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High temperature dehydroxylation of muscovite-2M₁: a kinetic study by in situ XRPD

Received: 24 April 1998 / Revised, accepted: 12 October 1998

Abstract Muscovite-2M₁ shows a major phase transition at about 800°C, which is generally attributed in the literature to the structural dehydroxylation process, although a number of structural models have been proposed for the dehydroxylated phase, and different transformation mechanisms have also been put forward. The observed first order transformation involves an increase in the cell volume, and it is not clear to date how the cell expansion is related to the loss of hydroxyl groups. The phase change has been re-investigated here by in situ high temperature powder diffraction, both in non-isothermal and isothermal modes, to combine for the first time the structural and the kinetic interpretation of the transformation. The results unequivocally confirm that the reaction taking place in the temperature range 700–1000°C is truly a dehydroxylation process, involving the nucleation and growth of the high temperature dehydroxylated phase, having Al in 5-fold coordination. Structural simulations of the basal peaks of the powder diffraction patterns indicate that the model originally proposed by Udagawa et al. (1974) for the dehydroxylated phase correctly describes the high temperature phase. The kinetic analysis of the isothermal data using an Avrami-type model yields values for the reaction order compatible with a reaction mechanism limited by a monodimensional diffusion step. Apparent activation energy of the process in vacuum is about 251 kJ/mol. Experiments carried out at temperatures much higher than the onset temperature of the reaction show that the dehydroxylation reaction overlaps with the reaction of formation of mullite, the final product in the reaction pathway.

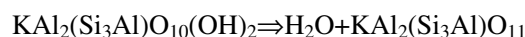
Key words Muscovite-2M₁ · In situ powder diffraction · Dehydroxylation · Kinetics · Structure simulation

Introduction

The structure of muscovite [ideally KAl₂(OH)₂(Si₃Al)O₁₀] can be described in terms of an Al-centered octahedral layer sandwiched between two (Si,Al)-centered tetrahedral layers so that the layer unit is a “true mica” 2:1 sheet whose overall charge is compensated by K cations in the interlayer region (Brindley and Brown 1980; Bailey 1984). In the octahedral layer only two out of three Al sites are occupied (labeled as M2 sites) inducing a relaxation of the framework around the vacant site (labeled M1). The apical 6-ring of tetrahedra displays a ditrigonal distortion in order to allow the fit between the tetrahedral and the octahedral sheets of the layer unit (Toraya 1981).

The understanding of the mechanisms controlling the transformation of muscovite at high temperatures has implications for the characterization of petrological and geological systems, especially for the classification of low-grade metamorphic rocks and their evolution in the frame of metamorphic processes, and it is important for industrial purposes as well, since muscovite is a major component in a variety of raw traditional and ‘high tech’ ceramic materials.

A number of diffraction studies have been devoted in the past to the investigation of the muscovite phase transitions either using single crystals (XRSD) or powders (XRPD). The structural studies have always been carried out separately from the kinetic studies, which have mostly been performed by thermogravimetry. The dehydroxylation reaction is chemically very simple:



and it involves condensation of two hydroxyl groups to form a water molecule. The reaction is qualitatively very similar to the decomposition reaction of pyrophyllite

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(Grim et al. 1951; MacKenzie and Milne 1953) and they both display DTA curves with very broad endothermic peaks because the reaction occurs over a wide temperature interval. Earlier single crystal structural studies on the dehydroxylation reaction of muscovite (Eberhart 1963; Nicol 1964), subsequently confirmed by Guggenheim et al. (1987), Catti et al. (1989), and Vassanyi and Szabo (1993) showed that the dehydroxylated phase has a larger cell volume with respect to the original phase, and the major increase in the cell dimensions is along the *c* axis. Eberhart (1963) observed a spinel-like phase forming above 1050°C. A structural model for the dehydroxylated phase has been proposed on the basis of single crystal diffraction data by Udagawa et al. (1974): the Al atoms switch from 6 to 5 coordination and have a very short bonding distance (1.69 Å) to the oxygen atom shared by two Al atoms, which is considerably charge undersaturated (Guggenheim et al. 1987). The 5-fold coordination group in a trigonal bipyramidal arrangement is similar to the one found in the dehydroxylated form of pyrophyllite (Wardle and Brindley 1972). The mixture of 5-fold and 6-fold coordinated site for the Al cations during the reaction produces an array of oxygen atoms with different charge saturation, and a variety of variously distorted Al sites. This is assumed to be the cause of the observed large temperature interval for the occurrence of the reaction. Abbott (1994) calculated the lattice energy of the commonly assumed model and postulated that the local distribution of tetrahedral Al may be important in determining the release sequence of the OH groups.

