

Mechanism of the $\text{H}_2\text{O}(\text{g})$ release during a dehydroxylation of montmorillonite

I. HORVÁTH and L. GÁLIKOVÁ

*Institute of Inorganic Chemistry, Slovak Academy of Sciences,
809 34 Bratislava*

Received 16 June 1978

Accepted for publication 9 November 1978

The mechanism of the water release during the dehydroxylation of a standard sample of montmorillonite, transformed into Li, Na, K, Cs, Ca, Mg, and Ba monoionic forms, has been investigated by an isothermal TG method. It turned out that the dehydroxylation of montmorillonite can be influenced by the kind of the exchangeable ion. The monoionic forms with monovalent exchangeable cations excepting the Na form released their water according to the mechanism of the first-order kinetics. The diffusion of the water molecules from the phase boundaries was the rate-controlling process for divalent cations and Na^+ in the interlayer region.

It can be assumed that the water transport through the interlayer region into the environment is decisively influenced by the strength of the electrostatic forces between the cation and the negatively charged oxygen atoms of the structure.

Методом изотермической гравиметрии был исследован механизм выделения воды при дегидроксилировании стандартного образца минерала монтмориillonита, переведенного в Li, Na, K, Cs, Ca, Mg и Ba-формы.

Было показано, что на дегидроксилирование монтмориillonита можно повлиять посредством вида обменного катиона. Моноионные формы с однозарядными обменными катионами, за исключением Na-формы, отщепляют воду по механизму реакции первого порядка. В случае двухзарядных катионов и Na^+ в межслойном пространстве самым медленным процессом оказалась диффузия молекул воды из межфазного слоя.

Можно предполагать, что на освобождение воды через межслойное пространство решающее влияние оказывает величина электростатических взаимодействий между катионом и отрицательно заряженными кислородными атомами в решетке минерала.

The release of the chemically bonded water from polycrystalline inorganic compounds during their thermal decomposition ranges among heterogeneous topochemical reactions in the solid state. An investigation of the kinetics of the

thermal decomposition of clay minerals facilitates the optimization of technological processes. Among clay minerals, montmorillonite can be regarded as an extreme example due mainly to very fine dispersion of crystallites and particles as well as very frequent occurrence of various structural defects.

The unit structure of an anhydrous montmorillonite (*i.e.* a montmorillonite without the interlayer water) has an ideal chemical composition

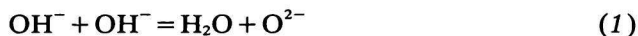


where Me^{+} is a monovalent interlayer cation balancing the negative charge caused by the isomorphous replacement Al—Mg in the octahedral sheet.

The dehydroxylation of montmorillonite takes place between 500—700°C yielding two H_2O molecules per unit structure, and dehydroxylated condensed phase.

According to *Taylor* [1] the dehydroxylation of sheet silicates is controlled mainly by two reaction mechanisms:

1. homogeneous — by the reaction of two OH groups, uniformly according to the equation



2. nonhomogeneous — by the migration of protons and central cations in the structure according to the equation



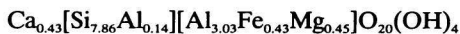
In the case (1) an interaction of two neighbouring OH groups is supposed; in the formation of H_2O according to (2) predominantly those OH groups participate which are in the reaction zones, *i.e.* at the surface of crystallites or at grain boundaries.

The investigation of the montmorillonite dehydroxylation has been based mainly on the results of DTA [2—4], *i.r.* spectroscopy and X-ray analysis [5, 6], and a dynamical TG [7] (TG analysis with constant heating rate). It turned out that the process of dehydroxylation — taking into account also the temperature range, thermal effect of the reaction, migration of protons and central atoms in the structure, and the character of the newly-formed phase — is greatly influenced by interlayer cations. After a removal of the interlayer water, these cations come into close contact with the basic framework of the structure, destroy its stability and influence thus the thermal decomposition of the mineral.

In this paper we present the results of isothermal measurements of the rate of the $\text{H}_2\text{O}(\text{g})$ release from the samples of monoionic forms of montmorillonite during a dehydroxylation, with the aim to contribute to the elucidation of the mechanism of this process.

Experimental

The montmorillonite Dakota from Belle Fourche, USA (Ward's Nat. Establ. Standard) has been chosen as model material. Its crystallochemical formula reads



The Li, Na, K, Cs, Mg, and Ba monoionic forms have been prepared by a saturation with the solutions of the respective chlorides (the starting Ca form has been prepared from the original bentonite in a similar manner).

