Thermochimica Acta, 194 (1992) 239–246
Elsevier Science Publishers B.V., Amsterdam

Thermal investigation of acid-activated attapulgites: influence of isomorphic substitution in the octahedral sheet

F. Gonzâlez, C. Pesquera and I. Benito

Dpto. de Química, Universidad de Cantabria, Avda. de los Castros s/n,
39005-Santander (Spain)

(Received 17 April 1991)

Abstract

Two samples of Spanish attapulgite with different degrees of isomorphic substitution in the octahedral sheet were studied. Both the aluminium-rich and magnesium-rich samples were activated with hydrochloric acid of various concentrations. TG and DSC curves of activated as well as natural attapulgite were obtained. From the analysis of these curves, the influence of the degree of isomorphic replacement of Mg^{2+} by Al^{3+} on the results of the acid activation was deduced.

INTRODUCTION

Attapulgite is a fibrous clay mineral composed of two tetrahedral silica sheets linked by magnesium cations in octahedral coordination, which presents capillary channels orientated in the longitudinal direction of the fibres [1]. The degree of isomorphic substitution of aluminium for magnesium in the octahedral sheet allows us to differentiate between aluminic and magnesic attapulgites. These materials are usually submitted to progressive acid treatment to enlarge their specific surface and porosity, and to improve their chemical reactivity. This process is known as activation [2–7]. Activated clays are of interest for later use in adsorption and catalysis.

In a previous work, we studied the influence of isomorphic substitution in attapulgites on the dehydration process [10], showing that there is a connection between the loss of the water coordinated to the edge octahedral cations and the chemical composition of the octahedral sheet. In the present work, two Spanish attapulgites, one magnesium-rich and the other aluminium-rich, were activated with hydrochloric acid. The structural changes in the mineral resulting from acid dissolution were studied by means of TG and DSC, and the differences in the evolution of the various samples are analysed.

EXPERIMENTAL

Starting material

The work was performed on two samples of Spanish attapulgite. One sample (A-I) came from Serradilla (Cãceres), and the other (A-II) from Sacramenia (Segovia).

Previous characterisation of the samples [7] gave the results below; thus A-II can be considered as magnesic whereas A-I is aluminic because of the amount of Al^{3+} ions replacing Mg^{2+} in the octahedral sheet.

Sample A-I

S_{BET} (m^2 g^{-1}), 71; fibre dimensions (Å), 1500–7000 and 260–400; cation exchange (mequiv. per 100 g), 42.5; mineralogical composition, 95% attapulgite, 5% mica and quartz traces; structural formula, $(Si_{7.91}Al_{0.09})_{Tetr}$-$(Mg_{1.69}Al_{1.62}Fe_{0.48})_{Oct}(Mg_{0.10}Ca_{0.003}K_{0.01}Na_{0.18})_{CC}O_{20}(OH)_2(OH_2)_4 \cdot nH_2O$.

Sample A-II

S_{BET} (m^2 g^{-1}), 138; fibre dimensions (Å), 350–3700, and 130–180; cation exchange (mequiv. per 100 g), 25.8; mineralogic composition, 85% attapulgite, 5% mica and 10% quartz; structural formula, $(Si_{7.25}$-$Al_{0.75})_{Tetr}(Mg_{3.18}Al_{0.90}Fe_{0.41}Ti_{0.05}Mn_{0.003})_{Oct}(Mg_{0.08}Ca_{0.03}K_{0.01}Na_{0.01})_{CC}O_{20}$-$(OH)_2(OH_2)_4 \cdot nH_2O$.

Apparatus and methodology

The samples were mechanically ground and particles < 0.40 mm in size were selected. This size fraction was put into contact with hydrochloric acid of various concentrations (1, 2, 3, 4 and 6 N), using a liquid/solid ratio of 10 cm^3 g^{-1} for sample A-II and 25 cm^3 g^{-1} for sample A-I, whose density is less. The activation was performed in a reactor at boiling temperature and with constant stirring for one hour. The reaction mass was cooled, while the stirring continued for 2 h. Next, it was sedimented for 48 h. Then, it was filtered and washed free of chloride and dried at 100 °C.

Silica extraction was performed by digestion with 1 N Na_2CO_3 at boiling point.