Concerning the kinetics, all previous works have been carried out by thermoanalytical or spectroscopic techniques, and were therefore focused on the study of the kinetic mechanism, independent of the structure model. Earlier findings by Holt et al. (1958, 1964) indicate an increase in the apparent activation energy of the process with time. This was interpreted on the basis of a strained lattice model. They found that the kinetic expression is simply a first order reaction and the apparent activation enthalpy of the dehydroxylation process in air is 377 kJ/mol. According to Gaines and Vedder (1964) the rate limiting step should be the diffusion of water molecules in the dehydroxylated structure. Kodama and Brydon (1968) concluded that the mechanism is controlled by the two-dimensional diffusion of the water molecules through a growing product layer. They found an apparent activation energy of the process in vacuum of 226 kJ/mol. According to Rouxhet (1970), the diffusion takes place parallel to the *c** direction, and the protons are transported in H₂O complexes, at least during the slowest step of the reaction.

There is no general agreement on the proposed kinetic and structural models. In particular the frequency factors and the reaction order of the kinetic process were never calculated directly, in order to assess the reaction mechanism. The present in situ powder diffraction study aims to the direct definition of the kinetic parameters, and to establish an experimental link between the structural inter-

pretation of the high temperature phase and its formation kinetics.

Experimental

The muscovite sample utilized for this study is a well-ordered 2M₁ polytype sample from Stoneham, Maine (USA) supplied by Ward's Natural Science Establishment, Rochester (USA). The sample has been characterized elsewhere by chemical analysis (Gualtieri et al. 1994) leading to the following formula unit:



Thermal analyses (TG, DTA) were carried out using a SEIKO SSC/5200 instrument in the temperature range RT–1250°C using a thermal gradient of 10°C/min. The DTA depicts a very broad endothermic peak in the temperature range 400–1100°C and a sharp exothermic peak at about 1100°C due to the nucleation of mullite. The DTG shows a maximum in the dehydroxylation rate at about 880°C. The total weight loss in the range 700–1000°C is about 4.5% which corresponds to the reported amount of hydroxyls lost during the transformation of muscovite (Eberhart 1963; Guggenheim et al. 1987).

Prior to the XRPD and thermal experiments the muscovite powder was hand ground in agate mortar and sieved to achieve a particle size distribution peaked at about 20 μm, with maximum grain size of about 40 μm. XRPD data were collected using a Siemens D500 powder diffractometer in parafocusing Bragg-Brentano geometry, equipped with a Bühler HDK-S1 heating chamber, and using graphite monochromatized CuKα radiation.

A preliminary non-isothermal run was performed by measuring the powder spectra in the angular range 16–48°2θ, under vacuum conditions of 3×10⁻³ torr, tube power 40 kV and 25 mA, angular step size 0.02°2θ, measurement time 1.5 s/step. Data were collected at RT, 350, 700, 725, 750, 775, 800, 825, 850, 875, 900, 925, 950, 975, 1000, 1025, 1050, 1100, 1150, 1200°C. Since during each data collection the temperature was kept constant, the experiment should actually be regarded as a temperature-resolved experiment, rather than a time-resolved non-isothermal measurement. Each temperature step involves a rapid temperature ramp of the order of few seconds, a 10 min dead time to let the sample temperature reach equilibrium, and a 40 min data collection time. This experiment allowed general evaluation of the reaction temperature and rate for the subsequent experiments, of the angular regions of the powder pattern to be analyzed in the isothermal runs, and measurement of the integrated intensity of several basal (00l) peaks of the two phases to be compared with the structural simulations.

