Effects of temperature and pH on the kaolinite crystallinity

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Kaolinite is common in weathering area. Crystallo-chemical characteristics of these natural occurring minerals have been widely studied by all current characterization methods and specially by X-ray diffraction and infrared spectrometry (e.g. Brindley *et al.*, 1986; Ambrosi and Nahon, 1986). However, our knowledge of the actual influence of the different conditions of kaolinite formation on its characteristics is only partial. In order to estimate these effects we realized an experimental study. Particularly, we determined the influence of synthesis temperature and pH on the crystallinity of kaolinite. Considering the kinetic slowness of kaolinite synthesis at low temperature (Espiau and Pedro, 1984), we used hydrothermal conditions to optimize the rate formation of kaolinite. Moreover, it appeared interesting to use as starting material a synthesized product including already a noticeable amount of synthesized kaolinite with a medium crystallinity to show up the possible transformation of this initial kaolinite.

Materials and methods

Hydrothermal syntheses were performed from 200 to 260°C ($\pm$ 3°C), under the equilibrium water pressure (respectively 15.5 to 47.6 bars), for a duration of 21 days, in bombs with metal bodies and removable Teflon liners (from 200 to 240°C), and for a duration of 14 days, in a titan bomb at 260°C. The initial pH at room temperature was adjusted to 1 to 14, directly in the bomb by addition of NaOH or HCl to distilled water before heating. The final pH was measured on quenched fluids.

The starting material is a partly developed silica-alumina synthetic gel (of atomic ratio Si / Al = 0.93). It is composed of about 50 % of fairly ordered kaolinite with a medium crystallinity, associated with pseudoboehmite and residual product. It has been obtained by hydrothermal treatment (220°C, 14 days, with distilled water, pHi = 5, pHf = 4) of a gel prepared by coprecipitation of sodium metasilicate and aluminum nitrate with soda additionned according to the atomic proportions Si/Al/Na = 2/2/2.

Starting material and synthesis products were characterized by X-ray diffraction (XRD) (Cu-$K\alpha$ radiation), Fourier Transformed infrared spectrometry (FTIR), differential and gravimetric thermal analyses (DTA-TGA) and transmission electronic microscopy (TEM). The chemical composition of the starting material and the hydrothermal fluids were measured by atomic absorption spectrometry (AAS).

Results

Kaolinite was obtained from the most acidic initial pH to pH value as high as 13 at 240°C (final pH =

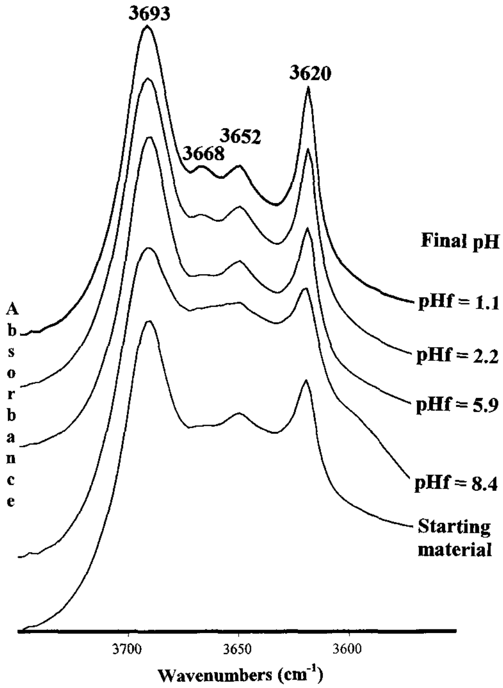

FIG. 1. Evolution of the hydroxyls configuration of kaolinite synthesized at 220°C as a function of the final pH.

TABLE 1. Synthesis conditions and crystallo-chemical characteristics of kaolinites formed, established by X-ray diffraction and differential thermal analyses

T (± 3°C)	Initial pH (± 0.2)	Final pH (± 0.2)	CS along c-axis (Å)	CS along V	Hi	R2	Tendo (°C)
	2.0	2.0	286	235	0.99	0.53	518
	4.5	5.5	266	241	0.86	0.40	511
	5.5	5.7	285	241	0.86	0.45	512
200	6.0	5.6	254	232	0.87	0.42	510
	6.5	5.8	242	244	0.85	0.45	511
	8.1	5.7	262	235	0.97	0.44	511
	10.4	6.1	250	241	0.86	0.53	510
	11.5	7.3	158	226	0.6	0.33	496
	1.0	1.1	286	238	0.99	0.67	516
	2.0	2.2	276	238	0.87	0.52	515
	4.5	5.5	262	235	0.90	0.42	511
220	5.5	5.9	258	241	0.85	0.43	508
	6.0	5.9	250	244	0.85	0.43	514
	6.5	6.0	258	232	0.91	0.43	512
	11.5	8.4	147	224	0.6	0.36	502
	1.0	1.0	296	251	1.09	0.82	525
	2.1	2.1	276	251	1.02	0.62	517
	3.6	4.0	307	244	0.97	0.65	518
240	5.1	4.7	276	251	0.96	0.50	516
	6.4	5.7	285	251	0.97	0.54	512
	8.1	5.6	262	258	1.02	0.50	514
	10.7	6.6	225	269	0.97	0.50	508
260	6.2	6.3	268	251	1.03	0.45	519

CS: Crystallite Size of synthesized kaolinites, calculated with the Scherrer formula - Hi: Hinckley index of crystallinity established by Hinckley, 1963 - R2: test of crystallinity established by Liétard, 1977 - Tendo: temperature of the endotherme of kaolinite dehydroxylation.

7.9) and to pH value of 11.5 for 200 and 220°C (final pH = 7.3 and 8.4 respectively). It is sometimes associated with small amount of boehmite. For final pH value upper than 12 feldspathoïdic minerals were formed (nephelite and cancrinite).

For the experimental conditions used, no influence of temperature on the crytallo-chemical characteristics of kaolinites has been observed. Contrary, final pH has a clear effect on the hydroxyls configuration of synthesized kaolinites as well as on their crystallinity, morphology, and thermal stability (Fig. 1, Table 1).

As a matter of fact, for acidic final pH (pHf < 4), kaolinite is well ordered, with a good crystallinity, a good thermal stability, a morphology of isotropic hexagonal crystals and extended crystal size coherencies. For intermediary final pH (4 < pHf < 6), kaolinite is fairly well ordered, with a fairly good crystallinity, a morphology of hexagonal crystals often anisotropic, a smaller thermal stability and smaller crystal size coherencies. Over a final pH range of 6–7, kaolinite is disordered, with a lath morphology and a low thermal stability.

All these results are in agreement with Satokawa *et al.* (1996) who studied the effects of acidity on the hydrothermal synthesis (220°C for 3 to 10 days) of kaolinite from silica-gel and gibbsite. They established that the rate of kaolinitization is affected by the pH condition of the reaction system but that difference in this rate cannot simply explain the variations in the crystallinity of synthesized kaolinites. In the light of our results, it can be proposed that the variations of kaolinite crystallinity are not only due to the rate of kaolinitization but also and probably essentially to the pH dependence of the critical nuclei nature.

An other point that must be underline is the fact that each kaolinite synthesized was obtained by total transformation of the starting material. In spite of the presence of about 50 % of only fairly ordered kaolinite with a medium crystallinity in the starting material, we obtained almost 100 % of well ordered kaolinite with a good crystallinity for acidic final pH and about 70 % of disordered kaolinite with a bad crystallinity for the most basic final pH.