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EFFECT OF STRUCTURE ON THE MECHANISM OF DEHYDRATION OF CLAY MINERALS

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ABSTRACT

The kinetics of the isothermal dehydration of two clay minerals, attapulgite and powdered vermiculite were studied both in vacuo and in the presence of constant water vapour pressure. The mechanism of dehydration was found to be interfacial where diffusion plays a dominant role and it is called"activated diffusion". A comparison is made with some layered structure clay minerals.

INTRODUCTION

The low temperature dehydration of three layered structure clay minerals[1] namely, vermiculite sheets, montmorillonite and illite was the subject of a previous study in this laboratory[2,3]. The study was concerned with the kinetics and the mechanism of their dehydration. Additional results are presented in this paper on the kinetics and mechanism of dehydration of a chain structure clay mineral, attapulgite, and powdered vermiculite where the layered structure of vermiculite was altered by grinding.

EXPERIMENTAL and MATERIALS

Attapulgite was obtained from Georgia, U.S.A., The vermiculite samples were provided from Vermiculite Industrial Corp. of Egypt and was fractionated to 0.5 mu equivalent spherical diameter.

The kinetics of an isothermal dehydration and thermogravimetric analysis (t.g.a.) were carried out by the use of silica spring of McBain-Bakr type of sensitivity 35 cm/g. Two series of experiments were conducted for each clay mineral, in vacuo, and in the presence of water vapour of pressure 4.8 mm Hg. The procedure for making an isothermal run is described elsewhere[2,3].

The t.g.a. curves were obtained by heating the samples from room temperature to 480°C with controlled linear rate of 2.0°/min.

RESULTS and DISCUSSION

Thermogravimetric analysis

T.g.a. for the two clay minerals studied is shown in Figure 1 where a complete loss of the total water content of the minerals could not be achieved in the temperature range investigated. Complete dehydration and dehydroxylation is achieved only above 800°C. The two thermograms show that the dehydration in vacuo is accelerated below 120°C, whilst beyond that temperature, the presence of water vapour seems to favour its removal, causing an intersection points between the two thermograms obtained in vacuo and in water vapour. Similar observations were reported for vermiculite sheets, illite and montmorillonite.[2,3]

Kinetics of isothermal dehydration

D.t.a. and t.g.a. results indicated that the suitable temperature ranges for the study were 90-260°C for attapulgite and 200-350°C for powdered vermiculite. A typical set of isotherms obtained is shown in Figure 2a for the dehydration of attapulgite heated in water vapour of pressure 4.8 mm Hg. The isotherms obtained were found to obey first order kinetics, Figure 2b. First order plots were also obtained for the dehydration of vermiculite sheets, montmorillonite and illite[2,3]. A summary of the velocity constants, k, and the extent of dehydration w_ℓ/w_o which indicates the ratio of the limiting amount of water lost (w_ℓ) to the total water content of the sample (w_o) obtained by ignition at 1000°C, are shown in Table 1. Table 1 also shows the (k) and w_ℓ/w_o values obtained for vermiculite sheets, montmorillonite and illite samples. The values obtained for the energy of activation were found to be 13-21 kJ mol^{-1} for the two clay minerals studied irrespective of the atmosphere prevailing during the dehydration.

Table 1 shows that the values of the rate constant ,k, and the extent of dehydration ,w_ℓ/w_o, are affected to various degrees by the presence of water vapour for the clay minerals studied. Similar behaviour was reported for the dehydration of kaolinite and bentonite[4,5] It might be argued in this respect that the presence of water vapour could lead to an acceleration of nucleation or nucleus growth[6], and would thus account for the observed effect of increasing the extent of dehydration. This argument does not seem to be valid in the case of clay minerals, because it would lead to a conclusion that a higher