Isothermal TG analyses have been carried out using a DuPont thermoanalyzer (with thermobalance TGA 951) and 16–19 mg samples at constant N_2 flow rate during all measurements. Before starting the measurements, the interlayer water was removed from each sample by achieving an equilibrium at 400°C directly in the thermobalance. 3–5 independent isothermal measurements have been made for each monoionic form.

Results

The results of the isothermal measurements have been plotted in the form of isothermal curves, as shown in Figs. 1 and 2 for Ca and K monoionic forms. These curves could then be used for the choice of the most probable mechanism controlling the way in which the water molecules formed in the process of dehydroxylation escape from the samples. In order to compare the experimental results with the model curves for the conversion α in the reduced time scale $\tau/\tau_{0.5}$ ($\tau_{0.5}$ is the time for $\alpha = 0.5$) the method described in [8] has been applied. The following possible reaction mechanisms have been chosen:

- a) F_1 — the first-order kinetics,
- b) A — the mechanism described by the Avrami—Erofeyev rate equation $[-\ln(1-\alpha)]^{1/2} = kt$,
- c) R — the mechanism controlled by displacement of the phase boundary,
- d) D — the reaction rate controlled by diffusion.

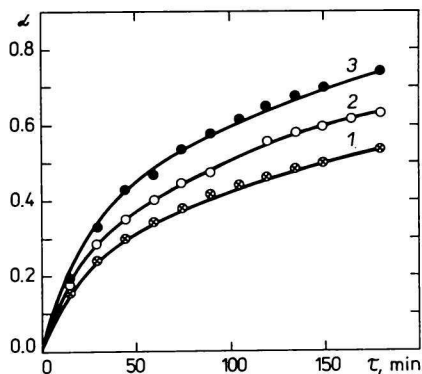


Fig. 1. Isothermal TG curves for the dehydroxylation of the Ca form of the Dakota montmorillonite.

1. 522°C; 2. 534°C; 3. 557°C.

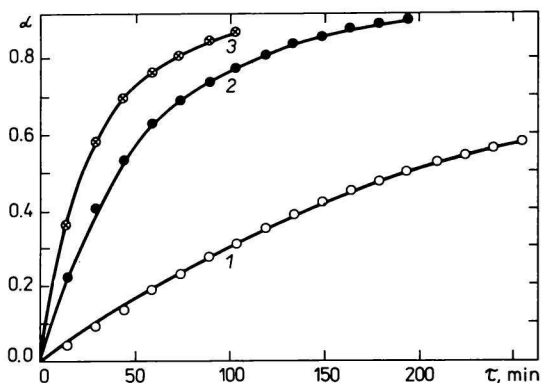


Fig. 2. Isothermal TG curves for the dehydroxylation of the K form of the Dakota montmorillonite.
1. 513°C; 2. 529°C; 3. 541°C.

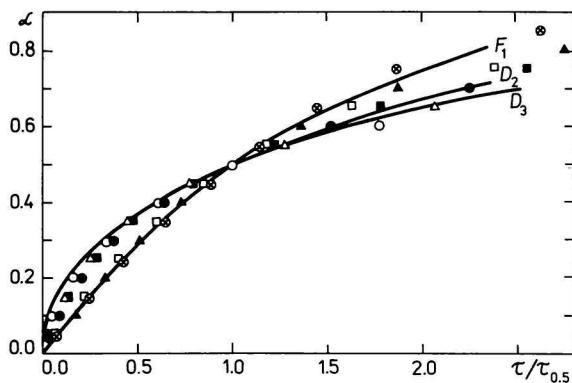


Fig. 3. Comparison of the experimental results with the model curves for the first-order kinetics (F_1), two-dimensional (D_2) and three-dimensional diffusion (D_3).

Experimental points corresponding to the individual monoionic forms:

- ⊗ Li (528°C); ■ Na (532°C); ▲ K (529°C); □ Cs (532°C); △ Mg (532°C); ○ Ca (534°C);
 ● Ba (535°C).

A comparison of the experimental results with the model curves of the probable mechanisms is shown in Fig. 3. The plots $\alpha = f(\tau/\tau_{0.5})$ constructed from the experimental results (for Fig. 3 isothermal measurements at about 530°C for each monoionic form have been chosen) comply closely with two reaction mechanisms:

1. The release of water from the monoionic forms Li, K, and Cs can be described by the equation of the first-order kinetics

$$F(\alpha) = \frac{d\alpha}{dt} = k(1 - \alpha) \quad (3)$$

2. The release of water from the monoionic forms Na, Mg, Ca, and Ba is controlled by diffusion and can be described by the equations

$$F(\alpha) = (1 - \alpha) \ln(1 - \alpha) + \alpha = \frac{k}{r^2} t \quad (4)$$

$$F(\alpha) = [1 - (1 - \alpha)^{1/3}]^2 = \frac{k}{r^2} t \quad (5)$$

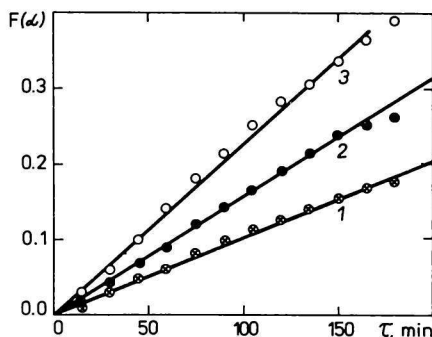


Fig. 4. Plot of $F(\alpha) = f(t)$ for the Ca form of the Dakota montmorillonite.