The time-resolved isothermal runs for the kinetic analysis were performed in the angular range 25–27°2θ in order to follow the temperature evolution of the (006) Bragg peak during the phase transformation. Data were collected under vacuum conditions of 10⁻⁴ mbar, tube power 40 kV and 20 mA, angular step size 0.02°2θ, measurement time 1.0 s/step. Isothermal runs were performed at 760, 780, 800, 820, 830, 840, 860°C around the onset temperature for the dehydroxylation reaction. The total duration of each isothermal experiment varied from 8 h at 760°C to 3 h at 860°C. The experimental time was sufficient to reach a steady state of the reaction. Given that the onset temperature of dehydroxylation is much lower than the temperature of the stability field of mullite, the latter was not observed in any of the isothermal runs.

The evolution of the reaction has been followed by measuring the integrated intensity of the (006) Bragg peak in time by an especially developed fitting routine (SRSFIT). In Fig. 1 a selected example of the observed and fitted powder peak profiles during the isothermal run at 830°C are shown. Mass balance renormalization was performed by assuming a constant sum of the intensities of the two peaks of the disappearing and newly formed phases. The normalized integrated intensities were then transformed into phase fractions and conversion values (α=the normalized fraction of reacted material).

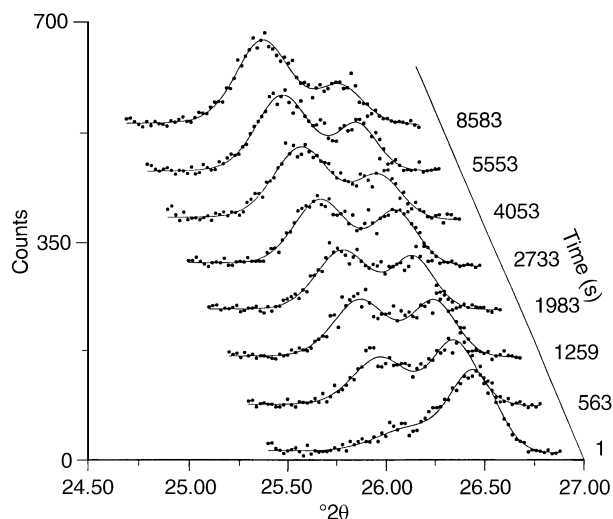


Fig. 1 Powder diffraction spectra of the isothermal run at 830°C: observed and fitted (006) peak profiles

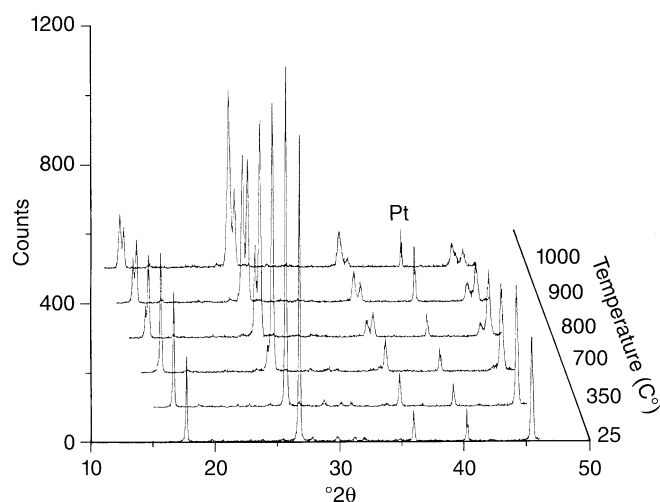


Fig. 2 Powder diffraction spectra of the non-isothermal run at selected temperatures (RT-1000°C). The duration of the whole experiment is about 9.5 h

Results

Non-isothermal runs and structural simulations

Figure 2 shows powder diffraction spectra at selected temperatures during the non-isothermal run from RT to 1000°C. The peaks of the high temperature phase appear in the powder patterns at about 700°C in the low angular tail of the basal reflections of the starting muscovite, and increase in intensity up to 1000°C. At that temperature, the peaks of both the original and the newly formed phases decrease in intensity and the mullite reflections appear.

The first observation to be discussed is the fact that the basal peaks of the two phases are always distinct at any stage of the process: a continuous process involving distortion of the muscovite structure or a close structural relationship between the two phases would imply a progressive splitting of the original muscovite (006) peak. The presence of a new peak even in the early stages of the transformation is a clear indication of the presence of a nucleation and growth mechanism.

