Influence of counterion species on the dehydroxylation of Ca^{2+} -, Mg^{2+} -, Na^{+} - and K^{+} -exchanged Wyoming montmorillonite

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ABSTRACT

The dehydroxylation of Ca-, K-, Mg- and Na-saturated Wyoming montmorillonite has been studied by thermogravimetry (TG), infrared (IR) spectroscopy and X-ray diffraction (XRD). Samples saturated with either Ca^{2+} or Mg^{2+} show a predominantly diffusion-controlled reaction step, whereas Wyoming montmorillonite with Na⁺ and K⁺ in the interlayer exhibit control closer to first order. The activation energy of dehydroxylation is not significantly correlated to the type of interlayer cation present, in turn demonstrating that the role of vacancy location in the octahedral sheet is more significant a control on dehydroxylation.

KEYWORDS: montmorillonite, IR spectroscopy, X-ray diffraction, dehydroxylation kinetics.

Introduction

PREVIOUSLY, differential thermal analysis patterns have been used to study water loss from montmorillonites during dehydroxylation. It has been reported that the behaviour of montmorillonites cation-exchanged with small cations (e.g. Li⁺ and Mg²⁺) cannot be distinguished readily from that observed for montmorillonites cation exchanged with larger cations such as Ca2+, Na+ and K⁺ (Koster van Groos and Guggenheim, 1989). Mackenzie and Bishui (1958) studied the differential thermal characteristics of a suite of cation-exchanged montmorillonites. They found minor variations in the temperature of the main dehydroxylation event. The dehydroxylation temperature ranged from 680 to 710°C, and a parabolic relationship between the temperature of the main dehydroxylation event and the ionic radius of the interlayer cation was observed. The main temperature of dehydroxylation increases to a maximum of 710°C as the ionic radius approaches 1.1 Å. In addition, Waclawska (1984) noticed that the temperature at which the dehydroxylation rate is a maximum was lower for smectites containing K^+ in the interlayer region. He did not note any correlation, however, between the dehydroxylation temperature and cation size in Ca²⁺, Na⁺ or Mg⁺ saturated montmorillonites.

Horvath and Galikova (1979) reported that dehydroxylation is first order controlled when montmorillonite contains monovalent cations other than Na⁺. They suggested that it is controlled by the diffusion of water molecules from a phase boundary when montmorillonites were saturated with divalent cations or Na⁺. Moreover, it has been postulated that the mechanism of water release is controlled by the interlayer cation and to some extent the negative charge on the outer basal oxygens (Horvath and Galikova, 1979; Koster van Groos and Guggenheim, 1986, 1987b). The dehydroxylation of montmorillonites and illites appears to be controlled by the evolution of water molecules from the octahedral sheet, through the cavities of the outer tetrahedral sheet, and their subsequent diffusion through the interlayer region (Bray et al., 1998; Bray, 1999). The relative importance of the influences of the tetrahedral sheet on the one hand, and the interlayer cation on the other, on the rate and energetics of dehydroxylation are not fully understood, however. Therefore, we have studied the effect of varying interlayer cation

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saturation on dehydroxylation by TG, IR spectroscopy, and XRD in an attempt to gain further insights in to the dehydroxylation process.

Experimental procedures

The <2 μ m fraction of Wyoming montmorillonite was left to equilibrate with 250 ml of 1 M chloride salt solutions (Ca²⁺, Mg²⁺, K⁺, Na⁺) for 24 h after which time the chloride solution was syphoned off and replenished with fresh 1 M solution. This process was repeated four times. The clay was then put in dialysis tubing and placed in distilled water. The water was changed daily until a stable electrical conductivity was reached indicating the absence of any residual chloride ions in solution.

The kinetics of dehydroxylation were investigated using a Stanton-Redcroft thermobalance. The samples were preheated at 350°C for 24 h in a muffle furnace, to ensure complete dehydration. They were then stored at 110°C until use. The sample size was kept between 9.7 and 10.2 mg. At the beginning of each isothermal experiment the sample was heated for 1 h at 350°C in the thermobalance under a constant N₂ gas purge. Then the temperature was raised (at 990°C/min) to the set temperature of between 500 and 700°C at which temperature isothermal dehydroxylation was observed as mass loss, following the approach of Redfern (1987). The in situ heating at 350°C ensured that any water absorbed whilst weighing the sample did not influence the mass change vs time data recorded. Samples were heated isothermally for up to 3 h with the mass recorded every 4 s.

