrous and smectitic clays it has been reported that optimal conditions for the activation of the surface of a given clay may be reached, but that treatment under more drastic conditions provokes a strong decrease in the surface area. For example, when treating a montmorillonite with 1$-$8 M HCl solutions at 80 °C, Mendioroz et al. reported a higher surface area (419 m^2/g) when treating the clay with the 4 M solution, which progressively decreased with more concentrated solutions, being 166 m^2/g when treated with the 8 M solution.[12] The same group reported similar behavior for another montmorillonite treated under reflux conditions, although in this second case, the maximum value of surface area (391 m^2/g) was found for the solid treated with the 5 M solution.[13] For the treatment of a sepiolite with HCl, Vicente et al.[15] reported a maximum surface area value of 549 m^2/g when using 1.25% HCl for 48 h, which decreased to ≈290 m^2/g (similar to the value of the parent sepiolite, 293 m^2/g) when the treatment was stronger.[15]

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Mendioroz et al.[12] suggested that this decrease in the surface area may be due to a "passivation" effect caused by the silica on the clay sheets; thus, when very strong conditions are used, a thick silica layer is formed, which prevents the access of protons to the clay layers that remain unaltered or only partially altered. This explanation does not seem to be valid for our samples. Such a passivation mechanism will involve a maintenance of unaltered sheets, and this may be correlated with a maintenance of octahedral cations in the chemical composition of the solids, as occurred in the samples prepared by Mendioroz et al.[12] But, for our samples, we observed that the removal of Al^{3+} cations continued from the samples treated under reflux conditions for 6 h (about 5% of Al_2O_3 not dissolved) to the samples treated for 24 h (only 1−2% of Al_2O_3 not dissolved). Only the samples obtained from MK-900 showed a different trend, but this was due to the already discussed low reactivity of this metakaolin. Thus, and considering that the samples obtained under the stronger conditions are composed up to 85% by silica, the decrease in the surface area may be due to the texture of this silica, which is different when obtained under very strong conditions, due to an "amorphization" of the silica, as will be discussed later. Thus, one can reasonably think that the very strong conditions negatively affect the structure of the silica generated, the amorphization of the silica is unimportant when the duration of the treatment is 6 h, but becomes very important when it is 24 h. Considering these results, a new question arises, whether the amorphization of silica is an abrupt or a gradual process. To answer this question, a series in which the samples treated for 6 and 24 h showed very different degrees of activation was selected to prepare two samples with an intermediate time of treatment, namely, samples MK-600-HCl-6-90-12 and MK-600-HCl-6-90-18; data of these samples are included in Tables 1−3. The comparison between all the samples showed that the amorphization was a rather fast process when critical conditions are exceeded, the solids treated for 12 and 18 h showing a high degree of alteration, with chemical composition, X-ray patterns, and textural parameters close to the solid treated for 24 h, and consequently, very different from the solid treated for 6 h.

Considering the very strong conditions needed for activating effectively the surface of metakaolin, the conditions in which the amorphization of silica begins are relatively close to the optimal activation conditions. That is, in contrast to what is observed for fibrous and smectitic clays, the conditions that give a good acid activation of kaolin are in a very narrow range and, consequently, these optimal activation conditions have to be carefully sought.

The SEM micrographs confirmed the different texture of the solids, which present these different values of surface area. For solids treated at room temperature, the form of the particles was very similar to that of the parent kaolin and of the metakaolins (Figure 5). In contrast, the solids MK-600-HCl-6-90-6, MK-700-HCl-6-90-6, and MK-800-HCl-6-90-6 showed the characteristic form of very porous and "spongy" silica particles, in agreement with the composition and the high surface area of these solids. The sample MK-900-HCl-6-90-6 was less attacked, in agreement with the low reactivity of

MK-900 metakaolin. The solids treated at reflux conditions for 24 h showed an aspect more similar to that of the metakaolins (Figure 5). From the aspect of the layers, one can even think that these layers were not attacked, although as indicated before almost all Al^{3+} was removed.

