Thermochimica Acta, 118 (1987) 295–303
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL BEHAVIOUR OF INTERCALATED KAOLINITE

P. SIDHESWARAN, P. GANGULI * and A.N. BHAT

Hindustan Lever Research Centre, Andheri (East), Bombay 400099 (India)

(Received 10 March 1987)

ABSTRACT

The thermal decomposition of potassium salts of acetic, malic, malonic, benzoic, succinic and butyric acids and urea was investigated using TGA, DTA and DSC, before and after intercalation with the hydrazine hydrate–kaolinite system. Substantial reductions in the temperature of decomposition of the salts were noticed for the intercalates and the mixtures. Smectites, SiO_2 and alumina, the building blocks of clays, also induced reductions in the temperatures of decomposition. The catalytic role of clays in lowering the temperature of decomposition of the potassium salts is thus clearly indicated.

INTRODUCTION

Certain organic compounds can enter into the kaolinite interlayer and expand the C spacing from the 7.13 Å of $d(001)$ to about 10.5 Å. This intercalation may be effected either by direct mixing (as in the case of urea) or by using an entrainer such as hydrazine hydrate, DMSO, etc. [1–4]. In an earlier investigation [5], infrared and XRD studies of intercalates of kaolinite with potassium salts of organic acids have been reported. Though the thermal behaviour of kaolinite has been well documented [6], thermal studies of intercalated kaolinites have not so far appeared. Hence, an attempt has been made to explore the behaviour of intercalated kaolinite.

Upon heating kaolinite, the hygroscopic moisture, if any, is lost at temperatures up to about 150 °C. The structural water expected from the formula $(OH)_8Si_4Al_4O_{10}$ amounts to 13.96% and the dehydroxylation occurs by an endothermic phase transition at 450–600 °C. Eventually metakaolinite is produced [6]. At higher temperatures ($> 1010\,^\circ C$) a characteristic reaction occurs which presumably results in mullite crystallisation.

The basic objectives of the present study are: (a) to examine the thermal behaviour of intercalated kaolinite in comparison with that of a physical mixture of the salts and kaolinite; (b) to explore the role of the substrates, if any, in the thermal decomposition patterns of the salt and the intercalate.

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* To whom all correspondence should be addressed.

0040-6031/87/$03.50

EXPERIMENTAL

Materials

Kaolinite was obtained from English India China Clay (Kerala). Urea, benzidine and potassium acetate were of reagent grade. In the case of the salts (such as succinate, malate, malonate, benzoate, and *n*- and *iso*-butyrates) the corresponding acid was neutralised with KOH solution to a pH of 8.7 ± 0.1 and the water removed by evaporation.

Intercalation

Intercalation was carried out as follows: 17 g of the salt was dissolved in 20 ml (in some particular cases, such as those of potassium benzoate and benzidine, 40 ml were used) of the entraining agent (hydrazine hydrate) and the solution was added slowly to 83 g of kaolinite with stirring. The reaction was highly exothermic and required cooling to maintain the temperature below 35 °C. In intersalation hydrazine hydrate was replaced by water and the products were dried at 105 °C for about 2 h.

Substrates

In addition to kaolinite, the following substrates were also used in the current investigations.

SiO_2: alkaline silicate (5% SiO_2) solution and dilute H_2SO_4 were mixed and the pH adjusted to 7.0. After overnight gellation, the gel was washed with distilled water and dried at 120 °C.

α-Alumina: Catapal SB (Conoco Chemical Co.) was heated to about 450 °C and the resulting product was used directly.

Silica–alumina: silica gel prepared as described above was mixed with $Al_2(SO_4)_3$ solution and allowed to age for a day, then filtered and washed free of the counterions. It was then dried at 110 °C and used.

Calcium bentonite: commercial bentonite (Asiatic Trading Co.) was Na exchanged by treatment with Na_2CO_3 solution. The solid portion of the resulting slurry was washed and dried before use.

Zirconium pillared clay: swelling type bentonite (Asiatic Trading Co.) was treated with $ZrOCl_2$ solution as described elsewhere [7] and the pillared smectite was washed free of the auxiliary ions and dried before use.

Instrumentation

Intercalation behaviour was monitored by XRD (D-500 Kristalloflex, Siemens X-ray diffractometer) using Cu$K\alpha$ radiation. Differential thermal analysis (DTA), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments on the salts, clay and their intercalates were performed using a 990 Du Pont Thermal Analyser.

