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THERMAL DECOMPOSITIONS OF KAOLINITE INTERCALATION COMPOUNDS

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Through a combination of X-ray diffraction and thermal analysis (simultaneous TG–DTG–DTA and quasi-isothermal TG), it was shown that the molar ratio intercalation agent/kaolinite in all intercalation compounds is approximately 1. In a saturated atmosphere of the corresponding intercalation agent, the intercalation compounds are stable up to more than 150 °C.

Decomposition of the potassium acetate intercalation compound proceeds simultaneously with the dehydroxylation of kaolinite at an extrapolated onset temperature of 360 °C. The high-temperature reactions (dehydroxylation and transformation) of kaolinite obtained through the decomposition of intercalation compounds with volatile intercalation agents depend on the conditions applied during decomposition.

The treatment of ordered kaolinite at room temperature with an excess of compounds which have a strong tendency to hydrogen-bonding (e.g. hydrazine or formamide) and/or dipole-dipole interaction (e.g. dimethylsulfoxide) leads spontaneously to the formation of kaolinite intercalation compounds (IC's). Similarly, salts of lower fatty acids with large cations (e.g. potassium acetate) also form IC's. From structural considerations [1–9], it follows that the molar ratio (MR) between the intercalation agent (IA) and kaolinite (formula unit $Al_2Si_2O_5(OH)_4$) in the IC's should be MR = 1. Only a few investigations are known which deal with the thermal behaviour of IC's [10, 11] and from which the MR can be confirmed. The thermal stabilities of IC's, the character of the solid decomposition products and the stoichiometry of the IC's form the subject of this investigation.

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Experimental

A washed kaolin from the Caminau deposit (GDR), with the mineralogical composition 87.5% kaolinite (well-ordered), 1.5% quartz and 11.0% mica, was used for the preparation of different IC's. The following IA's were applied: dimethylsulfoxide (DMSO), formamide (FA), hydrazine hydrate (HH) and potassium acetate (KAc).

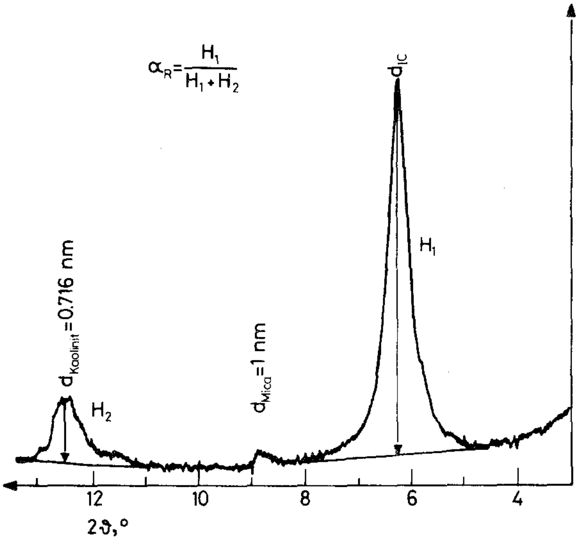

Fig. 1 X-ray diagram of IC to determine the degree of intercalation α_R. d_{IC}-values (in nm): kaolinite – DMSO = 1.12, —FA = 1.01, —H = 1.04, —KAc = 1.40 (CuK$_\alpha$ – radiation)

For the formation of the IC, 3 g of the kaolin was gently mixed with 6 ml of the IA in a mortar. The reaction process was followed by X-ray diffraction (XRD), with measurement of the intensities of the 001 reflexes of kaolinite and the corresponding IC (Fig. 1), and determination of the degree of intercalation α_R. These measurements indicated that the formation of the IC was completed after a standing period of 24 h at room temperature (or 80° in the case of DMSO) in a closed vessel. The thermal behaviour of the reaction products was investigated by using a Q 1500 D derivatograph (MOM, Budapest) under dynamic and quasi-isobaric quasi-isothermal conditions (Table 1).