The mid-IR absorption spectra of samples were obtained using a Bruker 66v Fourier transform infrared spectrometer, after each had been heated in the thermobalance. The basal spacings of the rehydroxylated samples were determined using a Guinier X-ray diffractometer. The samples were mixed with silicon (which acted as an internal standard) and diffraction patterns obtained between 6 and $30^{\circ}2\theta$. Data points were collected every $0.06^{\circ}2\theta$ with a counting time of 60 s.

Thermogravimetry

The isothermal experiments between 646 and $694^{\circ}C$ show that all the cation-exchanged Wyoming montmorillonites lose between 4 and 4.5 wt.% (relative to their initial mass) on dehydroxylation (Fig. 1). Mass loss did, however, occur before the target temperature

was reached, and the first 30 s of the reaction curves do not represent isothermal conditions. As the samples were fully dehydrated prior to heating to the target temperature, these first 30 s of data represent the loss of structural hydroxyls and were included in the analysis.

Rate controlling mechanism

To determine the average reaction order, n, the mass change vs time data for each isothermal temperature were fitted to a general rate equation (Fig. 2):

$$m_t = m_\infty + a e^{(\mathbf{k}t)^n} \tag{1}$$

where m_t and m_{∞} are the masses observed at time t and at the end of the reaction, respectively. The amplitude of the reaction is defined by a and the rate constant is k. Hydroxyl loss often commenced before the isothermal conditions of the experiments were reached and samples take ~ 30 s to reach the set temperature, a start point of $t_0 = 60$ s was chosen, beyond which point the sample can be assumed to be held under true isothermal conditions. The data were fitted over as wide a time interval as possible (3600 s for lower temperature experiments, only 1000 s at higher temperatures).

The average *n* value over the temperature region studied was calculated by fitting the data to equation 1; the results are presented in Table 1. It can be seen that the rate-controlling process lies intermediate between a first-order (n = 1) and a diffusion-controlled process (n = 0.5). The montmorillonites saturated with K⁺ or Na⁺ in the interlayer region show a rate-controlling step closer to first-order, while the value of *n* for the

TABLE 1. Reaction order (n) values as determined from fitting the data to the general rate equation (equation 1). Figures in parentheses represent one standard deviation error.

<i>T</i> °C	Reaction order (n)				
	Ca-Wy	K-Wy	Mg-Wy	Na-Wy	
646	0.74(2)	0.94(2)	0.74(2)	0.81(2)	
658	0.77(2)	0.94(3)	0.74(3)	0.85(4)	
670	0.78(2)	0.90(3)	0.69(2)	0.88(4)	
682	0.76(2)	0.95(5)	0.83(5)	1.01(8)	
694	0.69(3)	0.90(4)	0.75(6)	0.9(1)	
Average	0.755(9)	0.93(1)	0.72(7)	0.84(2)	



FIG. 1. Mass change vs time curves for (a) Ca-saturated, (b) K-saturated, (c) Mg-saturated, and (d) Na-saturated Wyoming montmorillonites.

TABLE 2. Rate constant (k) values for different Wyoming cation-exchanged samples determined from fitting the raw data. Figures in parentheses represent one standard deviation error.

Rate constant (k)						
$T^{\circ}C$	Ca-Wy	K-Wy	Mg-Wy	Na-Wy		
646	0.00125(2)	0.00193(2)	0.00202(4)	0.00440(6)		
658	0.00167(3)	0.00290(5)	0.00242(6)	0.0067(2)		
670	0.00267(5)	0.00436(8)	0.0044(1)	0.00109(3)		
682	0.0048(1)	0.0060(2)	0.0048(2)	0.0137(8)		
694	0.0061(2)	0.0104(2)	0.0060(4)	0.016(2)		

 Ca^{2+} - and Mg^{2+} -saturated samples is lower. This could be evidence that the rate controlling process is slightly affected by the type of interlayer cation present.

Apparent rate constants at each isothermal temperature were calculated by fitting the data to the general rate equation with a fixed value of n (Table 2). The fixed n value for each sample was taken as the average over the temperature range from 646°C to 694°C, as given in Table 1. Na-saturated Wyoming montmorillonite appears to dehydroxylate more rapidly than the other cation-saturated samples (Fig. 2, Table 2). Interlayer cations, such as Ca²⁺ and Mg²⁺, with stronger hydration properties, may impede the

migration of water molecules and lower the rate constants of the reaction.

Determination of activation energy

Activation energies for the dehydroxylation of the cation-saturated Wyoming montmorillonites were determined from the Arrhenius relation. Generally, it appears that the activation energies for the dehydroxylation of the Wyoming montmorillonites are not strongly dependent upon the type of interlayer cation present (Fig. 3, Table 3). We note, however, that the activation energy of the Mg-exchanged Wyoming montmorillonite is slightly lower than the other samples studied (Fig. 3, Table 3). The rate of dehydroxylation is also lower in this sample.

