Spontaneous Rehydroxylation of a Dehydroxylated Cis-Vacant Montmorillonite

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NOTE

SPONTANEOUS REHYDROXYLATION OF A DEHYDROXYLATED *CIS*-VACANT MONTMORILLONITE

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INTRODUCTION

In general, montmorillonite and other dioctahedral 2:1 layer silicates are characterized by dehydroxylation temperatures between 500–700°C (*e.g.*, Mackenzie, 1957; Grim and Kulbicki, 1961; Schultz, 1969; Guggenheim, 1990). Differences in dehydroxylation temperature are primarily related to the kind of octahedrally coordinated cations present and their distribution and movement in dioctahedral 2:1 layer silicates (Drits *et al.*, 1995), although the interlayer cation may have an effect also (*e.g.*, Guggenheim and Koster van Groos, 1992).

Trans-vacant (tv) smectites and micas are characterized by dehydroxylation temperatures which are 150–200°C lower than those for the same minerals consisting of *cis*-vacant (cv) 2:1 layers. Most montmorillonites consist of a mixture of cv and tv 2:1 layers and lose their hydroxyls in two steps near ~550 and ~700°C (Drits *et al.*, 1995). Hence, the investigation of the structure of dehydroxylated montmorillonite is of great interest to understand the dehydroxylation process (*e.g.*, Jonas, 1954; Heller *et al.*, 1962; Drits *et al.*, 1995).

Dioctahedral 2:1 layer silicates are expected to produce well defined dehydroxylates after heating for a short time at temperatures between 500–700°C and cooling under laboratory atmosphere (*e.g.*, Grim and Bradley, 1948; Heller-Kallai and Rozenson, 1980; Drits *et al.*, 1995). However, the heating rate (Hamilton, 1971) and duration of heating (Horváth, 1985) are important in determining if an anhydrous state is achieved. A slow heating rate lowers the apparent dehydroxylation temperature, which is a well known but often neglected phenomenon.

Emmerich *et al.* (1999) found that a completely dehydroxylated state of montmorillonites that are homoionic and *cis*-vacant was not attained after heating to 700°C (heating rate 150 K h^{-1}) for 20 h, because the dehydroxylated montmorillonites show a spontaneous rehydroxylation during cooling. The clays regained nearly 15% of the initial hydroxyls.

In this study, the state of dehydroxylation is investigated after heating a homoionic and cv montmorillonite at various temperatures for different times. Spontaneous rehydroxylation occurs under ambient conditions (at ~24°C) at a relative humidity (r.h.) of ~55%.

MATERIALS AND METHODS

The Ca^{2+}-rich form of the <2-μm fraction of a cv montmorillonite from Linden, Bavaria, was used in this study (Emmerich *et al.*, 1999). It has a chemical formula of $Ca_{0.185}[(Si_{3.95}Al_{0.05})(Al_{1.46}Fe_{0.18}Mg_{0.38})O_{10}(OH)_2]$.

Samples of 55–60 mg of the homoionic clay were heated at a heating rate of 2.5 K min^{-1} in streaming dry air (3 L h^{-1}) to 540 or 700°C. The final temperature was maintained for 0, 12, or 20 h. Thereafter, the samples were cooled and maintained at various periods for ≤8 d in an atmosphere of ~55% r.h. over a saturated $Mg(NO_3)_2$ solution (Table 1). Subsequently, samples were investigated in a Mettler thermobalance linked to a Balzers quadrupole mass spectrometer (MS) (Kahr *et al.*, 1996) with a heating rate of 10 K min^{-1} in the range from 30 to 1000°C. This combination makes it possible to register simultaneously selected masses of the evolved gases during thermal reactions in the thermobalance (Emmerich *et al.*, 1999). The mass loss between 350–1000°C was considered in determining the number of hydroxyl groups regained

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Table 1. Experimental data.