Table 1 Experimental conditions for Derivatograph Q 1500 D

Type of heating	Dynamic	Q
Sample size	0.2–0.4 g	0.2–0.3 g
Sample holder	corundum crucible Ø ~13 mm	labyrinth-crucible
Reference material	α-Al_2O_3	—
Furnace atmosphere	air, N_2	quasi-isobaric
Flowing rate	10 l/h	—
Heating rate	5 deg min^{-1}	quasi-isothermal

Results and discussion

1. Temperature region 20° to 300°

In DTA and DTG, 3 endothermic effects were observed for all mixtures (Fig. 2).

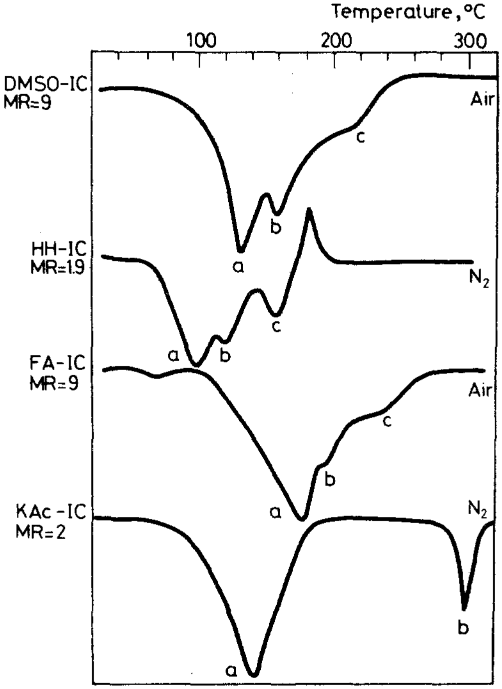

Fig. 2 DTA-curves in the region 20° to 300°
Explanation in the text.
KAc—IC: peak b = melting point of KA$_c$,
peak c above 300 °C (see Fig. 4)

The effects can be assigned to the following processes:

a) Evaporation of water + IA (or water influenced by IA).

b) Evaporation of IA or melting of IA (KAc).

c) Decomposition of IC.

The corresponding processes were also observed in the thermogravimetric curves taken under Q-conditions for IC's with volatile IA (see Fig. 3). From the Q-diagrams, it can be stated that, under a partial pressure of the IA of $p \approx 1$ bar, the IC's are stable up to the temperatures given in Table 2. Moreover, it follows that the molar ratio in all IC's is MR = 1.

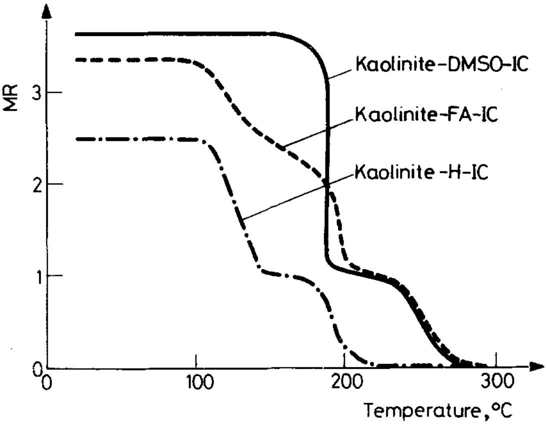

Fig. 3 Quasi-isobaric quasi-isothermal TG curves of: — kaolinite—DMSO—IC, — — — kaolinite—FA—IC, — · — kaolinite—H—IC

Table 2 Thermal stability of IC's

IC	Stable up to, °C	Conditions
Kaolinite-Hydrazine	160	closed system partial pressure ≈ 1 bar
Kaolinite-DMSO	220	
Kaolinite-FA	220	
Kaolinite-KAc	300	N_2-atmosphere, open system

The same conclusion can be drawn for the KAc–IC from DTA curves taken on a sample series with decreasing excess of KAc.