The activated samples were called A-I-1N, A-II-1N, A-I-2N, etc, according to the acid treatment received.

The thermic analyses were performed in a Setaram TG–DSC 111. The heating rate was 5 °C min^{-1}, under a dynamic flow of dry helium of 50 ml min^{-1}. The investigated range was from room temperature to 825 °C.

RESULTS AND DISCUSSION

Figures 1 and 2 show the TGA, DSC and DTG of the two attapulgites studied. The loss of mass in the different temperature intervals is shown in Table 1.

The first TGA step, which can be subdivided into two as is evident on the DSC and DTG curves, corresponds to the loss of surface-adsorbed water up to a temperature of 85 ° C. The mass loss in sample A-II is greater due to its larger external surface. The loss of weight between 85 and 180 ° C is attributable to zeolitic water within the structural channels of the silicate.

The second step, observed between 180 and 350 ° C, corresponds to the loss of a first water molecule coordinated to the end cations of the octahedral sheet.

The third step, between 350 and 650 ° C, is due to the loss of the second coordinated water molecule which overlaps with the water loss from the dehydroxylation of the octahedral sheet [8,9].

Based on the DSC curves, all of these steps are identified as endothermic. These curves also allow us to determine the maximum transformation temperature of each step (Table 1). In all cases, it can be seen that these temperatures are lower for sample A-II. In the first step corresponding to temperatures below 85 ° C, this fact is attributed to the greater influence of surface-absorbed water due to its larger external surface. In the second and third steps, this result is explained by the greater Mg^{2+} content in the octahedral sheet of A-II and the fact that the Mg^{2+}–OH_2 bond is weaker than that of Al^{3+}–OH_2, considering the higher charge and smaller radius of the Al^{3+} cation [10].

Figures 1 and 2 also show the TGA and DSC curves of samples A-I and A-II after being submitted to successive acid treatments. With respect to the 0–180 ° C interval, a change is observed in the slope of the curves of sample A-II from the 2 N treatment onward. This indicates an increase in loss of surface-adsorbed water at temperatures lower than 85 ° C, with respect to the zeolitic water, which is not appreciated in sample A-I. This fact is due to a greater creation of external surface on the A-II sample, whose surface area reaches a value of 399 m^2 g^{-1}, following 2 N treatment, while the A-I attapulgite surface area is only 139 m^2 g^{-1} [11]. This is confirmed in the DSC curve corresponding to sample A-II-2N, which shows the great influence of the increase in its surface area, with a decrease being observed in the maximum transformation at 84 ° C.

It can also be observed that in sample A-I the two peaks of the TG curves (peaks 3 and 4) assigned to the molecules of water coordinated to the octahedral sheet, are clearly maintained in all the samples after acid attack. In sample A-II, the slopes gradually become smoother as the acid attack increases. The DSC curves of samples A-II-2N, A-II-3N and A-II-4N confirm this by the lower intensity of these steps with respect to the natural

