DIFFERENTIAL SCANNING CALORIMETRIC STUDY OF THE KAOLINITE: *N*-METHYLFORMAMIDE INTERCALATE

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Abstract—The thermal decomposition of the kaolinite: *N*-methylformamide intercalate $[Al_2Si_2O_5(OH)_4 \cdot HCONHCH_3]$ has been studied by differential scanning calorimetry (DSC). The decomposition starts at 355 K, finishes at 450 K and follows Avrami–Erofeev kinetics for $\alpha = 0.04$–0.96. ΔH for the loss of organic is 19 ± 2 kJ mol^{-1}; the activation energy for the reaction is 30 ± 3 kJ mol^{-1}.

Key Words—Intercalate, Kaolinite, Methylformamide.

INTRODUCTION

The intercalation of polar organic molecules into kaolinite (Figure 1) has received much attention (Theng, 1974) and of these intercalates the *N*-methylformamide (NMF) complex is one of the most well studied. Infrared investigations (Olejnik et al., 1971; Cruz et al., 1970) have shown that the amide oxygen is an acceptor in the hydrogen bonds formed from the inner surface hydroxyls of the clay layer, but that technique was incapable of resolving whether the NMF is itself weakly associated when intercalated or whether weak N—H . . . O hydrogen bonds are formed between the amide and the tetrahedral oxygens of the next silicate layer. One-dimensional X-ray studies on this system (Olejnik et al., 1970; Weiss et al., 1963, 1966) show that the oxygen atoms of the NMF molecules are sufficiently close to the clay OH groups to accept hydrogen bonds. It is also clear that the molecules are oriented such that the N—H vector points towards the silicate oxygens, again suggesting the formation of N—H . . . O bonds. The kinetics of the intercalation process itself have been studied (Hach-Ali and Weiss, 1969) using X-ray powder diffraction as a monitor and have been shown to obey the Avrami–Erofeev equation $\{[-\ln(1 - \alpha)]^{1/2} = kt\}$ until $\alpha = 0.8$, with an activation energy of 149 kJ mol^{-1}.

In this investigation the stoichiometry of the intercalate was studied by thermo-gravimetric analysis (TGA) to ascertain if the type of bonding found in the dickite:formamide intercalate (Adams and Jefferson, 1976)—which implies a 1:1 clay:organic ratio—is also maintained with the larger but analogous molecule. The kinetics of the process of loss of organic from the intercalate were also studied by DSC to ascertain if diffusion control is important or whether other solid-state kinetic formulations are more applicable.

EXPERIMENTAL

The intercalate was prepared by immersing a sample of kaolinite (obtained from the Greensplatt pit, St. Aus-

tell) in excess NMF for 3 days. The liquid was decanted and the sample dried in an oven at 60°C. A Stanton–Redcroft TG-750 was used for TGA and a Perkin–Elmer DSC1b for the evaluation of solid-state kinetics using the method of Thomas and Clarke (1968). In both cases, heating rates were 2 deg min^{-1} with nitrogen flow rate of 25 cm^3 min^{-1}. A Philips PW1050 vertical diffractometer was used for powder X-ray data and a Pye Unicam SP1000 for infrared.

RESULTS

Initially the intercalate was dried for 2 days. A TGA run showed (Figure 2) that there were three weight loss processes: (i) 1½%, starting at room temperature, (ii) 7%, starting at 310 K, and (iii) 14% starting at 355 K. The initial change was taken to be due to loss of very loosely bound (physically adsorbed) material, the second loss to the rather more strongly bonded organic species and the final process to the decomposition of the intercalate. The stoichiometry of the intercalate then is $Al_2Si_2O_5(OH)_4 \cdot (HCONHCH_3)_{0.95}$. The sample was reheated at 60°C for a further 36 hr and the TGA trace now showed only the loss starting at 355 K. A powder X-ray pattern taken with this sample showed that the intercalate had not decomposed (i.e. the basal spacing was still 10.8 Å, with no 7.16 Å peak apparent) into kaolinite. Infrared spectra, both of the 2-day heated sample (I) and the final (3½-day heated) sample (II) showed the expected peaks due to NMF but for the final sample the peaks were much sharper. It appeared that shoulders were lost from the sides of the amide peaks after this further period of heating. For the C═O stretch at 1693 cm^{-1}, the shoulder for I was at 1675 cm^{-1} and was almost equal to the main peak in intensity.