2. Temperature region 300° to 600°

DTA/DTG measurements were performed to examine the influence of intercalation on the dehydroxylation of kaolinite. The reaction of kaolinite with

KAc primarily results in an IC in hydrated form (d_{001} = 1.40 nm). On heating, this IC underwent dehydration; up to 300°, the unhydrated IC with $d_{001} \approx 1.11$ nm is stable. At higher temperature, decomposition of the IC and dehydroxylation of kaolinite take place simultaneously (extrapolated onset temperature 360°). If the decomposition is performed in an N_2 atmosphere, the following reaction products occur: CO_2, $(CH_3)_2CO$, CH_3COOH, H_2O and amorphous $K_2O \cdot 2\,Al_2O_3 \cdot 4\,SiO_2$.

From IC's with volatile IA's heated under dry conditions and without an excess of IA up to 300°, a disordered kaolinite results. Further heating of this kaolinite leads to dehydroxylation at somewhat lower temperatures than for the original kaolinite (see Fig. 4).

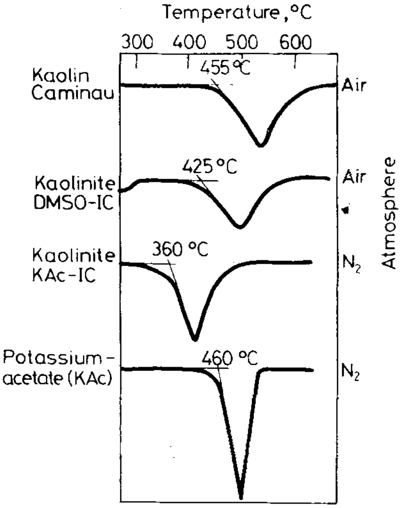

Fig. 4 DTG-curves in the region 300 °C to 600 °C. Explanation in the text

This behaviour is different from that of kaolinite obtained by decomposition of IC's at lower temperatures (< 150°) under normal atmospheric conditions and with vanishing partial pressure of IA. Under these conditions, IC's are decomposed slowly and the following steps have been observed via a combination of XRD and thermal analysis:

a) The molar ratio decreases (MR < 1), but the degree of intercalation remains constant ($\alpha_R \approx 1$).

b) At MR < 0.7, degeneration of 001 interferences to mixed-layer forms can be observed (depending on IA).

c) After the decomposition is completed, a disordered kaolinite remains. The high-temperature behaviour of these products shows no difference compared to the original kaolinite.

3. Temperature region 900° to 1000°

The exothermic peak for disordered kaolinites with lower dehydroxylation temperatures resulting from IC's is shifted by ≈40 deg to lower temperatures compared with the original kaolinite.

The products obtained through the decomposition of KAc–IC do not show any specific reaction in this temperature region.

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Zusammenfassung — Mittels Röntgenbeugung und thermischer Analyse (simultane TG–DTG–DTA und quasi-isotherme-quasi-isobare TG) konnte gezeigt werden, daß das molare Verhältnis Einlagerungsmedium/Kaolinit in allen Einlagerungsverbindungen etwa 1 ist. In gesättigter Atmosphäre des jeweiligen Einlagerungsmediums ist die Einlagerungsverbindung stabil bis über 150 °C. Die Zersetzung der Kaliumacetat-Einlagerungsverbindung läuft zusammen mit der Dehydroxylation des Kaolinits bei einer extrapolierten onset-Temperatur von 360 °C ab. Die Hochtemperaturreaktionen (Dehydroxylation, Phasenneubildung) von Kaolinit, der aus der Zersetzung von Einlagerungsverbindungen mit flüchtigen Einlagerungsmedien erhalten würde, werden von den Zersetzungsbedingungen beeinflußt.

Резюме — Комбинацией рентгено-диффракционного анализа и термического анализа (совмещенный метод ДТА, ТГ, ДТГ и квазиизобарной и квазиизотермической ТГ) показано, что во всех интеркаляционных соединениях каолина молярное соотношение интеркалирующий агент-каолин составляет приблизительно 1. В атмосфере, насыщенной соответствующим интеркалирующим агентом, интеркаляционные соединения устойчивы до температуры выше 150°. Разложение интеркаляционного соединения ацетат калия — каолин протекает одновременно с дегидроксилированием каолина с начальной температурой 360°, найденной экстраполяцией. Высокая температура реакций дегидроксилирования и превращения каолина, полученного разложением его интеркаляционных соединений, зависит от условий процесса разложения.