RESULTS AND DISCUSSION

Characterisation of kaolinite

In an earlier communication, certain aspects of the characterisation of kaolinite were described. The characteristics of the kaolinite sample used in the current studies were as follows: (a) C-axis spacing 7.2 Å (from XRD); (b) characteristic IR bands at 3696 (s), 3619 (s), 3670 (w) and 3653 (w) cm^{-1} (from FTIR); and (c) loss of weight due to dehydroxylation 13.96% (from TGA).

Endothermic dehydroxylation peaks at about 530–540 ° C were observed in DSC whereas in DTA this feature was noticed at 530 ° C (Fig. 1). DTGA showed an endothermal effect at about 525 ° C. The dehydroxylation temperature observed matches the range of values reported in the literature [3] for kaolinite. DTA also gave an exothermal peak at about 1010 ° C, associated with mullite crystallisation.

Metakaolinite formation was detected by the loss of the characteristic XRD pattern when kaolinite was heated to about 550 ° C; similar behaviour has been described elsewhere [3,4]. The clay used was free of quartz and crystobalite and thus the sample was pure enough for our studies.

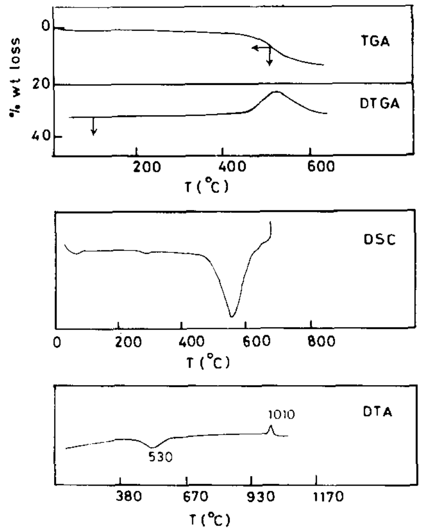

Fig. 1. Thermal behaviour of the kaolinite sample used.

Thermal behaviour of the salts

The pure potassium salts decompose on heating at significantly higher temperatures than the intercalated salts. Thus potassium acetate, for example, decomposes over the range 450–520 °C (Table 1). However, when this salt is entrained and intercalated in the kaolinite interlayer, its thermal behaviour (as measured by DSC) shows that the decarboxylation temperature has fallen to 385 °C — a significant drop. These results are presented in Table 1. It is evident that the endothermal dehydroxylation peak specific for kaolinite changes only marginally and remains in the range 520–550 °C. In a study carried out elsewhere [3] on kaolinites ground to various sizes, a variation of about 70 °C in dehydroxylation temperature has been recorded.

The TGA data for the salts are presented in Table 2. The loss on ignition (LOI) noticed with these salts was as expected on the basis of their structure; the ignition leads to K_2CO_3 as the final decomposition product.

Nature of the decomposition product

As the salts decompose, a basic material results. The exothermic decomposition of the potassium salts results in the formation of K_2CO_3. This was established in two different ways.

TABLE 1

Thermal data on intercalation [a]

System intercalated	Characteristic region sought			Remarks
	Kaolinite dehydroxylation peak (endo) (°C)	Decarboxylation peak of the entrained salt (exo)		
Kaolinite only	525–540	–	–	Exotherm at ~1010 °C
Potassium acetate	(525)	450–520,	(385)	–
Potassium succinate	(525)	520,	(220–400)	Broad exotherm for intercalation
Potassium malate	(530)	380–500,	(230–420)	–
Potassium malonate	(550)	400–560,	(375–450)	–
Potassium benzoate	(520)	480–575,	(430–530)	–
Urea	–	420,	(nil) –	No exotherm for decarboxylation of urea

[a] Results in parentheses are for intercalates.

TABLE 2

Thermal characteristics of the decomposition of butyrates, with and without support [a]

Compound	Support material	Thermal characteristics		Reduction in the decomposition temperature (°C)
		TGA: LOI, 700 °C (%)	DTA: decomposition peak temperature (°C)	
KBA	Kaolinite	30	370(495)	125
KIBA	Kaolinite	35	350(550)	200
KBA	Ca bentonite	27	358(495)	137
KIBA	Ca bentonite	27	360(550)	190
KBA	Zr PC	29	346(495)	149
KIBA	Zr PC	27	332(550)	218

[a] Temperatures in parentheses are for the salts alone.

(a) A known weight of the sample was ignited to about 700 °C in a muffle furnace and the weight of the final residue determined. The loss in weight corresponded to the formation of K_2CO_3. (b) The XRD pattern of the ash (Fig. 2) was identical with that of K_2CO_3.

TGA experiments confirm that the formation of K_2CO_3 is quantitative. In the cases of benzidine and urea, the salts decompose to give gaseous products.