When studying in detail the textural properties of the samples MK-600-HCl-6-90-6, MK-700-HCl-6-90-6, and MK-800-HCl-6-90-6, one observes that acid treatment produced the development of both the external and the internal surface of the solids (see Table 3). Thus, the external surface of these solids was 84−126 m^2/g (16.6 m^2/g for the parent kaolin and about 9 m^2/g for the metakaolins), while the micropore surface varied between 46 and 135 m^2/g (1.6 m^2/g for the kaolin and lower than 1 m^2/g for the metakaolins). The t plots of these samples, whose extrapolation did not pass through zero, clearly showed the important contribution of the internal surface to the total surface area. At the same time, the pore size distribution of these solids showed a maximum at 17−19 Å in diameter. The contribution of the internal and the external surface to the total surface area is ≈55 m^2/g, except for the sample MK-700-HCl-6-90-6, which presented a lower value of micropore area, 46 m^2/g. For the sample MK-900-HCl-6-90-6, which had a surface area of only 51 m^2/g, the micropore surface was not developed and almost all of the surface was due to the contribution of the external surface.

The concentration of acid centers was calculated from a very simple method, which has been shown to be very effective for clay minerals. The solids were exposed to cyclohexylamine vapor, and the amount of chemisorbed cyclohexylamine was determined by thermogravimetry. It is assumed that water and physisorbed cyclohexylamine are desorbed below 240 °C, while the cyclohexylamine chemisorbed on clay Brönsted acid sites is desorbed between 240 and 420 °C, each molecule of gaseous cyclohexylamine interacting with one surface-accessible Brönsted acid site.[32,33] This method has also been widely used for the determination of acid centers in acid-activated[34−38] and intercalated clays.[39−44]

The concentration of acid centers of some selected samples is given in Table 2. As observed, parent kaolin had a low number of acid centers, 0.1049 mmol/g, which strongly decreased for the metakaolins. The number of acid sites in the acid-activated solids again depended on the intensity of the treatment, but reached values up to 0.19 mmol/g, that is, twice the amount in the parent kaolin and up to 9-fold the acidity of the

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Table 2. Weightless % (TG) and Concentration of Acid Sites of the Solids Indicated

	weightless (wt %)			
sample	RT−120 °C	120−600 °C	600−1000 °C	acid centers (mmol/g)
K 2 μm	1.136	9.815	1.853	0.1049
MK-600	0.079	0.588	0.868	0.0426
MK-800	0.036	0.379	0.348	0.0212
MK-600-HCl-6-RT-6	0.968	1.331	1.117	0.1084
MK-900-HCl-6-RT-6	0.200	0.601	0.306	
MK-600-HCl-6-90-6	7.738	3.697	1.614	0.1855
MK-800-HCl-6-90-6	6.696	3.669	1.403	0.1866
MK-900-HCl-6-90-6	0.785	1.767	0.487	
MK-600-HCl-6-90-12	5.266	3.318	1.465	
MK-600-HCl-6-90-18	3.680	2.073	1.445	
MK-600-HCl-6-90-24	4.204	2.958	1.492	0.1404
MK-700-HCl-6-90-24	5.165	3.271	1.555	0.1270
MK-800-HCl-6-90-24	6.843	2.787	1.352	0.1260
MK-900-HCl-6-90-24	1.720	1.430	0.606	0.0699
MK-600-KOH-5-RT-6	2.436	2.790	0.973	0.1081
MK-700-KOH-5-RT-6	3.863	4.216	1.074	
MK-900-KOH-5-RT-6	1.857	2.266	0.764	
MK-600-KOH-5-90-6	5.129	4.645	3.875	0.1302
MK-700-KOH-5-90-6	6.445	3.681	5.627	0.1393
MK-800-KOH-5-90-6	6.390	6.457	5.625	0.1185
MK-900-KOH-5-90-6	7.122	4.925	2.881	0.2009
MK-600-KOH-5-90-24	6.251	5.589	2.430	0.0872
MK-700-KOH-5-90-24	5.954	5.152	2.763	0.1024
MK-800-KOH-5-90-24	7.549	4.540	7.753	0.0816
MK-900-KOH-5-90-24	11.059	3.909	5.537	0.0908