The c axis of the high temperature phase is longer than the c axis of the original muscovite phase, as reported in the literature. Figure 3 is a plot of the temperature behavior of the c cell parameter of the two phases. In the temperature range RT-700°C the measured linear thermal expansion coefficient of muscovite is $1.48(7) \times 10^{-5} \text{ K}^{-1}$, in good agreement with previous estimates (Guggenheim et al. 1987: $1.4\text{--}1.5 \times 10^{-5} \text{ K}^{-1}$). Nevertheless, above 700°C (in the range 700–1000°C) the coefficient decreases substantially [$6.0(7) \times 10^{-6} \text{ K}^{-1}$]. A possible cause may be the activation of new vibration modes in the low temperature phase during the transformation. The measured linear thermal expansion coefficient of the high temperature phase is $1.1(1) \times 10^{-5} \text{ K}^{-1}$.

Figure 4a and Figure 4b show the observed temperature dependence of the intensity of the basal (006),

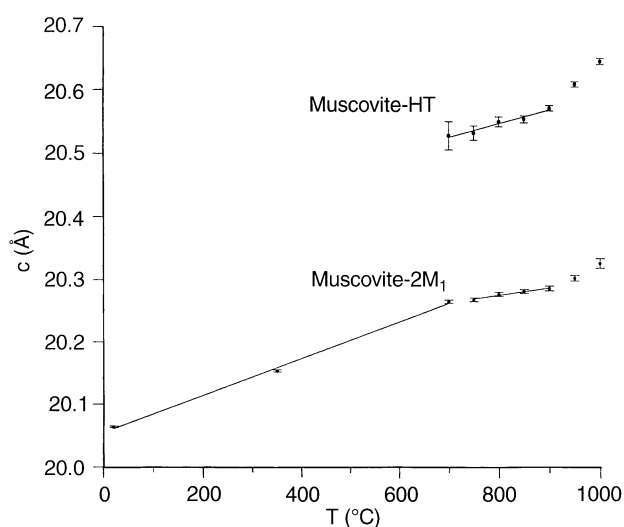


Fig. 3 Plot of c versus temperature of the two phases

(008), and (0010) peaks normalized with respect to the (004) peaks of the original and the high temperature phases, respectively. For both phases, the intensity of the (008) peak do not show appreciable changes, whereas the (006) and (0010) peak's observed structure factors (F_o^2) slightly change with temperature. Both peaks decrease in muscovite, while in the high temperature phase the (006) increases and the (0010) decreases. More important, it can be clearly observed that in the original muscovite the (0010) F_o^2 is constantly more intense at all temperatures than the (006) peak, while this is reversed in the high temperature phase. These key features enable us to distinguish among the proposed structure models of the high temperature phase.

Structural simulations of the powder diffraction patterns were performed in order to test the models of the

