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THERMAL ANALYSIS AS A TOOL FOR DETERMINING AND DEFINING SPHERICAL KAOLINITE

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Abstract—Samples containing spherical kaolinite, synthesized under hydrothermal conditions (T = 200 °C; t = 24 h, 192 h, 720 h) from gel with Si/Al = 0.84, were studied by differential thermal analysis/thermogravimetry (DTA/TG) to provide a contribution to the mineralogical characterization of this unusual morphology. The data clearly show that dehydroxylation temperature of spherical kaolinite is lower than that of platy/lath kaolinite. It can also be used to detect the presence of spheres in the presence of the other morphologies. A rough estimation of its quantity can be obtained by TG data if spheres are present in appreciable concentrations. The results also confirm microscopic observations previously reported in the literature: spherical morphology is a discrete and metastable phase, and it is gradually dissolved along hydrothermal treatments of gels.

Key Words—Spherical Kaolinite, Synthesis, Thermal Analysis.

INTRODUCTION

Kaolinite crystallizes under hydrothermal conditions both in geological environments and in laboratory synthesis. It can exhibit, besides the typical hexagonal outlines, elongated and spherulitic morphologies. Although studied less frequently than other morphologies, spherical kaolinite has been observed by electron microscopy as a product of the hydrothermal treatment of Si-Al gels or glasses (Rayner 1962; De Kimpe et al. 1964; Rodrique et al. 1972; Tomura et al. 1983, 1985; Huertas 1991; Fiore et al. 1995; Kawano and Tomita 1995). It is formed at the beginning of the synthesis process and is a metastable phase, intermediate between the starting material and the platelets of kaolinite. It has been suggested (Tomura et al. 1983, 1985) that the structure of the spheres does not correspond to the curved layer but to radiating crystals that have straight lattice images with 7-Å spacing. Regarding the formation mechanism, Fiore et al. (1995) recently proposed a solid-state mechanism for sphere formation, based on the arrangements of pre-ordered domains inside the gel. These domains give rise to the formation of proto-kaolinite, which emerges from the gel with spherical morphology.

The size of the spheres (0.1–0.6 μm in diameter) and their hypothetical "structure" (radiating or disordered aggregates of domains) accounted for a low crystallinity. Therefore, X-ray diffraction (XRD) cannot provide clear information, especially if both morphologies of kaolinite are present in the samples (Tchoubar et al. 1982; Plançon et al. 1988, 1989). The differences between spheres and platelets of kaolinite probably depend on energetic factors, as indicated by dissolution of spherical kaolinite along the hydrothermal experiments.

Knowledge of spherical kaolinite's mineralogical characteristics is important for understanding sphere-to-plate evolution and conditions of its formation in nature. It is also important because of implications for the preparation of high-performance ceramics. Therefore, thermal decomposition of spherical kaolinite was studied to provide a more detailed mineralogical characterization of this unusual morphology and to determine if thermal analysis could be used as a diagnostic tool for spherical morphology.

MATERIALS AND METHODS

The samples analyzed in this study are among those previously utilized by Fiore et al. (1995) for morphological investigation. They were hydrothermally synthesized at 200 °C from aluminosilicate gels with Si/Al = 1 and Si/Al = 0.84, in 0.1 M KOH solution (2.5 g/10 mL). Details of the synthesis procedure are given in Huertas et al. (1993). Samples consisted of mixtures of kaolinite (lath, platy and spherical morphologies) and unreacted gel; the proportion of each morphological type depended on temperature, time and initial gel composition (compare Fiore et al. 1995). Although the products synthesized from gel with Si/Al = 1 yielded the highest quantity of spherical kaolinite, the results will be shown for samples from gel with Si/Al = 0.84, as the DTA tracings of the latter exhibit the better resolution. Thermal analyses discussed here are of samples synthesized at: 1) 24 h, which contain a high quantity of spherical kaolinite; 2) 720 h, which contain a high quantity of platy/lath kaolinite; and 3) 192 h, in which the 2 morphologies are almost equally represented.

DTA and TG curves were recorded using a Netzsch simultaneous thermal apparatus (STA 409 PE) under