corresponding metakaolins. The samples prepared by reflux for 24 h, which presented an amorphization of the silica generated, showed a lower amount of acid centers than their counterparts prepared by treatment for 6 h, thus confirming the amorphization of the silica. It has been reported that this method gives high acidity for natural smectites; acidities of 0.4−0.6 mmol/g have been reported for natural samples, which was explained by Kooli and Jones as being due to the protonation of cyclohexylamine by the water molecules polarized by the exchangeable cations.[37] In the parent kaolin, the value is much lower than those reported for natural smectites, probably because of the very low amount of exchangeable cations in the kaolinite, most of them corresponding to the montmorillonite admixture. The removal of water made the metakaolinites have a very low acidity, close to zero, which strongly increased in the activated solids by the creation of specific acid sites on the surface of the silica generated.

3.3. Alkaline Treatments. Treatment with KOH at room temperature led to very weak alterations in the composition and structure of the solids; the fixation of about 3% K_2O was the main alteration. This was equivalent to about only 0.06 K atoms per Si atom and, as indicated, did not cause significant effects in the properties of the solids. For this reason, more efforts were devoted to the characterization of the samples treated under reflux conditions. For these solids, the first strong difference was observed in the XRD diffractograms; the characteristic patterns of the metakaolinites disappeared and patterns with new and very intense peaks were obtained (Figure 6). The comparison of the new diffractograms with the JCPDS data file showed that K−F zeolite was formed under these reaction conditions (JCPDS file 38-216).[45] To our knowledge, only Barrer et al.[47−49] have described the formation of K−F zeolite from metakaolinite by hydrothermal
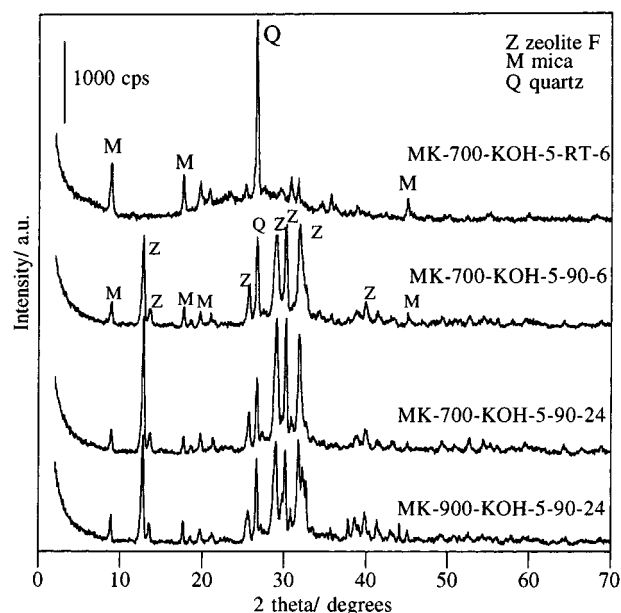

Figure 6. XRD patterns of some alkaline-treated solids.

treatment with KOH solution. They carried out their experiments in autoclaves, adding certain amounts of SiO_2 to the reaction medium, and obtained not only K−F zeolite but also other zeolitic phases, like K−I, K−M, and L-type, depending on the KOH concentration and on the amount of SiO_2 added in the reaction medium.

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Other authors working in a KOH medium have reported the synthesis of K–I and phillipsite zeolites.[46] On the other hand, the synthesis of zeolites from metakaolinite has been reported by other authors using NaOH as the reaction medium, obtaining LSX,[5] A,[4,8] X,[7] and KSO1[9] zeolites depending on the concentration of NaOH, the calcination temperature of the parent kaolin, and the time of the treatment. These data indicate that the formation of different zeolitic phases strongly depends on the treatment conditions and on the composition of the reaction medium, resulting, somehow surprising, in the obtention of very pure K–F phase in our experiments, carried out without the addition of external SiO_2. At the same time, under similar conditions to those used by us, Okada et al. have reported the selective leaching of SiO_2, obtaining Al_2O_3 with interesting textural properties as the main reaction product.[24–26]