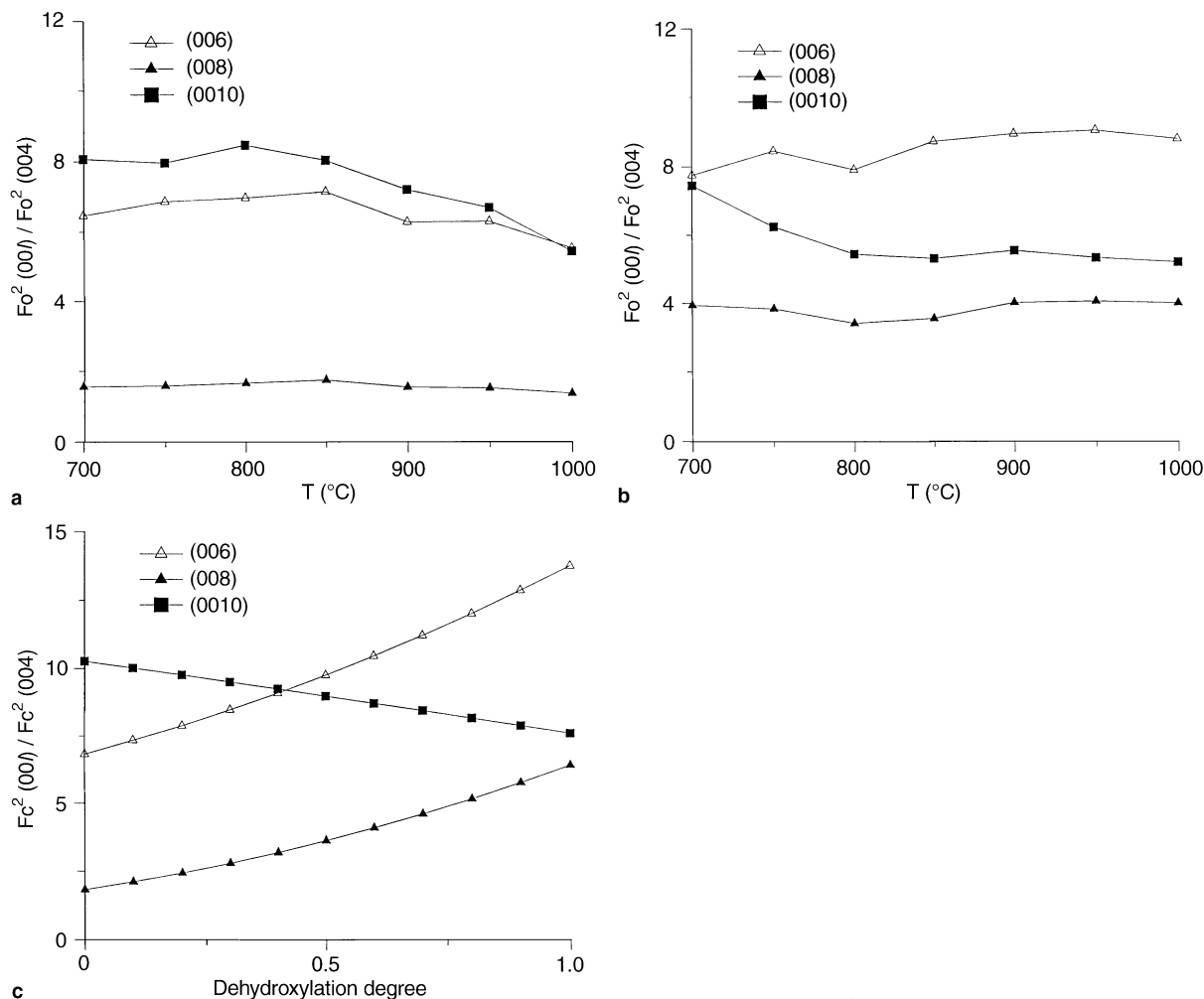


Fig. 4 **a** Variation of basal observed structure factors (Fo^2) in the original phase; **b** variation of basal observed structure factors (Fo^2) in the dehydroxylated phase; **c** simulated variation of basal peak calculated structure factors (Fc^2) versus degree of dehydroxylation

high temperature reaction product present in the literature: (1) 1M phase, according to the $2M_1 \rightarrow 1M$ transformation model of Gualtieri et al. (1994); (2) $2M_1$ phase with Al in octahedral coordination, according to the $2M_1 \rightarrow 2M_1$ transformation model of Eberhart (1963); (3) $2M_1$ phase with Al in 5-fold coordination, according to the $2M_1 \rightarrow 2M_1$ transformation model of Udagawa et al. (1974) and Guggenheim et al. (1987).

The powder pattern simulations of the high temperature phase were performed in the angular range $16\text{--}48^\circ 2\theta$ using the GSAS software package (Larson and Von Dreele 1998). The simulations based on the structural models of muscovite-1 M (atomic coordinates after Sidorenko et al. 1975) and of muscovite- $2M_1$ with 6-coordinated Al (atomic coordinates after Eberhart 1963) show rather different $Fo^2(00l) / Fo^2(004)$ ratios with respect to the observed ones shown in Fig. 4b. The simulation based on the third model, on the other hand, shows a satisfactory agreement with the observed intensity ratios. The calculations were per-

formed by assuming the residual oxygen position midway between the original positions of the two OH groups in the standard structure model of muscovite- $2M_1$ (atomic coordinates after Catti et al. 1989), according to Udagawa et al. (1974) and Guggenheim et al. (1987). The dehydroxylated form is obtained by gradually decreasing the site population of the OH groups, and by increasing the population of the residual oxygen. Figure 4c shows the change in the intensity ratio of the basal peaks as a function of the dehydroxylation degree: the relative structure factors of the renormalized (006), (008), and (0010) in the fully dehydroxylated form match well with those observed for the high temperature phase of muscovite. There is, therefore, little doubt that the studied phase change is the direct transformation of hydroxylated muscovite- $2M_1$ to dehydroxylated muscovite- $2M_1$, the latter being already fully dehydroxylated when the basal peaks appear in the powder pattern and having a structural arrangement very similar to the one proposed by Udagawa et al. (1974).