Infrared spectroscopy

Infrared spectroscopy was used to monitor the local changes in structure of the 2:1 layer clay mineral on dehydroxylation. Most absorption bands observed could be identified following the work of Farmer (1974). In the region between 400 and 650 cm⁻¹, absorption is due to the Si-O bending vibrations, which are coupled with the octahedral sheet (Stubican and Roy, 1961*a*,*b*) (Fig. 4). On increasing the temperature to 646° C the absorption band at 523 cm⁻¹ decreases in intensity and shifts to a higher frequency. The



FIG. 2. Rate constants (k) for the dehydroxylation of cation-exchanged Wyoming montmorillonites.



Fig. 3. Arrhenius plot giving the activation energy of dehydroxylation for different cation-saturated Wyoming montmorillonites.

small shoulder near 423 cm^{-1} on the main Si-O absorption band also splits into two sharper bands (Fig. 4).

The changes in vibrational modes between 400 and 650 cm⁻¹ in these cation-saturated Wyoming montmorillonites are similar to those seen in pyrophyllite spectra upon dehydroxylation (Bray, 1999), indicating that they may be associated with the formation of an anhydrous dehydroxylate phase. Single crystal XRD of anhydrous pyrophyllite has shown that the coordination of the previously octahedral M2 sites becomes five fold after the loss of structural hydroxyls (Wardle and Brindley, 1972). By analogy, it is reasonable to suppose that the coordination around the M2 sites

TABLE 3. Activation energies determined for the dehydroxylation of the cation-exchanged Wyoming montmorillonite.

Sample	Activation energy		
Ca-Wy	$261 \pm 22 \text{ kJ mol}^{-1}$		
K-Wy	$254 \pm 8 \text{ kJ mol}^{-1}$		
Mg-Ŵy	$175 \pm 20 \text{ kJ mol}^{-1}$		
Na-Wy	$251 \pm 17 \text{ kJ mol}^{-1}$		

becomes five-fold in the cation-saturated Wyoming montmorillonites samples as they are heated and dehydroxylate. All the Na-saturated samples that had been heated in the thermobalance between 646 and 694°C were analysed to determine any changes in the absorption bands over this temperature regime. A slight increase in intensity of the absorption band at 566 cm⁻¹ is seen. By analogy with the results for anhydrous pyrophyllite, this increase reflects changes in the amount of ^[5]Al, suggesting an increasingly reorganized dehydroxylated phase is formed at higher temperatures of reaction (Fig. 4).

The hydroxyl bending absorption bands, seen from 840 to 940 cm^{-1} , reduce in intensity on dehydroxylation (Fig. 5). In addition, new absorption bands, indicative of a dehydroxylated phase, are observed at 731 and 864 cm^{-1} . The changes in Si-O stretching frequencies, noticeably those between 1070 to 1150 cm^{-1} , appear to be dependent on the type of interlayer cation present (Fig. 5). For the Wyoming montmorillonite with either Mg^{2+} or Ca^{2+} in the interlayer region the Si-O_{apical} absorption band near 1080 cm^{-1} at room temperature shifts to 1122 cm⁻¹ at 694°C. This has also been observed in the pyrophyllite samples (Bray, 1999). At higher temperatures (694°C), montmorillonites saturated with K⁺ or Na⁺ show a broad shoulder



FIG. 4. Mid-IR absorption of the four samples before and after dehydroxylation, showing absorption due to Si-O bending modes which are coupled with the octahedral sheet of the cation-exchanged Wyoming montmorillonites. The additional peaks which develop on dehydroxylation are shown by markers in the higher temperature spectra, and may indicate the development of five-fold coordinated cations in the former octahedral sheet.



Fig. 5. Mid-IR absorption at $\sim 1000 \text{ cm}^{-1}$ in the four cation-exhanged montmorillonites before and after dehydroxylation. On dehydroxylation, a broad shoulder emerges on the main Si-O stretching band of the Wyoming montmorillonites containing monovalent interlayer cations. Montmorillonites saturated with divalent cations show an increase in the frequency of the Si-O vibration at 1120 cm⁻¹ (marked by dashed lines and arrow), which may simply be a sharper version of the shoulder seen in the monovalent-saturated samples. Solid lines mark new absorption bands associated with the dehydroxylated phase. Q marks absorption bands due to quartz within the sample.