The formation of K–F zeolite was observed in a similar way for all the samples treated with 5 M KOH both for 6 and 24 h. The theoretical formula of this zeolite is $KAlSiO_4 \cdot 1.5H_2O$. The amount of K_2O fixed by the solids was similar in all cases, between 26 and 31%. This is equivalent to about 1 atom of K for Si atom, and the Si/Al ratio in the treated solids always remained close to the value in the parent kaolin, that is, 1. Thus, the Si/Al/K ratios are in all cases close to 1:1:1, but with small differences in some samples. In general, the amount of Si, in number of atoms, is slightly higher than the amount of Al, in a ratio of about 1.0:0.9, thus suggesting that a small amount of free silica is present in the samples besides some remaining unaltered metakaolin layers and the zeolite formed. This small amount of SiO_2 may be derived from the free silica and quartz present in the parent solid. However, in the sample MK-900-KOH-5-90-6 the amount of Al was higher than that of Si (Si/Al = 1:1.81), which may correspond to a partial leaching of silica, with the generation of alumina particles, as described by Okada et al.[24–26] This agrees with the fixation of potassium, lower in this sample than in their counterparts, and thus this sample may be mainly composed of zeolite but with a low amount of alumina, although this supposition has not been confirmed because alumina was not detected by X-ray diffraction.

At the same time, the K/Si ratio was higher than 1.0 in all samples except MK-600-KOH-5-90-24 (0.945). In the rest of the samples, this ratio varied between 1.13 and 1.63. This suggested that, besides the formation of the zeolite phase from the metakaolinites, an additional amount of K^+ is fixed in interstitial positions, compensated by the fixation of OH^- anions from the solution and/or carbonate anions from the atmosphere. (The treatments were carried out in contact with ambient air.) The fixation of carbonate is undoubtedly proven by FT-IR (vide infra) but the presence of KOH or K_2CO_3 phases in the dried solids could not be demonstrated.

The thermal analyses of the alkaline-treated samples showed more complex curves when the intensity of the treatment increased (Figure 7). Thus, the weight loss increased to values of about 14–18%, even reaching 20.5% for the sample MK-900-KOH-5-90-24. The curves showed a strong effect at low temperature, between room temperature and 250 °C, and another at high
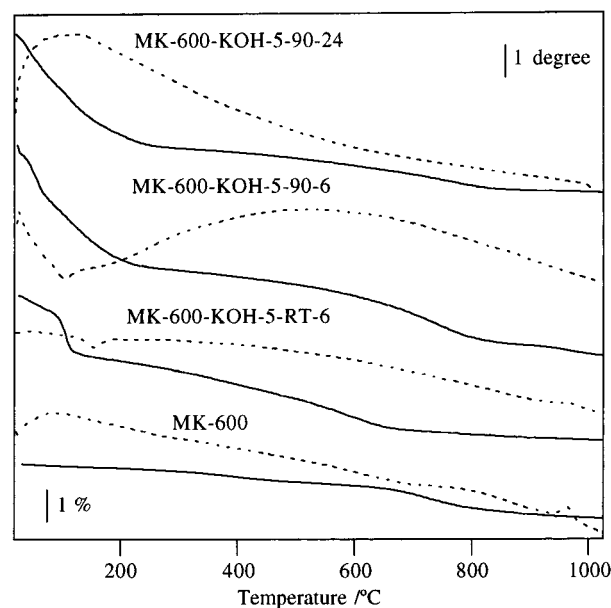
Figure 7. Thermal curves of some alkaline-treated solids.
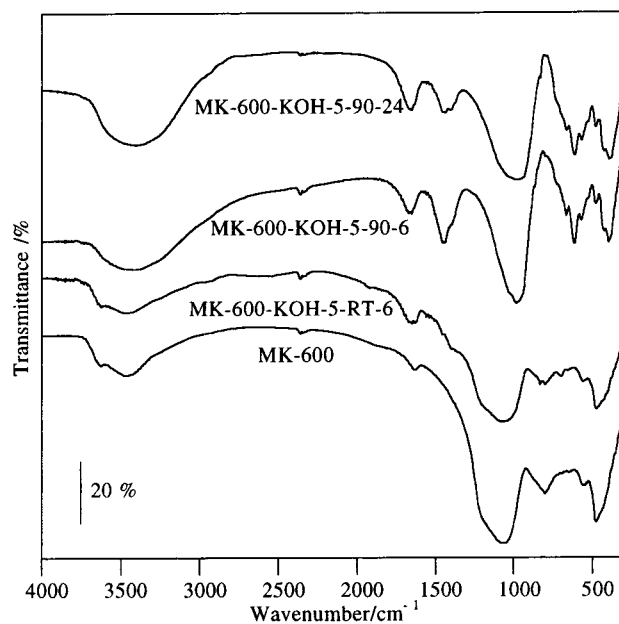