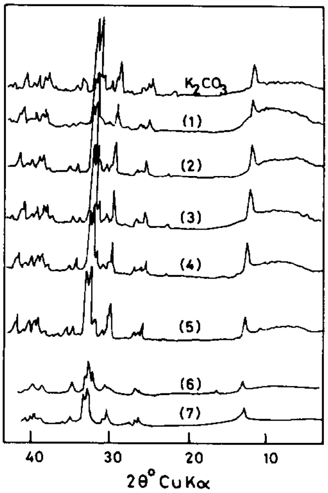

Fig. 2. XRD patterns of ignited (700 °C) masses of K_2CO_3 and of various potassium salts: (1) succinate, (2) malonate, (3) malate, (4) benzoate, (5) acetate, (6) *n*-butyrate, (7) *iso*-butyrate.

Thermal behaviour of intercalates

In an earlier study we noted that certain organic salts do not become intercalated in the interlayer, in spite of using an entrainer like hydrazine hydrate. Typical examples of this category are potassium salts of *n*- and *iso*-butyrates and benzidine. However, certain other organic salts, such as the potassium salts of acetic, succinic, malic and benzoic acids and urea can readily form intercalates. Potassium malate may be taken as a fairly typical example for the present discussion. It decomposed over the temperature range 380–500 ° C when heated alone (Table 1). However, upon intercalation the decarboxylation phenomenon took place at a much lower temperature (230–420 ° C, Fig. 3). Similar reductions in the temperatures of decomposition were also found for other organic acid salts in the form of intercalates (Table 1).

By and large, the decarboxylation temperature was altered significantly in all cases, while the dehydroxylation temperature changed by only about 30 ° C. Minor changes around this figure for the dehydroxylation temperature can be ascribed to variations in particle size, as shown by earlier studies elsewhere [3]: thus, for example, a variation of about 90 ° C was reported recently by Aglietti et al. [7].

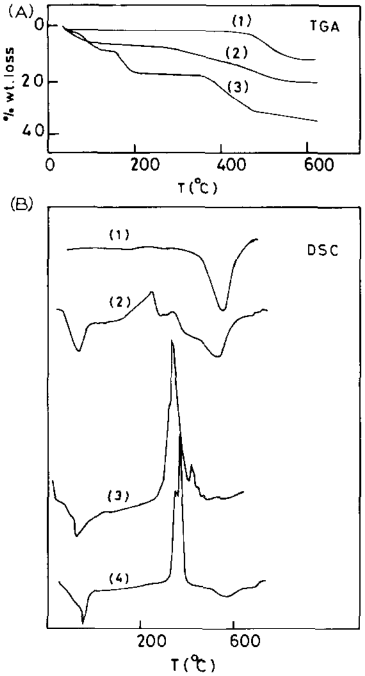

Fig. 3. Thermal patterns ((A) TGA and (B) DSC) of the potassium malate system: (1) kaolinite, (2) intercalated malate, (3) potassium malate, (4) physical mixture of kaolinite and potassium malate.

Thermal behaviour of non-intercalating systems

Attempts at intercalating the potassium salts of malonic and butyric acids, etc., with kaolinite via the hydrazine hydrate route failed. It was, however, considered worthwhile to investigate the thermal behaviour of these systems. The results obtained for the butyrates are presented in Fig. 4. The TGA and DTA studies made with potassium butyrate (KBA) and potassium isobutyrate (KIBA) show the following: (a) though KIBA as such decomposes at 550 °C upon "mixing" with kaolinite, the decomposition temperature drops to 350 °C (DTA) as shown in the TGA curves; (b) the drop in decomposition temperature in the case of KBA is about 125 °C. The data obtained for the butyrates are also listed in Table 2.

Role of clay-based substrates

Since the decomposition temperatures of the potassium butyrates fell in the presence of kaolinites, the study was extended to include the use of

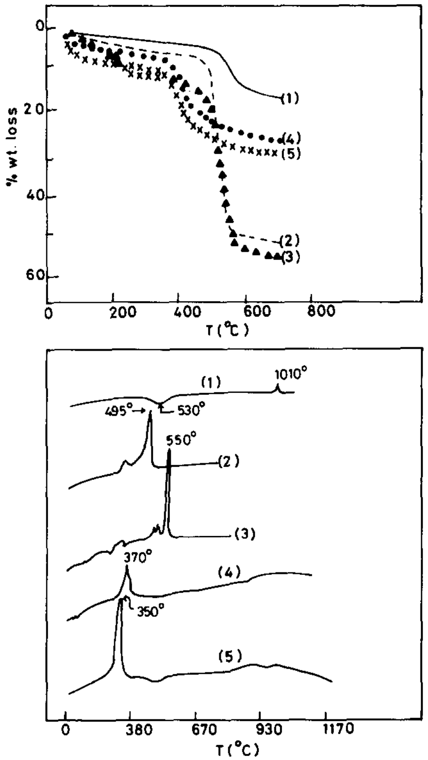

Fig. 4. Thermal behaviour of the potassium butyrate (non-intercalating) systems: (1) kaolinite (K), (2) KBA (potassium butyrate), (3) KIBA (potassium isobutyrate), (4) K + KBA, (5) K + KIBA.