Sample	Thermal treatment: Heating rate [K min⁻¹]	Final temperature [°C]	Time maintained at final temperature [h]	Time stored at ~55% r.h. at room temperature [h]	Thermal analysis: Heating rate [K min⁻¹]	Heating range [°C]	Regained OH groups [%][1]
1	2.5	540	0	0	10	30–1000	66.0
2	2.5	540	0	8	10	30–1000	80.7
3	2.5	540	0	24.5	10	30–1000	82.2
4	2.5	540	0	49	10	30–1000	81.8
5	2.5	540	0	168	10	30–1000	79.8
6	2.5	540	12	0	10	30–1000	22.0
7	2.5	540	12	4	10	30–1000	39.5
8	2.5	540	12	24	10	30–1000	n.d.
9	2.5	540	12	48.7	10	30–1000	42.1
10	2.5	540	12	174	10	30–1000	42.9
11	2.5	540	20	0	10	30–1000	18.5
12	2.5	540	20	10.3	10	30–1000	35.1
13	2.5	540	20	24	10	30–1000	n.d.
14	2.5	540	20	48	10	30–1000	37.1
15	2.5	540	20	168	10	30–1000	38.2
16	2.5	700	0	0	10	30–1000	5.0
17	2.5	700	0	12	10	30–1000	20.6
18	2.5	700	0	24.3	10	30–1000	23.0
19	2.5	700	0	48.4	10	30–1000	23.6
20	2.5	700	0	192	10	30–1000	25.8
21	2.5	700	12	0	10	30–1000	0.6
22	2.5	700	12	10	10	30–1000	12.0
23	2.5	700	12	23.3	10	30–1000	12.7
24	2.5	700	12	48	10	30–1000	13.8
25	2.5	700	12	168	10	30–1000	15.8
26	2.5	700	20	0	10	30–1000	0.7
27	2.5	700	20	10	10	30–1000	11.6
28	2.5	700	20	24	10	30–1000	12.3
29	2.5	700	20	48	10	30–1000	13.5
30	2.5	700	20	168	10	30–1000	15.9

[1] 4.85 wt. % of the initial formula unit is equal to 100% OH groups.

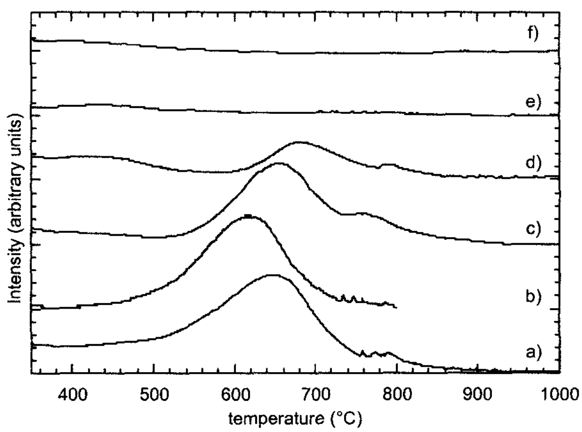

Figure 1. MS curves of the evolved water-mass fragment 18 mass/charge of the initial Ca^{2+}-rich montmorillonite heated at a rate of a) 10 K min^{-1} and b) 2.5 K min^{-1}. MS curves of the Ca^{2+}-rich montmorillonite stored at ~55% r.h. for 8 and 10.3 h, respectively, after heating at 540°C for c) 0 h (Table 1, sample 2) or d) 20 h (sample 12). MS curves of the Ca^{2+}-rich montmorillonite stored at ~55% r.h. for 192 and 168 h, respectively, after heating at 700°C for e) 0 h (sample 20) or f) 20 h (sample 25).

and the MS curves were used to determine dehydroxylation temperatures.

RESULTS AND CONCLUSIONS

Initially, the montmorillonite lost 4.85 ± 0.1 wt. % as the result of dehydroxylation between 350–1000°C. This result is identical to the theoretical OH content of this dioctahedral smectite. The peak temperature of the dehydroxylation peak of the initial cv clay (at 10 K min^{-1}) was ~670°C and the temperature of the return to baseline (reaction completed) was ~780°C (Figure 1, trace a). Complete dehydroxylation was not reached until ~1000°C. The peak temperature decreased to ~625°C with a heating rate of 2.5 K min^{-1} and the reaction was nearly complete at ~750°C (Figure 1, trace b).