Figure 8. FT-IR spectra of some alkaline-treated solids.

temperature. It may be considered that the fixed carbonate anions contributed in a small amount to the weight loss. The DTG curves showed that the weight loss effect at low temperature was really composed by two effects at about 60 and 100 °C, while the DTA curves showed two endothermal effects at about 115 and 175 °C. The weight loss at high temperature was located between 750 and 800 °C, although it had no clear thermal effect associated with it. The weight loss in these samples was close to the theoretical value in K–F zeolite, calculated to be 22.3%. In the samples in which the kaolinite–zeolite transformation had occurred to a lesser extent, the behavior was similar, but with a lower amount of water, because the untransformed metakaolinite layers fixed very small water amounts.

The FT-IR spectra of the solids treated with concentrated KOH showed the characteristic patterns of zeolitic materials, while the spectra of the solids treated under milder conditions resembled those of metakaolins
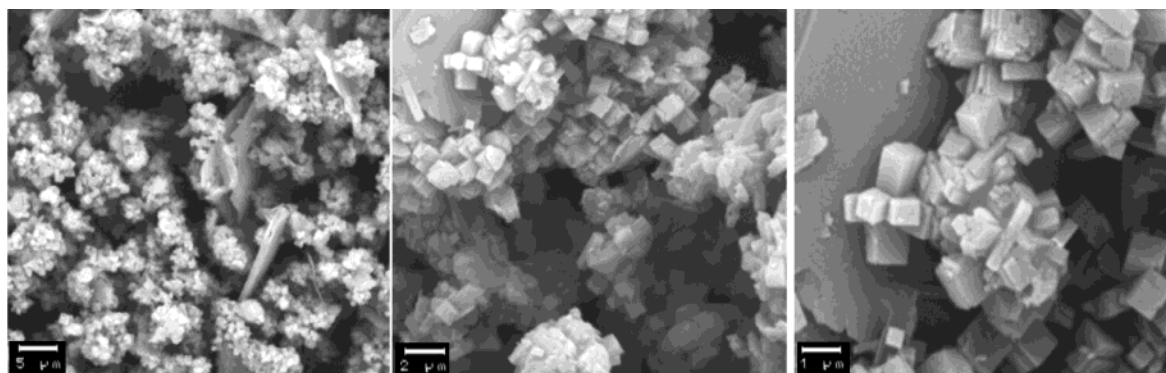
Figure 9. SEM micrographs of MK-800 treated with 5 M KOH under reflux conditions for 24 h; the micrographs correspond to the same sample with amplifications of 2000 (left), 5000 (center), and 10000 (right).

Table 3. Textural Properties Derived from the Nitrogen Adsorption Isotherms of the Different Solids