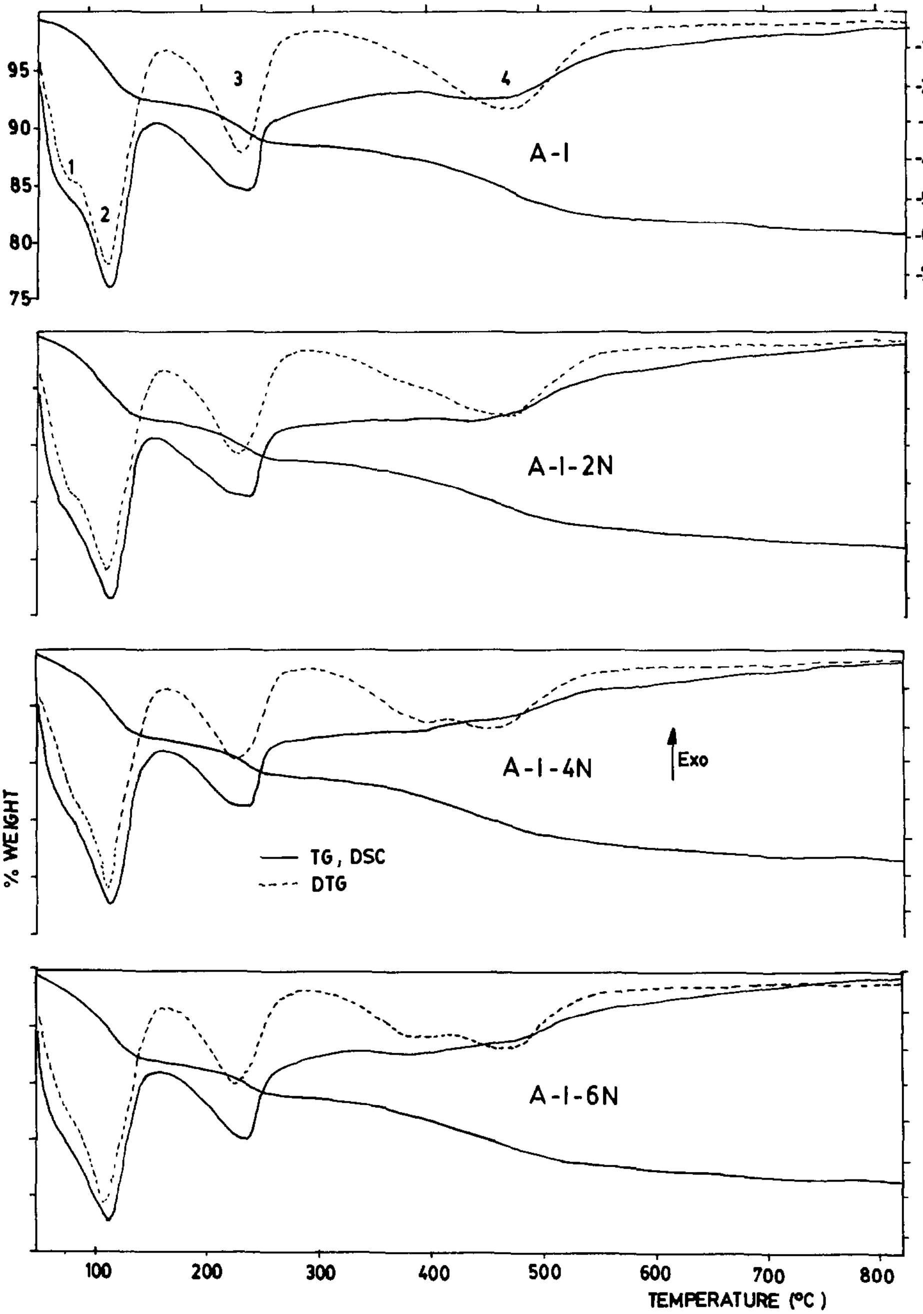

Fig. 1. TG and DSC curves of natural and activated A-I samples.

sample A-II (Fig. 2). This shows that a greater dissolution of the octahedral sheet occurs in the magnesium-rich sample (A-II), which implies that a lower percentage of coordinated water remains in this sample than in the

