Thermochimica Acta, 148 (1989) 431–438
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

INTERACTION OF KAOLINITE WITH ORGANIC AND INORGANIC ALKALI METAL SALTS AT 25-1300 °C

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ABSTRACT

The reactions of Georgian kaolinite with saturated solutions of alkali metal chlorides, potassium acetate and with solid salts resp. were followed by XRD, FTIR and TA-MS methods. The results show that in the case of solid MCl and solutions thereof already at room temperature alkali metal ions have been incorporated into kaolinite. The quantity of incorporated cations increased with rising temperature. CH_3COOK was intercalated into the interlayer spaces. The solid state reactions and the gaseous reaction products up to 1000°C were followed by different methods. The crystal phases formed in the course of the reactions between kaolinite and the decomposed salts have been investigated up to 1300°C. The reaction mechanisms on the basis of experimental data and literature are discussed.

INTRODUCTION

The reaction of kaolinite with alkali metal salts was investigated by thermal methods as well as by infrared spectroscopy (1,2,3). The mechanism of the reaction of kaolinite with organic and inorganic alkali salts does not seem to be well understood. Therefore we continued our previous work (4) in studying the reactivity of kaolinite towards alkali salts in solid state and in solutions. The investigated interactions may play a role in several practical applications from soil research to ceramics.

Thermal Analysis Highlights, 9th ICTA, Jerusalem, Israel, 21–25 August 1988.

0040-6031/89/$03.50

EXPERIMENTAL

The kaolinite used in the investigation was from Georgia (4). The alkali salts were of A.R. grade (Reanal). The air-dried kaolinite sample was mixed in an agate mortar with solid alkali chlorides. Other aliquots of kaolinite were treated with saturated salt solutions at room temperature according to Wiewiora et al (5). The K^+- and Na^+-forms of kaolinite were prepared from 1 M alkali metal chloride solutions. The air-dried kaolinite was immersed in alkali metal salt solution in water and shaken for 12 hours. The samples were centrifugated, excess liquid removed and washed out of the electrolyte with isopropyl alcohol. When the test for chloride in the leachate was negligible the kaolinite samples were dried at 100 °C.

XRD studies were performed on a Philips powder diffractometer using CuKα radiation. IR spectra of samples contained in KBr discs were taken on a Digilab FTS 20C and Nicolet FT spectrometer between 4000-40 cm^{-1}. The thermoanalytical investigations were carried out on a Mettler TA-1 instrument connected to a Balzers quadrupole mass spectrometer. The alkali content of some samples was measured by a Perkin Elmer 5000 atomic absorption instrument.

RESULTS AND DISCUSSION

TABLE 1

X-ray powder diffraction data of kaolinite pretreated by potassium salts solutions under heat treatment

Run	Samples pretreated	heat treated up to °C	Main crystalline phases
1		-	kaolinite, TiO_2
2	-	600	metakaolinite, TiO_2
3		1300	sillimanite
4		-	kaolinite, TiO_2, KCl
5	KCl	600	metakaolinite, TiO_2, KCl
6		1300	Al_2O_3, (sillimanite)
7		-	kaolinite-CH_3COOK complexes, kaolinite, CH_3COOK
8	CH_3COOK	600	$KHCO_3$, K_2CO_3
9		1300	$KAlO_2$, (sillimanite)

1/ The kaolinite samples treated by saturated solutions of KCl (pH$\sim$6), CH_3COOK (pH$\sim$9) resp. at 25 °C were examined with XRD. The results (Table 1. Run 4 and 7) show that in the case of KCl the kaolinite phase did not change. In contrast with CH_3COOK kaolinite-acetate complexes were formed. The data revealed the intercalation of CH_3COOK into the interlayer spaces which prises apart the silicate layers. According to a known method (6) at the given experimental conditions the degree of intercalation was only $\sim$58 %, i.e. some part of kaolinite did not react. This means the investigated kaolinite has varying chemical reactivity towards CH_3COOK. Some literature data also showed that the maximum degree of reaction of many kaolins remains below 100 %, even after very long reaction times.