DSC runs on I showed two overlapping endotherms which corresponded to the 7 and 14% weight loss processes. The final sample (II) only showed one endotherm (Figure 3) which started at the same temperature as the high weight loss process (as recorded by TGA).
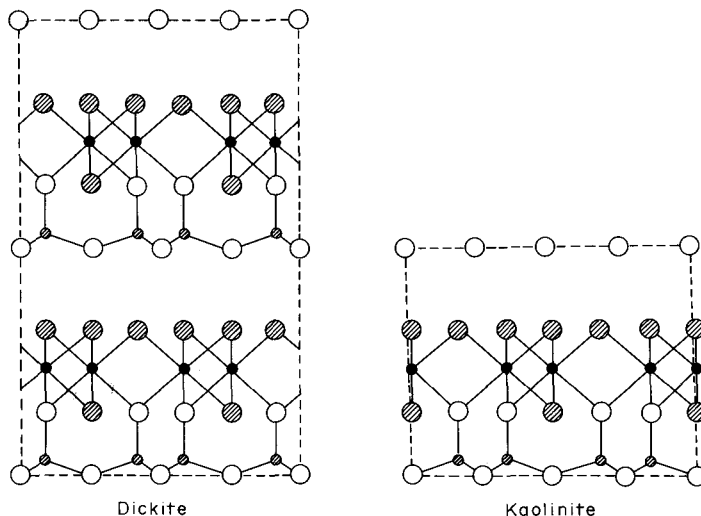
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Fig. 1.   Projection of the structures of kaolinite and dickite along the a-axis.

Provided that the sample was well powdered, the baseline under the peak could be interpolated easily. The area of the peak gives directly ΔH for the reaction provided the instrument is calibrated with a known standard (tin was used—the known heat of fusion is 60.7 J g^{-1}). Over many runs $\Delta H = 19 \pm 2$ kJ mol^{-1}.

The processing of the kinetic data was undertaken following the methods of Thomas and Clarke (1968) and Guarini and Spinicci (1972).

We have for DSC

$$d\alpha/dt = 1/\Delta H \; dH/dt,$$

where α is the fraction of reaction completed at time t.

Now (see Figure 3)

$$\Delta H = A \; R/S \; 1/W,$$

where A is the total peak area (cm^2), R is the sensitivity

(mJ s^{-1}), S is the chart speed (cm s^{-1}), W is the chart width (cm), and

$$dH/dt = R/W \; h_t,$$

where h_t is the deflection of the peak from the baseline at time t (cm). Therefore

$$d\alpha/dt = 1/A \; S h_t.$$

For the Avrami–Erofeev kinetic law (Gawley and Jacobs, 1960) with $n = 2$ [a kinetic formulation often followed for solid-state reactions, especially for reactions involving intercalation (Hach-Ali and Weiss, 1969; Riekel and Schöllhorn, 1976)] i.e. $-\ln(1 - \alpha) = (kt)^2$ we can obtain by substitution