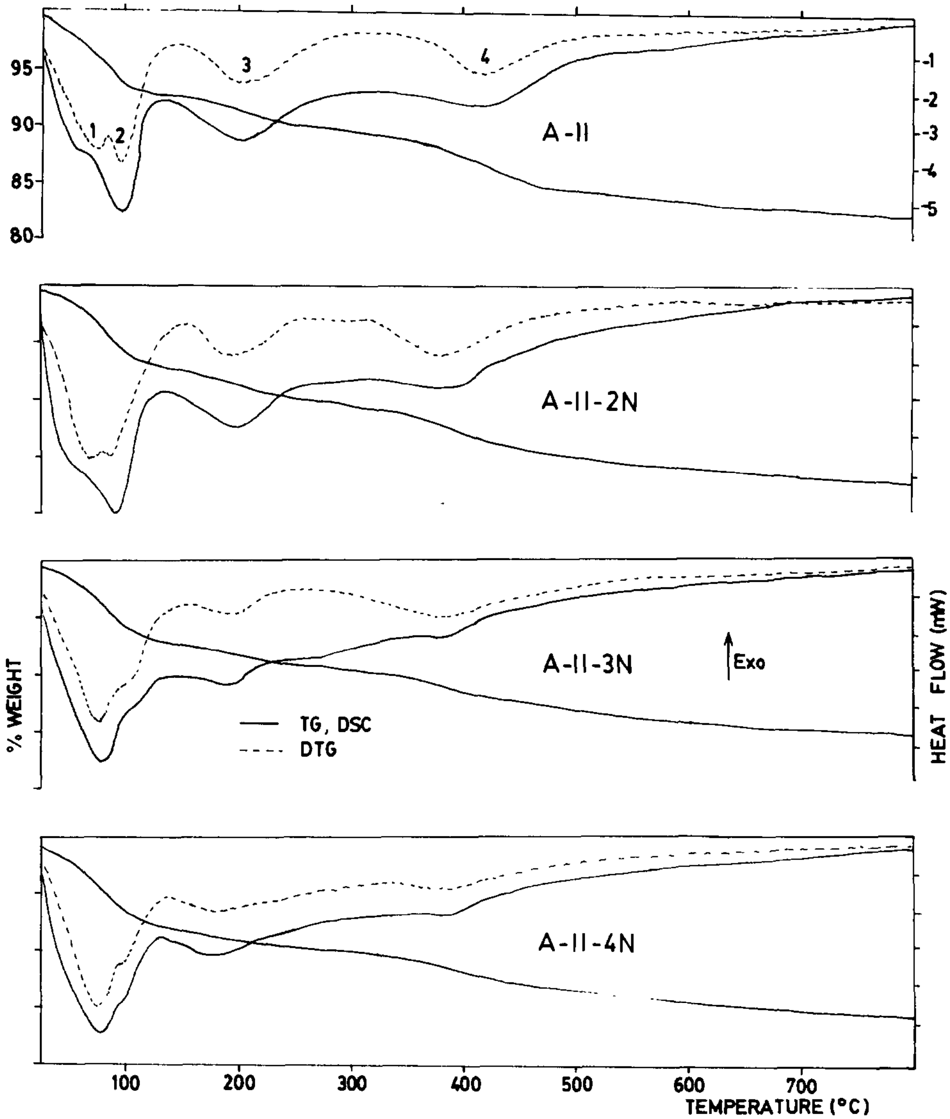

Fig. 2. TG and DSC curves of natural and activated A-II samples.

aluminium-rich sample (A-I). The destruction of the octahedral sheet leads to the formation of free silica chains with OH groups [12] resulting from acid hydrolysis, as is shown in the diagram of Fig. 3. These OH groups could explain the different shapes of peak 4 in the DTG curves of A-I and A-II acid-treated samples. This peak splits in two in samples A-I-4N and A-I-6N (Fig. 1), one at ≈ 450 °C and the other at ≈ 395 °C. The former is attributable to the second water molecule coordinated to the octahedral cations and the latter (≈ 395 °C) to the dehydroxylation of the silica. In samples A-II-3N and A-II-4N (Fig. 2), only the peak at ≈ 390 °C is

TABLE 1

DSC and TG of the natural samples

Step	Range (°C)	Sample A-I		Sample A-II	
		WL (%) [a]	T (°C) [b]	WL (%) [a]	T (°C) [b]
1	25– 85	2.69		5.58	
2	85–180	6.09	122	5.47	108
3	180–350	3.72	258	4.33	218
4	350–650	5.83	499	4.96	454

[a] WL (%), loss of weight.

[b] T (°C), maximum transformation of DSC.

observed. This could be explained by the greater percentage of silica (Table 2) generated and the greater destruction of the octahedral sheet by acid treatment of this magnesium-rich sample.

The corresponding mass losses of the acid-treated samples for the intervals 180–350 °C and 350–650 °C are shown in Table 2, expressed as percentages of the sample weight at 180 °C.