that appears between 1070 and 1150 cm^{-1} (Fig. 5). This broad perturbation on the Si-O stretching bands may be understood as a consequence of interlayer K⁺ and Na⁺ distorting the SiO₄ network. The large ionic radius of K⁺ (1.33 \AA) makes its penetration into the cavities of the tetrahedral sheets difficult. The same type of broad absorption is also seen in the Na-saturated sample, but is not seen in the Ca-saturated sample. This is despite the fact that Na⁺ has a radius of 0.97 Å, which is much smaller than the radius of Ca^{2+} (0.99 Å), and must imply that Na^{+} resides in a similar environment to the interlayer K^+ in the anhydrous phase. Ca^{2+} and Mg^{2+} can reside at the base of the tetrahedral cavities and the increase in frequency of the vibration at 1080 cm⁻¹ could correspond to the shortening and strengthening of the Si-O_{apical} bonds as the interlayer cation moves towards the octahedral sheet. It seems, from these results, that the main control on the final location of the alkaline earth or alkali cations is their valence rather than their ionic radius.

XRD

The dehydroxylated cation-exchanged Wyoming montmorillonite samples were cooled in air, and then left to rehydrate at room temperature and pressure over 7 days. The basal spacing of these clavs was then recorded on a Guinier X-ray powder diffractometer. The Wyoming montmorillonites with Na⁺ and K⁺ have larger (decrease in 2 θ) d spacings than the Wyoming saturated with Ca²⁺ or Mg^{2+} (Fig. 6) and show broader reflections. This could indicate that, even though Na^+ and K^+ have lower hydration energies than Ca^{2+} or Mg^{2+} , the position of the Na^+ and K^+ interlayer cations is such that rehydration is possible. In contrast, Mg^{2+} and Ca²⁺ appear to have penetrated into the cavities of the outer tetrahedral sheets and cannot readily form hydration spheres.

Conclusions

Generally, montmorillonites lose between 4 and 4.5% of their initial mass upon dehydroxylation.



FIG. 6. XRD patterns (Cu- $K\alpha_1$ radiation) of dehydroxylated montmorillonites left to rehydrate in air for 7 days, showing the basal 001 reflection below 9°2 θ . It appears that the Na⁺- and K⁺-saturated samples rehydrate to some extent, even though these interlayer cations have lower hydration energies than either Ca²⁺ or Mg²⁺.

Only the interlayer countercation type has been varied in this study, so any observed differences are presumed due to the type of interlayer cation present. By fitting the raw mass change vs time data to the general rate equation (equation 1), the reaction order has been determined. Ca- and Mgsaturated Wyoming montmorillonites dehydroxvlate with a predominantly diffusion-controlled (nearer to n = 0.5) rate-determining step. On the other hand, K- and Na-exchanged samples show more first order control during dehydroxylation. None of the models given in Hancock and Sharp (1972) to explain empirical kinetics fully describes the data. Never the less, a valid calculation of activation energy can be made from an Arrhenius plot. The activation energy does not appear to be greatly influenced by the type of interlayer cation present, and is ~250 kJ mol⁻¹ for the K-, Na- and Ca-saturated samples independent of saturating species.

An explanation of the difference in proposed rate-controlling processes could lie in the relationship between the interlayer cations and the collapse of the basal spacing. On dehydroxylation, divalent interlayer cations are positioned at the bottom of the pseudo-hexagonal cavities of the tetrahedral sheet. The spacing of the interlayer region is reduced and the movement of the water molecules formed through the interlayer is characteristically more diffusion controlled. In contrast, monovalent cations such as Na⁺ and K⁺ act as interlayer pillars since they do not migrate into the base of the tetrahedral cavities and, accordingly, the interlayer region does not collapse to the same extent. The movement of water molecules is governed by a first-order control. There is, however, little influence on the activation energy determined.

It is postulated that the SiO_4 network also affects the migration of the water molecules formed, and the activation energy of the process (Bray, 1999). In cis-vacant 2:1 layer silicates, e.g. montmorillonites, the tetrahedral cavities become more distorted, associated with a decrease in the b lattice parameter on dehydroxylation. For clays with trans (M1)-vacant 2:1 layers, such as illites, the tetrahedral sheets are believed to approach a hexagonal arrangement on dehydroxylation (Brav, 1999). The cavities of the tetrahedral sheets are less distorted in illites than in montmorillonites. Furthermore, the activation energy for dehydroxylation in montmorillonites is much greater than for illlites. Therefore, the energetics of the reaction are affected by the

position of the octahedral vacancies, which in turn determines how the tetrahedral sheets distort on dehydroxylation. In general, the rate-controlling process of dehydroxylation is linked to the migration of the water molecules. It appears to be influenced by two major factors: (1) the distortion of the tetrahedral sheet; and (2) the configuration of the interlayer region, for example the close approach of the 2:1 layers. Our studies indicate that the former has a greater influence on the overall activation energy.

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