After heating the sample to 700°C at a rate of 2.5 K min^{-1}, 4–6% of the initial hydroxyls remained in the structure. These OH groups were not released until the clay was heated for 1.5–2 h at 700°C. Heating for 12 or 20 h at 700°C produced a true anhydrous montmorillonite structure.

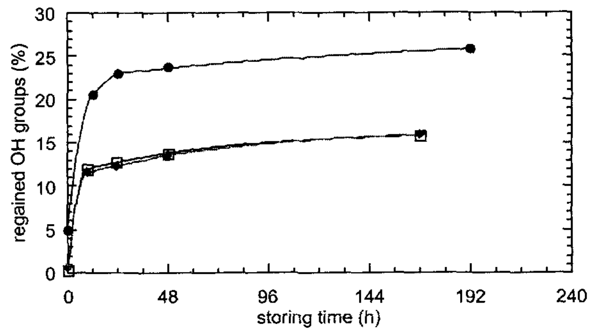

Figure 2. Regained hydroxyl groups for Ca^{2+}-rich montmorillonite after heating to 700°C and maintaining at 700°C for -●- 0 h (Table 1, samples 16–20), -⊟- 12 h (samples 21–25), or -◆- 20 h (samples 26–30) and after storing at ~55% r.h. for ≤192 h in a desiccator.

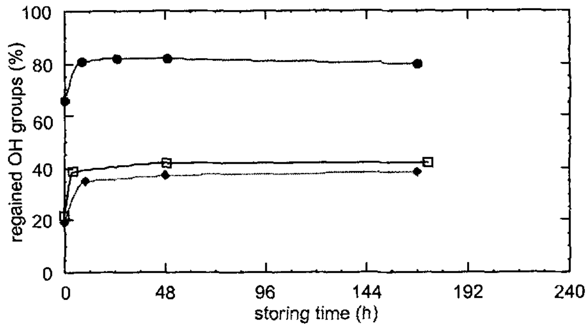

Figure 3. Regained hydroxyl groups for Ca^{2+}-rich montmorillonite after heating to 540°C and maintaining at 540°C for -●- 0 h (Table 1, samples 1–5), -⊟- 12 h (samples 6–10), or -◆- 20 h (samples 11–15) and after storing at ~55% r.h. for ≤174 h in a desiccator.

Uptake of OH groups under 55% r.h. was observed within 48 h after dehydroxylation (Figure 2). Thereafter, the percentage of regained hydroxyl groups approached ~26 for those samples that were subsequently removed from the furnace after heating to 700°C. In contrast, for those samples maintained at 700°C for 12 or 20 h the regained hydroxyl groups approached ~15 (Table 1). The low dehydroxylation temperature of <500°C of these rehydroxylated samples (Figure 1, trace e and trace f) may indicate that restoration of hydroxyl groups occurs first at the edges of the dehydroxylated layers.

If heating was terminated at 540°C, samples retained 65–67% of the hydroxyl groups. Presumably, the provided thermal energy was not sufficiently high to remove all the OH groups. However, 17–19% of the hydroxyl groups remained in the structure even after heating the samples for 20 h at 540°C.

Rehydroxylation under 55% r.h. was nearly complete within 10 h for samples heated to 540°C and maintained for 12 or 20 h at this temperature. For samples immediately cooled after heating to 540°C, 82% of the initial hydroxyl groups were regained (Figure 3). In contrast, samples maintained for 12 or 20 h at 540°C regained only 42 and 38%, respectively (Table 1). Note, that the peak temperature of the high-temperature dehydroxylation peak occurs at ~690°C, an increase of ~30°C after rehydroxylation (Figure 1, trace d). Rehydroxylation with steam at 200°C also increases the subsequent dehydroxylation temperature and enhances the hydroxyl-water uptake to ~90% (Emmerich *et al.*, 1999).

The results of this study show that heating rate and duration of heating are important to prepare dehydroxylated cv montmorillonites. Heating a cv montmorillonite with a rate faster than 150°C h^{-1} to 700°C and maintaining the sample at 700°C for <12 h is not sufficient to remove all OH groups. In addition dehydroxylated and also partly dehydroxylated samples must be cooled and stored under an inert atmosphere to prevent rehydroxylation under ambient conditions.

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