sample	S_{BET} (m²/g)	C^a	S_{ext}^b (m²/g)	S_{int} (m²/g)	V_T^c (cm³/g)	$V_{\mu p}^d$ (cm³/g)
K	11.8	125	11.6	0.21	38	0.00004
K 2 μm	18.2	193	16.6	1.6	80	0.00073
MK-600	10.6	160	9.8	0.8	42	0.0003
MK-700						
MK-800	9.8	133	9.4	0.37	37	0.0001
MK-900						
MK-600-HCl-6-RT-6	13.4	706	10.4	3.0	39	0.0015
MK-700-HCl-6-RT-6	9.7	−279	e			
MK-800-HCl-6-RT-6	9.2	−276				
MK-900-HCl-6-RT-6	6.9	−210				
MK-600-HCl-6-90-6	219	−436	84.6	135	146	0.065
MK-700-HCl-6-90-6	172	224	126	45.9	141	0.022
MK-800-HCl-6-90-6	209	−878	105	104	145	0.051
MK-900-HCl-6-90-6	50.7	192	49.9	0.8	71	0.0005
MK-600-HCl-6-90-12	25.6	171	23.1	2.5	67	0.0011
MK-600-HCl-6-90-18	24.2	197	21.5	2.7	67	0.0013
MK-600-HCl-6-90-24	22.1	157	20.5	1.6	66	0.0007
MK-700-HCl-6-90-24	21.9	266	18.4	3.5	64	0.0017
MK-800-HCl-6-90-24	23.1	218	20.2	2.9	69	0.0014
MK-900-HCl-6-90-24	23.0	172	21.1	1.8	57	0.0008
MK-600-KOH-1-RT-6	6.8	−190				
MK-700-KOH-1-RT-6	6.4	−198				
MK-800-KOH-1-RT-6	6.5	727				
MK-900-KOH-1-RT-6	7.9	100				
MK-600-KOH-1-90-6	9.2	−291				
MK-700-KOH-1-90-6	8.5	−187				
MK-800-KOH-1-90-6	11.9	−389				
MK-900-KOH-1-90-6	7.4	133				
MK-600-KOH-5-RT-6	5.4	−113				
MK-700-KOH-5-RT-6	0.3	−15				
MK-800-KOH-5-RT-6	8.7	−191				
MK-900-KOH-5-RT-6	7.0	93				
MK-600-KOH-5-90-6	4.1	104	4.1	0.0	7.9	0.0
MK-700-KOH-5-90-6	3.7	61	3.7	0.0	8.1	0.0
MK-800-KOH-5-90-6	3.6	−302	2.4	1.2	10.0	0.0006
MK-900-KOH-5-90-6	16.5	132	16.5	0.0	26.6	0.0
MK-600-KOH-5-90-24	2.4	−73				
MK-700-KOH-5-90-24	3.4	−146				
MK-800-KOH-5-90-24	3.7	18				
MK-900-KOH-5-90-24	0.1	−7				

[a] Langmuir *C* value, characteristic of the intensity of the adsorbate−adsorbent interactions. [b] From t method. [c] From volume adsorbed at relative pressure 0.99. [d] From t method. [e] Missing values were not determined; in these samples, the surface area was determined from a BET treatment of four adsorption points.

(Figure 8). Thus, the solids prepared under reflux conditions showed wide water bands centered at about 3420 and 1655 cm⁻¹, the asymmetric stretching of the tetrahedral units at 985 cm⁻¹ with a shoulder at 1020 cm⁻¹, the symmetric stretching at 665 cm⁻¹, and the bending at 478 cm⁻¹. Other zeolite characteristic bands were found at 665, 615, 570, and 481 cm⁻¹. Moreover, the presence of carbonate groups was clearly shown by the ν_3 mode of this anion as a wide band centered at 1440 cm⁻¹, while the ν_2 and ν_4 modes were observed only as shoulders on the strong lattice vibrations in these regions.

The formation of zeolite crystals was clearly shown by SEM micrographs; some examples are given in Figure 9. Up to three levels of particles can be distinguished: Primary particles are lamellar ones, although their thickness is quite appreciable; these particles are stacked, forming secondary particles with a cubelike shape. Finally, these cubelike particles are forming tertiary particles, quasi-spherical clusters. When samples submitted to an intermediate treatment were studied, it was observed that the crystals seemed to grow from an initial nucleus formed at the edges of the kaolinite sheets (see Figure 9, left, center), and thus a continuity kaolinite sheet−zeolite crystal is observed in all the micrographs. For the formation of LSX zeolite by treatment of metakaolin with NaOH, a mechanism based on the dissolution of the metakaolin sheets, formation of a gel containing an aluminosilicate phase, and later crystallization of zeolite particles has been proposed.[5] In our case, for samples submitted to intermediate treatments, a coexistence of unaltered metakaolin layers and of well-ordered zeolite crystals was observed (Figure 9); no evidence of the formation of any other phase could be obtained. It was also observed that the progression of the metakaolin → zeolite transformation depended directly on the intensity of the treatment.