calcium bentonite and zirconium pillared clays as substrates. Even these clay-based substrates showed a behaviour similar to that of kaolinite. This gave us a clue that substrate participation is vital in the clay-catalysed decomposition of organic salts. The results are presented in Table 2.

Participation of the components of clay

The decomposition temperatures of the organic salts were reduced in both intercalates and non-intercalated systems by the presence of kaolinite and smectite-based clays. As the major components of these materials are silica and alumina, an examination of the influence of these ingredients individually on the thermal decomposition of the organic salts was also undertaken. Potassium succinate was chosen for this part of the study and was mixed with alumina, silica and alumina–silica. The DSC results are presented in Figs. 5 and 6.

In all the cases examined, the catalytic influence of these surfaces was reflected in a decrease in the decomposition temperature of potassium succinate. Thus the clay catalysis may occur because of the presence of silica

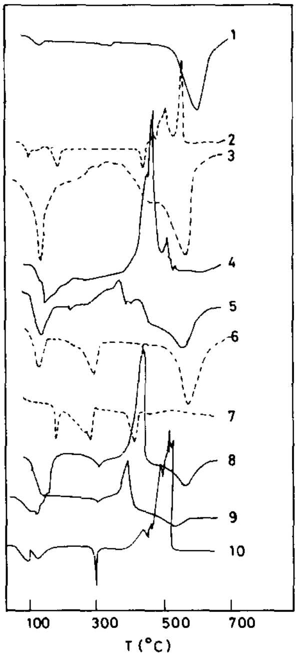

Fig. 5. DSC curves of the clay–organic systems: (1) kaolinite, (2) potassium succinate, (3) potassium succinate intercalate, (4) potassium malate, (5) potassium malate intercalate, (6) urea intercalate, (7) urea, (8) mixture of potassium acetate and kaolinite, (9) potassium acetate intercalate, (10) potassium acetate.

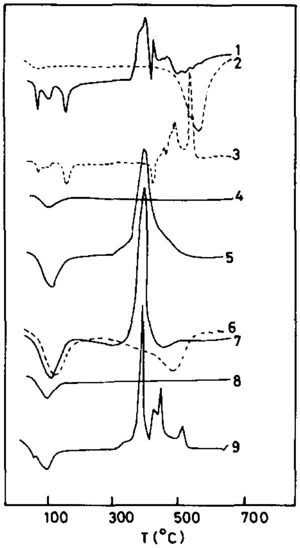

Fig. 6. DSC studies of the role of the inorganic matrix: (1) potassium succinate–kaolinite mixture, (2) kaolinite, (3) potassium succinate, (4) silica, (5) potassium succinate + SiO_2, (6) alumina; (7) alumina + potassium succinate, (8) silica–alumina composite, (9) mixture of silica–alumina composite and potassium succinate.

and alumina, the building blocks of kaolinite and smectites. Presumably the surface acidity of the solid matrices triggers the mechanism of clay catalysis — an aspect which has not yet been investigated. Further study along these lines will be required to establish a detailed mechanism for the phenomena observed.

REFERENCES

1 B.K.G. Theng, The Chemistry of Clay–Organic Reactions, Adam Hilger, London, 1974.
2 L. Fowden, R.M. Barrer and P.B. Tinker, Clay Minerals: Their Structure, Behaviour and Use, Proc. R. Soc. London Discuss. Meet., 9–10 November, London, 1984, The Royal Society, London.
3 R.E. Grim, Clay Mineralogy, McGraw-Hill, New York, 1968.
4 R.W. Grimshaw, The Chemistry and Physics of Clay and Allied Ceramic Materials, Ernest Benn, London, 1971.
5 P. Sidheswaran, S.V. Ram Mohan, P. Ganguli and A.N. Bhat, Indian J. Chem., in press.
6 R.C. Mackenzie, The Differential Thermal Investigations of Clays, Mineralogical Society, London, 1957.
7 E.F. Aglietti, J.M. Porto Lopez and E. Periera, Int. J. Miner. Process., 16 (1986) 125.