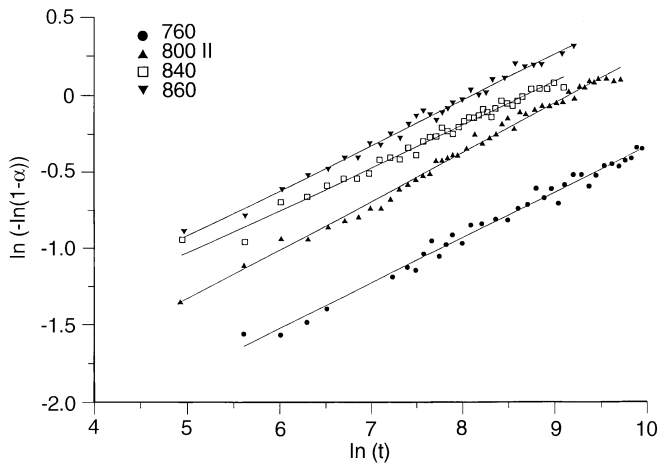


Fig. 5 Determination of the reaction order (n), only a few of the experimental runs are shown for clarity

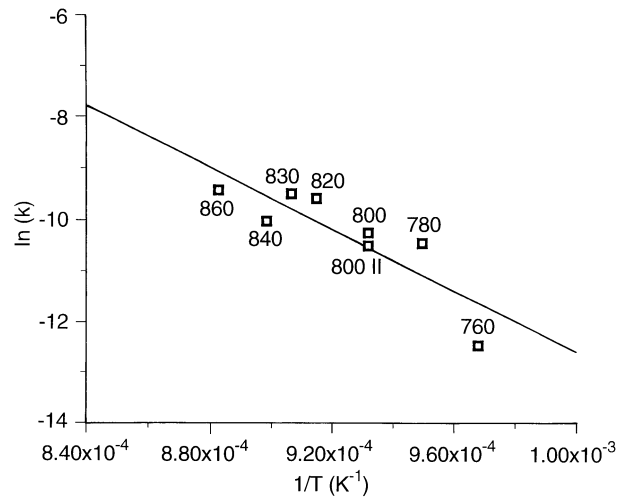


Fig. 6 Arrhenius plot for the calculation of E_a from the slope of the linear fit $\ln(k)$ versus $1/T$. The points refer to all isothermal runs

Isothermal runs and kinetic analysis

The kinetic analysis of the process leads to the interpretation of the mechanism of the reaction and to the estimation of the apparent activation energy. The data analysis was performed following the standard procedure after Hancock and Sharp (1972), and includes the plot of the quantity $\ln(-\ln(1-\alpha))$ versus $\ln(t)$, with α the conversion factor, and t the time. The resulting plots are linear in the conversion range $0.15 < \alpha < 0.5$ and are shown in Figure 5. The slope of the regression line fitted through the points of each isotherm is characteristic of the kinetic

Table 1 Values of the reaction orders and the regression coefficients. The run at 800°C was duplicated to check the reproducibility of the data

T (°C)	n	r^2
760	0.294(6)	0.98
780	0.293(4)	0.99
800	0.289(4)	0.99
800 II	0.315(5)	0.99
820	0.289(3)	0.99
830	0.262(6)	0.98
840	0.266(6)	0.98
860	0.289(5)	0.99

Table 2 Values of the rate constants and the regression coefficients

T (°C)	k (10^{-5})	r^2
760	0.380(7)	0.99
780	2.84(3)	0.99
800	3.48(4)	0.99
800 II	2.72(4)	0.99
820	6.83(8)	0.99
830	7.5(2)	0.98
840	4.41(8)	0.99
860	8.0(1)	0.99

expression and it is commonly defined n or the *reaction order* (Bamford and Tipper 1980). Table 1 reports the values of n for each isothermal run and the regression coefficients. The average value of n is 0.29(1) (arithmetic mean). This value unambiguously indicates that the rate limiting step of the reaction is a one-dimensional diffusion. Higher dimensional diffusion or different mechanisms would imply much higher values of n (Hulbert contribution in Bamford and Tipper 1980). In fact, the obtained value (0.29) is even smaller than the theoretical value for one dimensional diffusion (0.5) and this implies an instantaneous nucleation (zero order) or a deceleratory rate of nucleation of the reaction product.