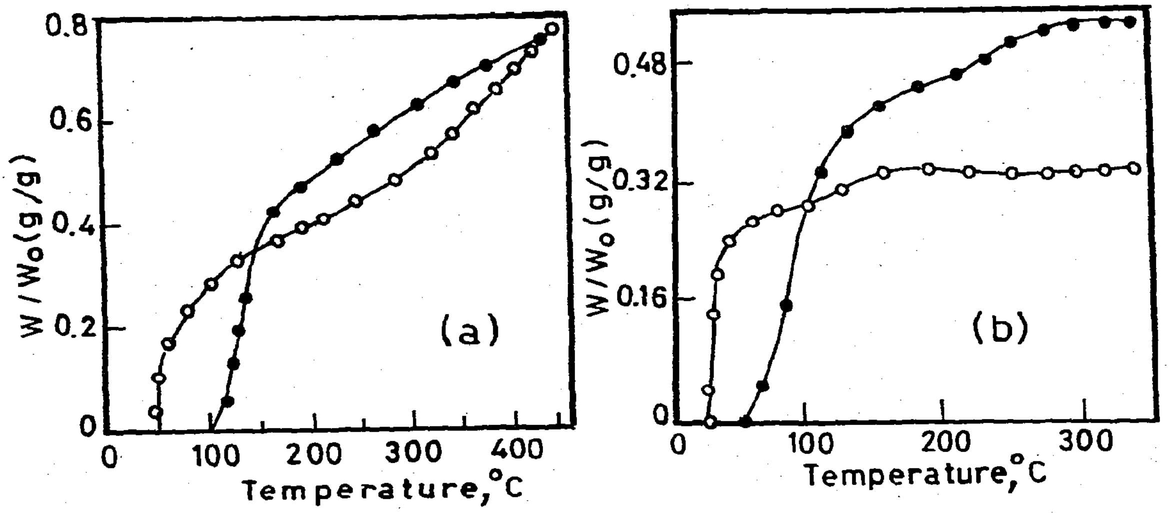

Fig. 1 Thermogravimetric analysis of(a) attapulgite; (b) vermiculite powder, w weight of water lost at a particular temperature; w_o total water content of the sample. o in vacuo; ● in water vapour.

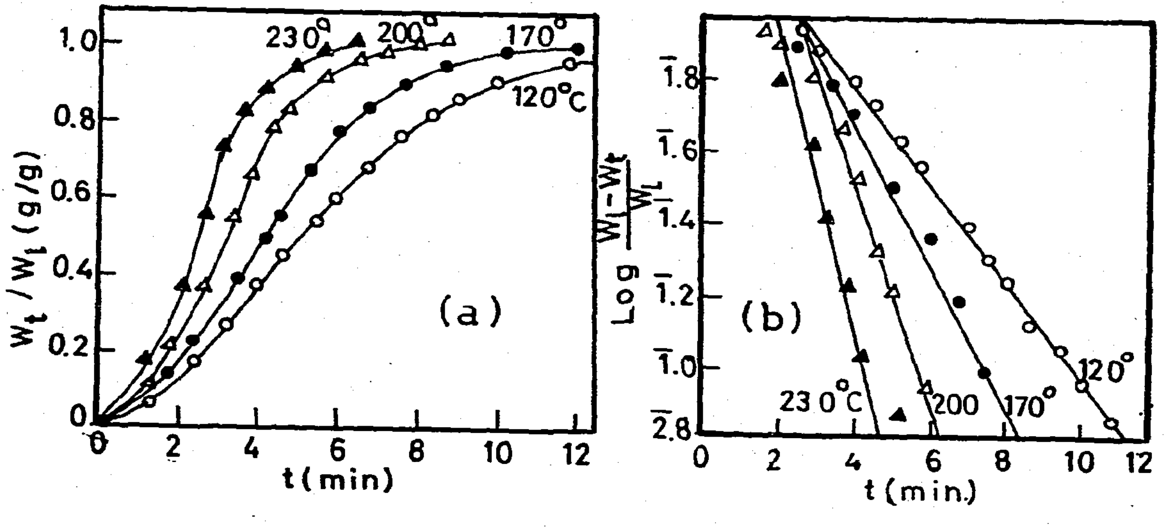

Fig. 2 Isothermal dehydration of attapulgite in water vapour (a) rates; (b) first-order plots. w_t=weight of water lost at a time t; w_ℓ=weight of water lost at a limiting value ℓ.

dehydration rate is expected in the presence of water vapour. In fact the presence of water vapour resulted in a decrease in the rate of reaction and an increase in the extent of dehydration. The explanation suggested is primarily related to the collapse of the

TABLE 1

VELOCITY CONSTANTS(k), THE EXTENT OF DEHYDRATION (w_l/w_o) AND ENERGIES OF ACTIVATION FOR THE DEHYDRATION OF SOME SELECTED CLAY MINERALS.