It can be observed that increasing the acid concentration leads to a reduction in the percentages of loss in the first interval. This is more accentuated in sample A-II, due to a greater dissolution in the octahedral sheet, as we have commented previously. In the interval 350–650 °C, increasing the acid treatment also results in a progressive reduction in the

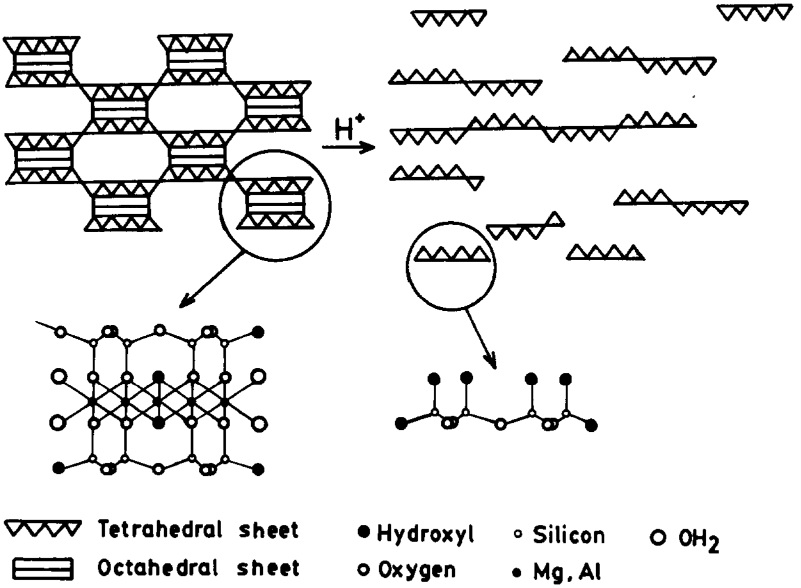

Fig. 3. Scheme of the structural evolution of acid-activated attapulgite.

TABLE 2

TG of the activated samples and percentage of silica extracted

Samples	Loss of weight (%)		Silica extracted (%)
	180–350 ° C	350–650 ° C	
A-I	4.08	6.39	–
A-I-1N	3.78	5.31	9
A-I-2N	3.70	5.03	13
A-I-3N	3.21	4.95	17
A-I-4N	3.21	4.88	19
A-I-6N	3.16	4.73	18
A-II	4.87	5.58	–
A-II-1N	3.45	4.95	27
A-II-2N	2.24	4.22	40
A-II-3N	1.79	4.18	43
A-II-4N	1.85	4.11	43
A-II-6N	1.75	4.03	42

percentages of mass loss, but in this case there are no significant differences between the series A-I and A-II. The reduction in mass loss should be equal in the two temperature intervals as both percentages are linked to be dissolution of the octahedral sheet. The fact that this is not so may be due to the accumulation in the second interval of the water loss corresponding to hydroxyls generated in the silica chain of the tetrahedral sheet, upon destruction of the octahedral sheet by the acid treatment. This has a greater incidence in sample A-II.

From the thermic analysis, it can be deduced that the isomorphic substitution of Al^{3+} for Mg^{2+} in the octahedral sheet produces less stability in the silicate network. Sample A-I, with a greater aluminic content, shows a greater resistance to acid attack, while sample A-II, with a greater magnesic content, undergoes an important dissolution of its octahedral sheet even with weak acid treatments.

REFERENCES

1 W.F. Bradley, Am. Mineral., 25 (1940) 405.
2 Y. Nathan, Israel J. Chem., 6 (1968) 275.
3 E. Mendelovici, Clays and Clay Mineral., 21 (1973) 115.
4 M.B. Makki and C. Flicoteaux, Bull. Soc. Chim. Fr., 1 (1976) 15.
5 A. Corma, A. Mifsud and E. Sanz, Clay Min., 22 (1987) 225.
6 N. Sarier and C. Güler, Thermochim. Acta, 119 (1987) 293.
7 F. González, Ph.D. Thesis, University of Oviedo, Spain, 1988.
8 H. Hayashi, R. Otsuka and N. Imai, Am. Mineral., 53 (1969) 1613.
9 Z. Gerstl, Clays and Clay Mineral., 29 (1981) 53.

10 F. González, C. Pesquera, I. Benito, S. Mendioroz and J.A. Pajares, Thermochim. Acta, 167 (1990) 139.
11 F. González, C. Pesquera, C. Blanco, I. Benito, S. Mendioroz and J.A. Pajares, Appl. Clay Sci., 4 (1990) 373.
12 F. González, C. Pesquera, I. Benito, S. Mendiroz and J.A. Pajares, Clays Clay Mineral., 37 (1989) 258.