The resulting values of n allows us to assess the kinetic model and the best kinetic expression to be employed to fit the α versus time data. The kinetic expression related to the diffusion process is: $n[-\ln(1-\alpha)]^{1/n} = kt$ with $n=0.29$. The plots of $n[-\ln(1-\alpha)]^{1/n}$ versus t allow the calculation of the rate constants k for each isothermal run. The data are shown in Table 2 together with the regression coefficients. The values of the obtained rate constants are then used in the plot of $\ln(k)$ versus $1/T$, the logarithmic form of the Arrhenius equation:

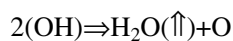
$$k = A \exp(-E_a/RT)$$

with A =frequency factor, E_a =apparent activation energy of the process, R is the gas constant, T is the absolute temperature. The Arrhenius plot for the muscovite dehydroxylation experiments is depicted in Figure 6. The resulting value of E_a is 251(63) kJ/mol with a regression coefficient of 0.73.

Discussion

The results of the powder pattern simulations indicate that the structural model which best fits the observed data is

based on a dehydroxylation process where the original muscovite-2M₁ undergoes cell volume expansion and then, at about 700°C transforms into a dehydroxylated muscovite-2M₁ form according to the structural model of Udagawa et al. (1974) and Guggenheim et al. (1987). A similar model has been proposed for the dehydroxylation process of pyrophyllite (MacKenzie and Milne 1953; Grim 1968; Wardle and Brindley 1972). The dehydroxylation process can be summarized as:



where the release of two hydroxyl groups as a water molecule implies the presence of a structural residual oxygen atom located in the center of the octahedral edge shared by two Al octahedra. The change of the Al coordination from 6- to 5-fold triggers the distortion of the octahedral layer, and the rearrangement of the adjacent tetrahedral layer. Rotation of the tetrahedra is necessary to compensate the misfit with the distorted octahedral layer.

As far as the kinetic mechanism is concerned, the obtained values of n are characteristic of a reaction in which the rate limiting step is one-dimensional diffusion. The previous kinetic studies on muscovite (Sabatier 1955; Eberhart 1963; Holt et al. 1958, 1964; Gaines and Vedder 1964; Kodama and Brydon 1968) by different methods all found that diffusion is the rate limiting step of the reaction kinetics, albeit the detailed conclusions differ, especially concerning the dimensionality of the diffusion mechanism, and the physical interpretation of the process. Possible mechanisms are: (1) diffusion of the hydroxyl groups out of the unit layer and water condensation in the interlayer region; (2) proton hopping between oxygen atoms of the octahedral layer and condensation of the water molecules at the crystallite surface; (3) intralayer condensation of the water molecules and diffusion of H₂O species out of the unit layer. Rouxhet (1970) for the first time advanced the hypothesis that the diffusion path-way is in one-dimension along the c^* axis. The activation energy he reports for diffusion and deuteration in a muscovite mica is 197 kJ/mol. This is in agreement with the value of 226 kJ/mol obtained in vacuum by Kodama and Brydon (1968) and about half the value of 377 kJ/mol obtained in air by Holt et al. (1958). Kodama and Brydon (1968) thoroughly discussed the differences in the measured E_a based on earlier considerations of Brindley et al. (1967) upon the effect of partial water pressure on the reaction. The value of the apparent activation energy measured by us in vacuum by XRPD ($E_a = 251$ kJ/mol) is in perfect agreement with the literature estimates obtained in vacuum by thermogravimetry and IR spectroscopy.