$$k = h_t S/2(A - A_t) \cdot /\ln[A/(A - A_t)]^{1/2}$$

where A_t is the area of the curve integrated up to time t.
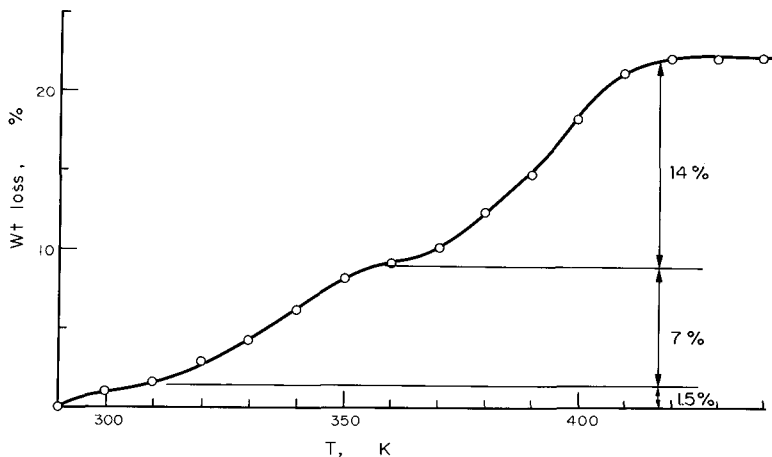

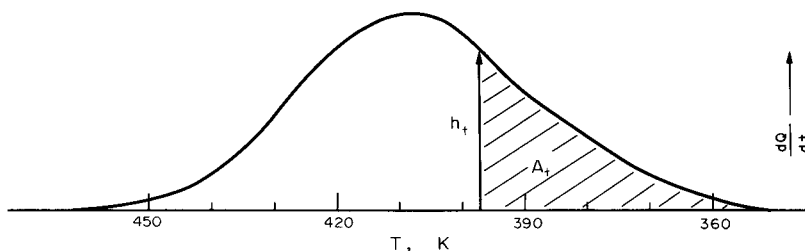Fig. 2.   TGA trace for the kaolinite:NMF complex (dried at 60°C for 2 days).

Fig. 3. DSC curve for the loss of NMF from the intercalate.

Similar expressions can be derived for other kinetic formulations.

Using data from the endotherms (Figure 3) and equations for k derived in the manner outlined above, plots of $\log k$ vs. $1/T$ were made. It was found that the plots gave straight lines over a wide range of α (0.04–0.96) for the Avrami–Erofeev law with $n = 2$ (Figure 4), whereas other kinetic equations gave nonlinear plots. The activation energy derived for the loss of the NMF from the kaolinite was found to be 30 ± 3 kJ mol^{-1}.

DISCUSSION

The orientation of the NMF molecules with respect to the aluminosilicate layers deduced previously from X-ray powder diffraction patterns resembles that found for formamide in the kaolinite:formamide complex. The distance of the molecules from the layers is also similar. Now the full three-dimensional crystal structure of a kaolin mineral:formamide intercalate has been elucidated [for dickite:formamide (Adams and Jefferson, 1976)] and the bonding from the organic to the octahedral layer of the mineral is known (Figure 5). An analogous bonding scheme would give a stoichiometry $Al_2Si_2O_5(OH)_4 \cdot NMF_{1\cdot 0}$, which is in satisfactory agreement with the experimental value. This stoichiometric

factor, then, while not of itself confirming this type of bonding, when combined with the X-ray evidence, certainly supports it.

The activation energy for the loss of the organic from between the sheets is much less than the activation for the reverse process (30 kJ mol^{-1}, 149 kJ mol^{-1}). This is not altogether surprising since this activation energy is likely to be related to the energy required to break the bonds between single NMF molecules and the clay sheets—whereas in the intercalation process itself, the first prising open of the layers requires either (with rigid sheets) the breaking of all the bonds between the sheets or the breaking of some of these bonds together with distortion of the sheets themselves.