1. 522°C, $k_{522} = 0.00096 \text{ min}^{-1}$; 2. 534°C, $k_{534} = 0.0015 \text{ min}^{-1}$;
3. 557°C, $k_{557} = 0.0022 \text{ min}^{-1}$

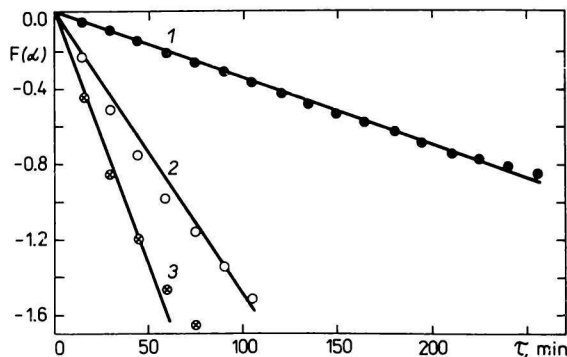


Fig. 5. Plot of $F(\alpha) = f(t)$ for the K form of the Dakota montmorillonite.

1. 513°C, $k_{513} = 0.00345 \text{ min}^{-1}$; 2. 529°C, $k_{529} = 0.01485 \text{ min}^{-1}$;
3. 541°C, $k_{541} = 0.0264 \text{ min}^{-1}$

Eqn (4) has been derived for a diffusion in a cylinder with radius r [9] and, according to our observations, it holds for the diffusion of $\text{H}_2\text{O}(\text{g})$ from the Na and Ca forms of montmorillonite. Eqn (5) has been derived by Jander [10] for a diffusion in a spherical particle with radius r , and it holds for the dehydration of the Mg and Ba monoionic forms. The validity of the proposed mechanisms is documented by the linear character of the dependence $F(\alpha) = f(t)$ in the conversion range $0 < \alpha < 0.7-0.8$, as shown for the Ca and K forms in Figs. 4 and 5.

Discussion

Neglecting small variances in the amount and shape of sample, the only variables in the series of our measurements are the kind of the exchangeable cation and the temperature of the isothermal heating. The exchangeable cations are placed mainly in the interlayer region of the montmorillonite structure (for the sample of Dakota 0.86 for a monovalent cation and 0.43 for a divalent cation per unit structure, respectively). After a removal of the interlayer water (at 300—350°C) these cations occupy the energetically most favourable positions in the ditrigonal cavities formed by the basal oxygen atoms of the adjacent silicate sheets [11] (Fig. 6). In the course of further heating they can — depending on their respective ionic radii — migrate closer to the octahedral positions in the structure [2, 3, 11], 1/3 of which being vacant in dioctahedral montmorillonites. The exchangeable cations with larger radii cannot migrate in this way for sterical reasons; they remain in the interlayer region, more or less “immersed” in the cavities mentioned above. They are bonded by electrostatic forces to the basal oxygen atoms of the two adjacent tetrahedral sheets influencing thus their distance. The smaller becomes this

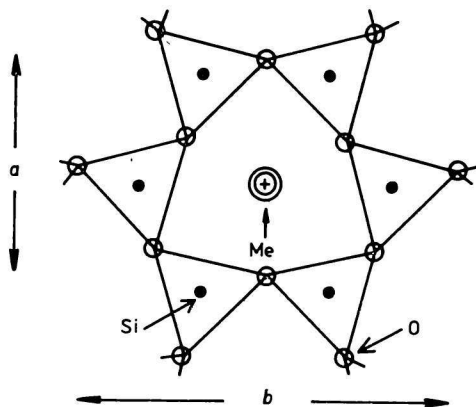


Fig. 6. Arrangement of the basal oxygen atoms in a tetrahedral sheet of the montmorillonite crystal structure, forming a ditrigonal cavity.

distance, the more increases the resistance against the diffusion of the H_2O molecules formed in the process of dehydroxylation from the structure of the mineral.