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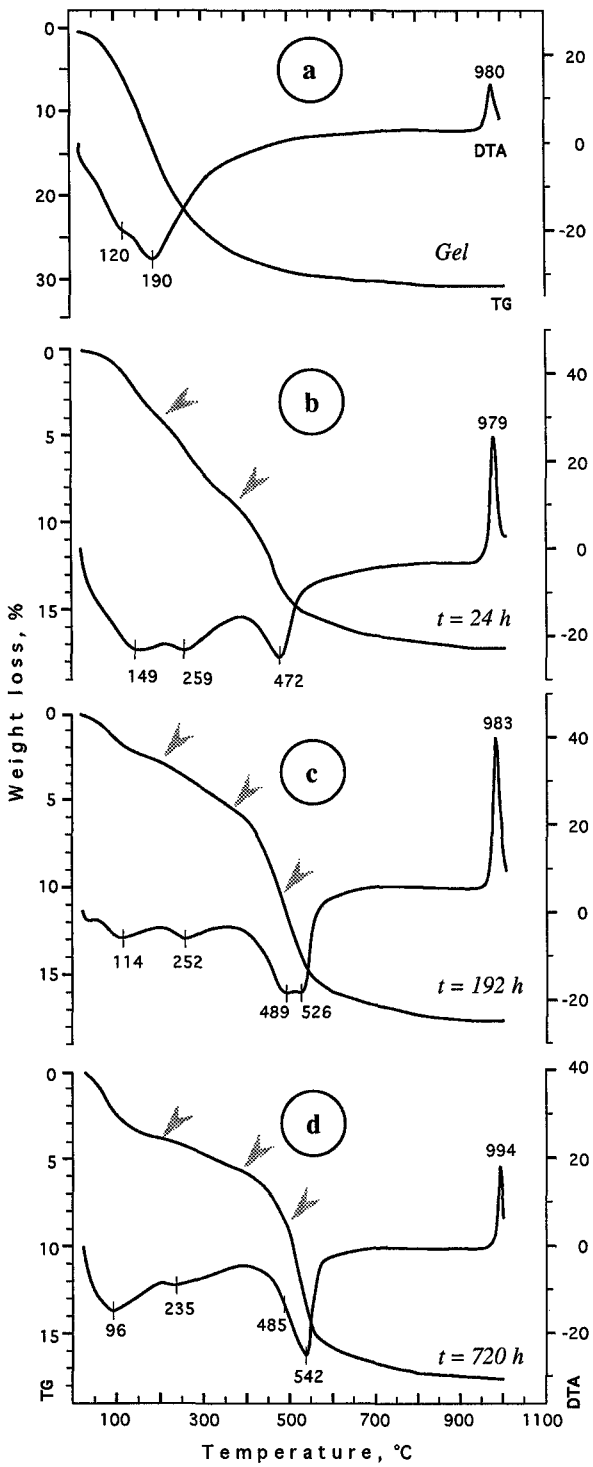


Figure 1. DTA and TG curves of the studied samples. Arrows label the slope changes on TG tracings. (a) Starting gel with Si/Al = 0.84. The 2 endothermic bands with maxima at ≈120 and ≈190 °C are due respectively to adsorbed water and to hydroxyls. (b) Products synthesized at 200 °C for 24 h and containing the highest concentration of spherical kaolinite. (c) Products synthesized at 200 °C for 192 h. Two endothermic peaks due to dehydroxylation of kaolinite evidence the coexistence of spherical and platy/lath morphologies. (d) Products synthesized at 200 °C for 720 h and containing the highest concentration of platy/lath kaolinite. A shoulder at ≈485 °C indicates that a small amount of spheres is still present.

the following working conditions: sample weight, ≈100 mg; thermocouples, Pt-Pt/Rh; references, Al_2O_3; temperature range, 20–1020 °C; heating rate, 10 °C; DTA sensitivity, 400 μV; TG sensitivity, 50 mg; static air atmosphere.

RESULTS AND DISCUSSION

DTA patterns of kaolinite are characterized by the presence of 2 effects: a strong endothermic peak at 500–700 °C (resulting from a dehydroxylation reaction) and a less intense exothermic one at 900–1000 °C (reflecting the crystallization of mullite—Holdridge and Vaughan 1957; Lemaitre et al. 1982). Another endothermic deflection may also appear at low temperature (about 100–150 °C) in hydrothermally synthesized products (Miyawaki et al. 1991; Satokawa et al. 1994). The position of the dehydroxylation peak maximum, as well as its shape and symmetry, are influenced by grain size and degree of structural disorder (Smykatz-Kloss 1974). The position of the peak increases with increasing size and crystallinity (Grim 1968), whereas a more asymmetric peak is caused by smaller and more disordered materials (Bramao et al. 1952), although asymmetry should not be considered an infallible criterion (Mackenzie 1970). Dehydroxylation peak area can be used for a semiquantitative mineral estimation because it is directly proportional to the amount of the mineral (Sand and Bates 1953).

DTA and TG curves of the samples studied are shown in Figures 1a–d, and DTA and TG data are summarized in Table 1.

As was expected, the Si/Al gel (Figure 1a) shows the presence of a broad endothermic band at low temperature, between 100 and 300 °C, which takes its origin from 2 reactions, the 1st having a maximum at ≈120 °C and the 2nd at ≈190 °C. The IR spectra for analogous materials (Huertas et al. 1993) indicated that the 1st reaction is due to the presence of absorbed water and the 2nd to gel hydroxyls, as evidenced by absorption bands at 3400 and 3600 cm^{-1} (Van der Marel and Beutelspacher 1976). After the 2 endothermic events, only an exothermic one at 980 °C, indicating the transition to the spinel phase, is recorded. The TG curve gradually declines, with 2 different slopes in correspondence with the endothermic events. The total weight loss is 31%.

The DTA curve of the sample containing the higher quantity of spherical kaolinite (t = 24 h; Figure 1b) is comparable to "typical" curves of kaolinite, but the

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Table 1. DTA and TG data, and estimated amount of synthetic kaolinites synthesized from gel with Si/Al = 0.84 at 24 h, 192 h and 720 h.