The Avrami–Erofeev kinetic law is based on random nucleation (no preferential surface growth) followed by growth of the nuclei, at the later stages of which it is assumed that nuclei overlap. In other terms, the process in this case might be typified, (i) loss of a part of the NMF between some of the layers (nucleus formation), (ii) increase in the loss of NMF in the layers where there are already nuclei and concurrently loss of some organic from between the layers previously not affected (growth of nuclei and also more nucleus formation) and, (iii) eventually between each layer there will only be a
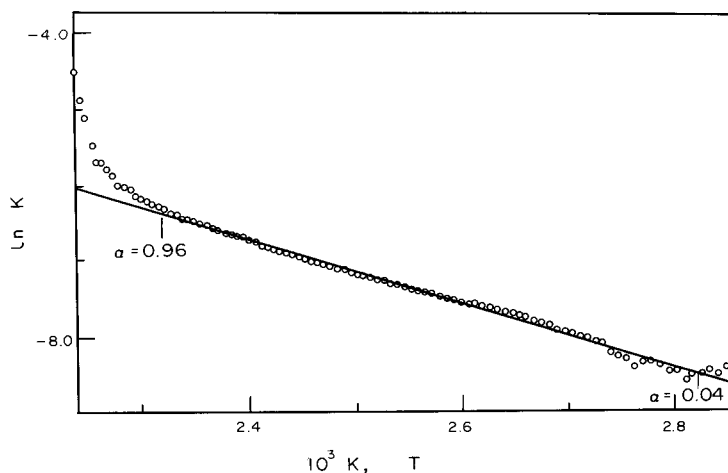

Fig. 4. Arrhenius plot from the DSC data of Figure 3. Avrami–Erofeev kinetics ($n = 2$).
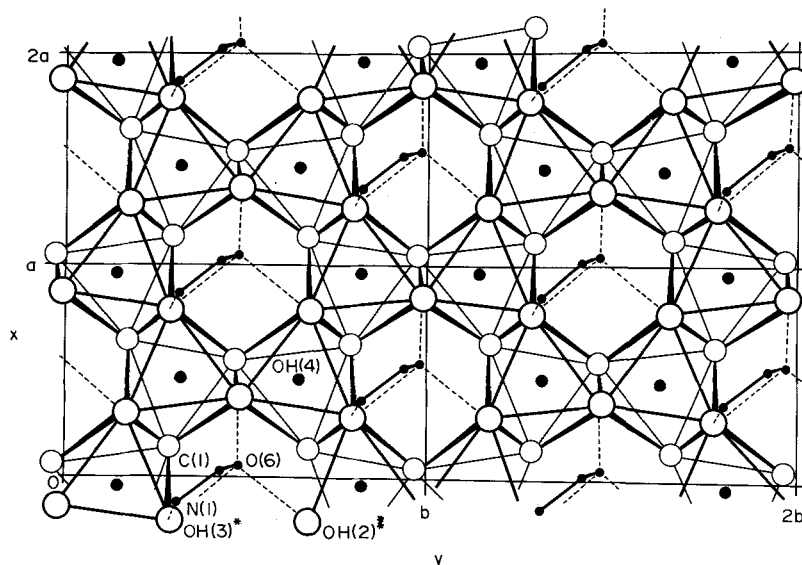
Fig. 5. Projection of the formamide molecules and the octahedral part of the clay layer on to the basal surface for the dickite:formamide intercalate.

few organic molecules left propping the layers apart (the nuclei have overlapped). These last molecules leave and the layers collapse.

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Резюме– С помощью термического разложения каолинита изучались прослойки N-метилформамида ($Al_2Si_2O_5(OH)_4 \cdot HCONHCH_3$) методом дифференциальной развертывающей калориметрии. Разложение начинается при 355°К, заканчивается при 450°К и следует кинетике Аврами-Ерофеева для $\alpha = 0,04-0,96$. ΔН в связи с потерей органики равно 19 ± 2 кдж мол$^{-1}$. Энергия активации для реакции равна 30 ± 3 кдж мол$^{-1}$.

Kurzreferat– Der thermische Zerfall des Kaoliniten: N-methylformamid-zwischengelagert ($Al_2Si_2O_5(OH)_4$ $HCONHCH_3$) ist mit Differentialkalorimetrie untersucht worden. Der Zerfall beginnt bei 355 K, endet bei 450 K und folgt Avrami-Erofeev Kinetik für $\alpha = 0,04-0,96$. ΔH für den Verlust von organischen Material ist 19 $\pm$2kJ Mol^{-1}. Die Aktivierungsenergie für die Reaktion ist 30 $\pm$3kJ Mol^{-1}.