The mere presence of exchangeable cations in the cavities between basal oxygen atoms does not obviously prevent the motion of water molecules from within the 2 : 1 layer into the interlayer region, since the majority of such cavities in montmorillonites with small total charge on layers (compared with micas, vermiculite, beidellite, illites) is empty.

An analysis of the experimental reaction rates of the $\text{H}_2\text{O}(\text{g})$ release from the monoionic forms of the Dakota sample leads us to the conclusion that — excepting the Na form — the reaction mechanism depends on the valence of the interlayer cations. The monoionic forms with monovalent cations Li, K, and Cs release the $\text{H}_2\text{O}(\text{g})$ according to the first-order kinetics. If the interlayer region contains divalent cations and Na^+ the controlling mechanism is diffusion.

For an explanation of these facts we have used the following hypothesis: The transport of the water molecules formed in the process of dehydroxylation from a layered structure of montmorillonite towards phase boundaries, proceeds obviously through the oxygen cavities and the interlayer region parallel to the layer plane. We suppose that in the case of the Dakota sample the presence of monovalent cations in the interlayer region did not prevent the transport of the water molecules due to the weak coulomb forces between monovalent cations and basal oxygen atoms of the tetrahedral sheets. For the anomalous behaviour of the Na^+ form however, we cannot offer an explanation as yet.

Divalent cations Mg, Ca, and Ba cause stronger bonding between the two adjacent tetrahedral sheets. The slowest process is thus the diffusion of the H_2O molecules away from the phase boundary.

It is first of all the two-dimensional diffusion through the interlayer region of the montmorillonite structure in the direction perpendicular to the stacking direction of layers (*i.e.* parallel to the layer plane), which is most important for the object of the study. A diffusion of the H_2O molecules from the Mg and Ba forms, controlled by a three-dimensional diffusion process (5) should however be also taken into consideration. It would obviously be a diffusion from polycrystalline aggregates of montmorillonite approximately spherical in shape. Similar mechanism has been derived by *Brindley et al.* [12] for the release of the H_2O molecules formed during a dehydroxylation of kaolinite.

The first-order kinetics for the release of $\text{H}_2\text{O}(\text{g})$ molecules from the Li, K, and Cs forms of montmorillonite documented by our experimental results does not prove the homogeneous character of a dehydroxylation according to eqn (1). In order to prove also this assumption, a confrontation of the experimental results of different methods is needed — first of all the study of the properties of the dehydrated phase.

Conclusion

The mechanisms of the release of $\text{H}_2\text{O}(\text{g})$ formed during a dehydroxylation of montmorillonite can be modified by the kind of the interlayer cation. In investigating this process on the monoionic forms of montmorillonite Dakota, a dependence between the reaction mechanism and the valence of the exchangeable cation has been found. The investigated monoionic forms of monovalent cations (excepting the Na form) release water according to the mechanism of the first-order kinetics. The process of the water release for the case of divalent cations and Na^+ in the interlayer region proceeds according to the rate equations for two- and three-dimensional diffusion. We assume that this phenomenon is caused by the electrostatic attractive forces between the negatively charged oxygen atoms of the two adjacent silicate sheets and the exchangeable cations in the interlayer region. In the case of divalent exchangeable cations, these forces are sufficiently strong and can thus prevent a free movement of water molecules through the interlayer region towards the phase boundaries.

References

1. Taylor, H. F., *Clay Min. Bull.* **5**, 45 (1962).
2. Green-Kelly, R., *Clay Min. Bull.* **1**, 221 (1951).
3. Green-Kelly, R., *Clay Min. Bull.* **2**, 52 (1953).
4. Mackenzie, R. C. and Bishui, B. M., *Clay Min. Bull.* **3**, 276 (1958).
5. Heller, L., Farmer, V. C., Mackenzie, R. C., Mitchell, B. D., and Taylor, H. F., *Clay Min. Bull.* **5**, 56 (1962).
6. Russel, J. D. and Farmer, V. C., *Clay Min. Bull.* **5**, 443 (1964).
7. Horváth, I., *Mineralia Slovaca* **10**, 239 (1978).
8. Sharp, J. H., Brindley, G. W., and Narahari Achar, B. N., *J. Amer. Ceram. Soc.* **49**, 379 (1966).
9. Holt, J., Cutler, I. B., and Wadsworth, M. E., *J. Amer. Ceram. Soc.* **45**, 133 (1962).
10. Jander, W., *Z. Anorg. Allg. Chem.* **163**, 1 (1927).
11. Calvet, R. and Prost, R., *Clays and Clay Min.* **19**, 175 (1971).
12. Brindley, G. W., Sharp, J. H., Patterson, J. H., and Narahari Achar, B. N., *J. Amer. Ceram. Soc.* **52**, 201 (1967).

Translated by S. Ďurovič