The overall kinetic model we assume on the basis of the resulting kinetic parameters (see Table 1) follows the general model of Rouxhet (1970), and is compatible with the structural model assumed for the transformation. The kinetic models involving proton hopping in the octahedral layers or two dimensional diffusion of the water molecules in the interlayer region would involve a two di-

mensional diffusion process as the rate limiting step of the reaction. This is clearly ruled out by the obtained values of n .

The reaction is a multi-step process encompassing:

- The early condensation of two adjacent hydroxyls in the octahedral layer to form a water molecule;
- The monodimensional diffusion of the water molecule throughout the 6-ring of the tetrahedral layer, that is the actual escape window to the interlayer space;
- The diffusion of the water molecule in the interlayer region to reach the surface of the crystallite.

The kinetic data confirm that a monodimensional diffusion process is the slower step of the reaction, that is the water molecule is inhibited by the small size of the tetrahedral 6-ring during diffusing out of the T-O-T unit layer. If we consider the diameter of an ideal 6-ring of tetrahedra at RT, its length is about the same of the Van der Waals diameter of the water molecule and diffusion is therefore precluded. The opening space at RT is further reduced by the actual ditrigonal distortion of the 6-ring in the tetrahedral layer. On the other hand, at high temperature the thermal expansion and the decrease in the ditrigonal distortion of the 6-ring opening make the diffusion possible to a water molecule having a substantial thermal energy. The observed apparent activation energy thus refers to the process of water molecules jumping from the octahedral layer to the interlayer region through the opening of the tetrahedral 6-rings, and this is the rate limiting step of the overall reaction. During the phase transition there should be a decrease of the tilting angle α in temperature, that is, the tetrahedral 6-ring should become more hexagonal, with an increase of the size of the internal cavity, and a consequent increase of the probability of the molecules to go through.

The sluggishness of the reaction shown by the thermal analysis can be interpreted in terms of layer distortion in the reacted phase (i.e., the layer distortion induced by the change in coordination of Al in the dehydroxylated phase, produces a reacted layer which is effectively closed to H₂O diffusion) or in terms of charge saturation of the chemical species involved (Guggenheim et al. 1987: the presence of nearby 5-fold and 6-fold coordinated Al sites produces four apical oxygen atoms per 6-fold site which are positively oversaturated; the octahedral Al therefore moves towards the two hydroxyl groups away from the apical oxygens, in order to compensate the residual electrostatic charge, and the increased attraction between the Al cation and the coordinated hydroxyls effectively delays further dehydroxylation). Whatever the preferred interpretation, the kinetic analysis clearly points to the deceleratory character of the nucleation rate of the high temperature phase, which is the cause of the large temperature interval during which the reaction occurs, and it is reflected in the broad endothermic band measured by thermal analysis. Early suggestions that the reaction is non-homogeneous (Nicol 1964) and maybe partially controlled by crystal defects and dislocations (Holt et al. 1964) cannot be completely ruled out by the present data.

This would imply that the dehydroxylation process does not occur uniformly in the muscovite crystallites, and as the reaction progresses domains of unreacted phase are left together with the newly formed phase by a nucleation and growth mechanism. Evidence of the non-homogeneous character of the reaction under certain conditions derives from a Mössbauer study of Fe-containing muscovite (Heller-Kallai and Rozenson 1980), whereas the electron spin resonance study of Kalinichenko et al. (1997) indicate a continuous nucleation process.

Conclusions

Re-investigation of the process of dehydroxylation in muscovite-2M₁ by in situ high temperature XRPD allowed a coherent structural and kinetic interpretation of the process. For the first time with a unique set of experimental data it has been possible to control the structural model of the high temperature dehydroxylated phase, and the kinetic model of the reaction.

A model implying condensation of the hydroxyl groups into water molecules in the mica intralayer region, and diffusion of the molecules in the interlayer region through the tetrahedral 6-rings seems to adequately account for the structural, geometrical, and kinetic parameters extracted from the diffraction data collected in isothermal and non-isothermal mode.

A natural development of this study would be a high temperature study by dynamic XRPD, in order to have diffraction data of sufficient quality for the complete structural refinement of the high temperature phases by Rietveld techniques.

Acknowledgements Financial support is acknowledged from Italian MURST and CNR. Part of the work has been performed by EM during his dissertation work towards a Laurea Degree at the Università di Milano.

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