The surface area of the solids in which the formation of zeolite was the predominant phenomenon was about 2−4 m²/g (Table 3), which may be attributable to the very crystalline aspect of the particles and their large size. Only the sample MK-900-KOH-5-90-6 showed a higher value of surface area (16.5 m²/g), which agreed with the possible formation of alumina particles, as has already been commented on. As can be expected from the size of the crystals, the surface area was completely due to the contribution of the external surface.

The alkaline-treated solids showed low concentrations of acid sites between 0.08 and 0.13 mmol/g, for all samples except MK-900-KOH-5-90-6, which showed a higher value, 0.20 mmol/g. These values are between 2- and 3-fold the concentration of acid centers in the metakaolins. Bearing in mind the composition of these solids, the acid positions must be located on the edges of the particles and in water molecules bonded to the accessible K^+ cations and polarized by them. The high value found for the MK-900-KOH-5-90-6 sample agreed with the hypothesis of the formation of a small amount of alumina particles in this solid.

With all these data, it is remarkable that the reactivity of the four metakaolins under alkaline conditions is very similar, contrary to the trend observed for the acid treatments, although, as indicated before, the solid MK-900-KOH-5-90-6 showed an unexpected high alumina content. The different behaviors of the various metakaolins under acid and alkaline conditions may be explained by the different dissolution processes in both cases. In the acid treatments, the protons have to access the octahedral layers to extract the octahedral Al^{3+} cations, while the tetrahedral silica structure is not soluble; the nature of the MK-900 sample hinders this process. In contrast, in alkaline conditions, both the aluminic and the silicic part of the metakaolin are dissolved, the particles being dissolved from the edges to the center as observed in the SEM micrographs;

hence, the nature of MK-900 does not strongly condition this dissolution process.

4. Conclusions

The metakaolins prepared by calcination of a natural kaolin at four different temperatures, 600, 700 800, and 900 °C, were submitted to acid and alkaline treatments. The extension of the alterations in the structure of the solids and of the change in their physicochemical properties depended on the metakaolin employed and on the intensity of the treatments, which may be summarized in the following points:

(i) Acid activation with 6 M HCl solutions at room temperature did not produce significant alterations either in the structure or in the composition or properties of the metakaolins.

(ii) Acid activation with 6 M HCl under reflux conditions for 6 h removed about 90% of the octahedral Al^{3+} cations, thus producing a high surface area amorphous silica phase (S_{BET} up to 219 m²/g), with similar properties to the silica obtained by acid activation of smectites or fibrous clays. The improvement in the textural properties is due both to the development of the external surface area and to the creation of microporosity.

(iii) Acid activation with 6 M HCl under reflux conditions for 12, 18, or 24 h removed about 95% of the octahedral Al^{3+} cations, but the silica obtained did not show a development of the surface properties; an abrupt amorphization of the silica obtained under such strong conditions is proposed to explain this observation.

(iv) The metakaolins synthesized by calcination of kaolin at 600, 700, and 800 °C showed similar reactivity under acid conditions. The metakaolin prepared by calcination at 900 °C was much less reactive probably because of an incipient sinterization during calcination at this temperature.

(v) Alkaline activation with KOH solutions showed the formation of K−F zeolite, which appeared as large and well-formed crystals. The progressive dissolution of the metakaolinite layers and the formation of zeolite crystals were observed depending on the intensity of the treatments. Because of this high crystallinity, the treated samples showed a very low surface area.

(vi) The four metakaolins showed similar reactivity under alkaline treatment; this reactivity did not depend on the temperature of synthesis of the metakaolins, although the treatment of MK-900 under reflux conditions for 6 h led to an Al-rich solid.

(vii) Acid treatment in strong conditions of metakaolins with HCl is a promising method for the obtention of active silica from natural kaolin samples, while the treatment with KOH in strong conditions allows K−F zeolite to be obtained in an effective way.

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