In vacuo			In water vapour		
Temp. (^oC)	$w\ /w_o$ (g/g)	k x 10^3 (sec.$^{-1}$)	Temp. (^oC)	w_l/w_o (g/g)	k x 10^3 (sec.$^{-1}$)
Attapulgite					
90	0.401	3.7	120	0.406	2.7
120	0.463	5.7	150	0.482	5.9
150	0.474	6.9	200	0.496	7.7
200	0.522	9.6	260	0.513	13.0
230	0.523	12.1			
E_a=13.4 k.J. mol.$^{-1}$			E_a=20.2 k.J. mol.$^{-1}$		
Vermiculite powder					
200	0.441	1.3	240	0.560	1.8
242	0.504	1.7	290	0.614	2.6
290	0.541	1.9	328	0.650	3.1
343	0.636	3.1			
E_a=14.7 k.J. mol.$^{-1}$			E_a=15.5 k.J. mol.$^{-1}$		
Vermiculite sheets					
210	0.497	2.2	200	0.615	1.7
235	0.516	3.4	230	0.638	3.7
277	0.526	8.8	270	0.770	9.2
323	0.530	20.0	340	0.846	12.3
E_a=51.7 k.J. mol.$^{-1}$			E_a=51.7 k.J. mol.$^{-1}$		
Montmorillonite					
90	0.510	2.6	102	0.627	0.12
120	0.510	3.0	132	0.627	0.64
157	0.607	4.7	148	0.632	1.30
185	0.608	6.7	175	0.712	2.57
220	0.613	9.6	190	0.712	5.37
E_a=18.5 k.J. mol.$^{-1}$			E_a=63.8 k.J. mol.$^{-1}$		
Illite					
82	0.145	3.6	98	0.220	0.23
115	0.200	5.0	134	0.330	1.01
185	0.254	6.9	148	0.440	2.30
240	0.273	12.3	170	0.450	3.65
300	0.370	17.2	192	0.475	4.10
E_a=12.6 k.J. mol.$^{-1}$			E_a=52.9 k.J. mol.$^{-1}$		

structure during dehydration and the role played by water vapour is obviously a retarding effect to the mechanical collapse of the structure leading to the acceleration of the water lost. This argument was supported by Walker[7]. Such an interpretation would in fact lead to a loss of a larger fraction of water without affecting the mechanism of the reaction as measured by the values of the energy of activation, Table 1, this is true for vermiculite and attapulgite. As for montmorillonite and illite, the mechanism of dehydration was found to be sensitive to the presence of water vapour.

Interlayer water in clay minerals is held by adsorption forces[8]. Desorption of water is expected to be the rate determining step, unless diffusion barriers are introduced, which would cause the mechanism to be diffusion-controlled[4]. In the presence of water vapour, values of 50-65 k.J. mol.$^{-1}$ were obtained for the energy of activation for vermiculite sheets, montmorillonite and illite, which is comparable with the latent heat of evaporation of water. The desorption of water seems to be the rate determining step. The fact that in the presence of water vapour, the mechanism is not diffusion controlled seems to be associated with a mechanical effect, the water molecules impede the mechanical collapse of the structure on the ellimination of interlayer water, leading to an open structure with no diffusion barriers. The dehydration of an open structure might lead to an apparent increase in the extent of dehydration, representing apparent equilibrium in the adsorption-desorption of water molecules. In vacuo, the mechanism of dehydration for montmorillonite and illite became diffusion controlled, Table 1, is attributed to the collapse of the structure as a result of the contraction of the layer structure providing diffusion barriers to the desorption of water. Since ordinary gaseous diffusion has no energy of activation, thus in the present case the mechanism is "activated diffusion" or "surface diffusion" along the grain bountaries of the product.

As already indicated, a layer structure is absent in attapulgite, and accordingly the "activated desorption" mechanism is absent as well and the "activated diffusion" mechanism became the rate determining step. As a support for this view, when the layer structure of vermiculite was destroyed upon grinding, the value of the energy of activation was reduced to 15 k.J. mol.$^{-1}$, needed for the surface diffusion mechanism.

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