Sample	Thermal reaction (°C)				Weight loss (%)			Estimated kaolinite (%)	
	Adsorbed water	Gel dehydration	Kaolinite dehydroxilation	Mullite formation	20–1020 °C	20–360 °C	360–1020 °C	Spheres	Plates/laths
Gel	120	190	—	980	31.5	—	—	—	—
24 h	149	259	472	979	17.5	9.0	8.5	61	n.d.†
192 h	114	252	489, 526	983	17.8	6.0	11.8	43	42
720 h	96	235	≈485, 542	994	17.5	5.4	12.1	23	64

† n.d. = not detected.

dehydroxylation effect occurs at a much lower temperature (472 °C). The TG curve correspondingly changes, recording a clear deflection in correspondence with the 472 °C peak, a more gradual and lower weight loss in the region 20–360 °C and a displacement of the 190 °C peak to 259 °C. As aging time is increased (192 h; Figure 1c), there appear 2 peaks at 489 and 526 °C. The peak at the higher temperature most probably displaced the previous peak at 472 °C upwards, but was itself pulled down by the same peak.

The endothermic effect at 489 °C tends to disappear on the DTA tracing of the samples synthesized for a longer time (720 h; Figure 1d) and containing the higher quantity of platy kaolinite. It shows 1 peak at 542 °C and a shoulder at a lower temperature (about 485 °C), confirming that spheres are metastable and tend to disappear, whereas plates/laths become more and more abundant. The doublet at 485–542 °C is accompanied by a slight, but well-identifiable, change of slope on the TG curve.

Displacement of dehydroxylation peak temperature in products synthesized from gel has been previously reported, although it was not related to variation in morphology. De Kimpe et al. (1981), for example, showed that the endothermic effect recorded for "amorphous with *hk* bands" product occurred at 425 °C and that it was displaced at higher temperatures as kaolinite developed. Also, DTA curves reported by Miyawaki et al. (1992, 1993, 1995) contain the same features. The coexistence of 2 endothermic effects was not previously reported, perhaps because of low instrumental resolution.

It should be noted that the synthesis products contain much lower amounts of H_2O (see Table 1) than the initial gel. This can be ascribed to a contraction of the gel after hydrothermal treatment; it loses its spongy aspect and becomes more compact (Fiore et al. 1995).

If we assign the peak at ≈470 °C to spherical kaolinite and the peak at 526–542 °C to platy/lath kaolinite, the quantity of each morphological type can be estimated by weight loss (Table 1). For these calculations, we assume that the H_2O content of both morphologies is comparable. Spheres decrease in concentration from 61 to 23% as reaction time increases from 24 to 720 h, whereas laths/plates increase to 64%. It should be noted that the total yield of kaolinite does not change from 192 to 720 h, confirming that, although gel grains are still present, the most important contribution of Si and Al to the solution originates from dissolution of spherical kaolinite. This result supports Fiore et al. (1995), who suggested that the quantity of dissolved spheres may control the chemical potential difference of the solution and, consequently, the morphology of the precipitating crystals (lath or plate).

The lower temperature of the spherical kaolinite dehydroxylation peak with respect to platy morphology can be ascribed to differences in fine grain size and crystallinity. Yet, in our study, the influence of grain size is small or negligible because dimensional differences between spheres and plates are small (compare Smykatz-Kloss 1974). As regards influence of crystallinity, Smykatz-Kloss (1974) reported a range of 530–555 °C for strongly disordered kaolinite and a value <530 °C for extremely disordered kaolinite. He suggested the latter temperature as a "zero-value" for the determination of the degree of disorder. In our samples, decomposition of spherical kaolinite occurs at a much lower temperature; therefore, it should not be related to structural disorder in the strict sense of Smykatz-Kloss (1974). However, if we take into account the fact that spheres are aggregates of domains and not curved layers, as for halloysite (Tomura et al. 1983; Fiore et al. 1995), then their decomposition temperature should be effectively much lower than that for platy kaolinite.

CONCLUSIONS

The results of the DTA-TG study of kaolinite samples synthesized from gel under hydrothermal conditions and containing spherical and platy/lath morphologies can be summarized as follows:

1) The DTA curve of spherical kaolinite is characterized by the presence of an endothermic effect at ≈470 °C (dehydroxylation event) and an exothermic effect at ≈980 °C (crystallization of a spinel phase). The lower temperature of the spherical kaolinite dehydroxylation peak with respect to the platy one is due to crystallinity rather than grain size.

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2) The endothermic effect tends to disappear as the synthesis time increases, confirming that spherical kaolinite is a metastable phase. However, the amount of kaolinite (spheres + plates) does not change with time. This implies that, although gel grains are still present, the concentration of Si and Al in solution is controlled mainly by sphere dissolution.

3) The endothermic peak can be used to detect the presence of spherical kaolinite in the presence of other morphologies, as well. Furthermore, estimation of the amount of spheres is possible using TG data.

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