2/ The results of our FTIR measurements in the middle and far-IR are presented in Table 2. The spectral features of Na^+- and K^+-kaolinites in the middle IR range are similar to the original clay, while in the far-IR differences were observed. The appearance of new bands at 180, 150 cm^{-1} resp. is accompanied by reduction of the intensity of the band at 195 cm^{-1} which was attributed to interlayer vibration of kaolinite lattice (7). The reduction intensity of the latter band may be the result of incorporation of alkali ions, capable of causing distortion of interlayer vibration. Thus the band at 150 and 180 cm^{-1} may be due to vibrations of Na^+ and K^+ in the interlayer spaces of kaolinite. The reduced intensity of the interlayer vibration band indicates the smaller amount of incorporated Na^+ in comparison with K^+. By chemical analysis it was proved that the Na^+-kaolinite contains 1.75 % Na^+, while the K^+-form had 4.42 % K^+. The original kaolinite contained 0.04 % Na^+ and 0.05 % K^+. By heating the mixture of kaolinite + NaCl at 400 °C for 60 min about 1.7 % Na^+ incorporation has been achieved. Spectra in middle- and far-IR of kaolinite pretreated with saturated salt solutions and heated up to 400 °C revealed also that, in comparison with Na^+- and K^+-kaolinites prepared by ion exchange method, alkali metal ions have been incorporated in larger amounts into kaolinite.

The most interesting IR features were observed for kaolinite pretreated with saturated CH_3COOK solution. The spectra showed four bands in the OH region which is in accordance with an earlier report (8). The disappearance of the band of hydrogen-bonded OH within the layers, the increasing intensity of the hydrogen-bonded OH between layers and also the occurence of three new bands indicate the formation of the acetate-kaolinite complex. The presence of the triplet and a doublet

TABLE 2

Position IR bands (in cm^{-1}) for kaolinite samples pretreated with the saturated solutions of salts at 25^0 and thermally treated

Pure kaolinite		K$^+$-kaolinite	Na$^+$-kaolinite	Kaolinite +10% NaCl (mixture)		Kaolinite with KCl solut.		Kaolinite with NaCl solut.		Kaolinite with CH$_3$COOK solution				Assignment bands
25^0	400^0	25^0	25^0	25^0	400^0	25^0	400^0	25^0	400^0	25^0	400^0	600^0	1000^0	
3700	3700	3700	3700	3700	3700	3700	3700	3700	3700	3700	-	-	-	Inner surface hydroxyls
3620	3620	3620	3620	3620	3620	3620	3620	3620	3620	3620	-	-	-	Inner hydroxyls
3670	-	-	3670	3670	3677w 3672w 3657w	3670w 3662w	3675sh 3670vw 3675vw	3685w 3675w 3660w	3675sh 3670vw 3660vw	-	-	-	-	Hydrogen-bonded hydroxyls
3650	3650br	3650br	3650	3650		3645 3640	3650sh	3650	3650	3655 3650 m	-	-	-	Hydrogen-bonded hydroxyls
										3600w	-	-	-	
-	-	150m	100w	-	100w	150w	150s	-	100s	150s	150vs			Vibrations of K$^+$- and Na$^+$-ions in the lattice of kaolinite
										1560 1535	1575 free ion			$\nu_{as}COO^-$ Hydrogen-bonded
										1470 1450 1430	1405 free ion			$\nu_{sym}COO^-$ acetate-ion
											1650 1630			$\nu_{as}COO^-$ In potassium
											1405 1370			$\nu_{sym}COO^-$ bicarbonate
													1420 1380	ν_3 For potassium

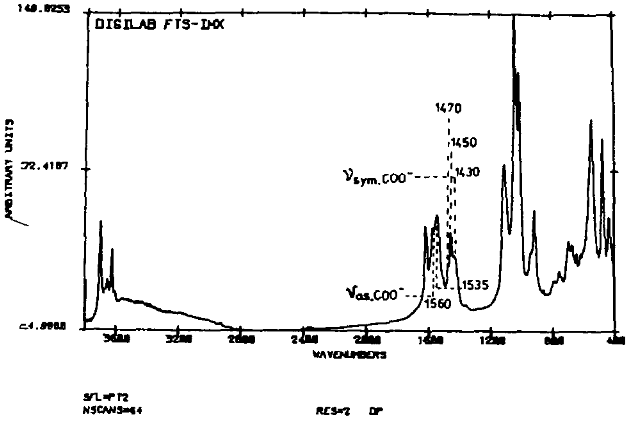

Fig. 1. IR spectra of kaolinite pretreated with saturated CH_3COOK solutions at 25 ^0C

(see Fig. 1. and Table 2) confirm the very strong hydrogen-bonded acetate-ion, which is different from the bands of CH_3COOK (9). Far-IR spectrum of intercalated kaolinite is characterized by the presence of a strong band at 150 cm^{-1}. Remarkable changes appeared in the spectrum on an intercalated sample heated at 400 ^0C for 60 min. In this case the kaolinite structure was completely absent and six new bands appeared which are characteristic for $KHCO_3$ (9), while a band at 1575cm^{-1} indicated the residue of acetate ions being already a free acetate, i.e. non-bonded by hydrogen. Further heating up to 600 ^0C did not cause any changes in the spectra, while according to the XRD spectra no metakaolinite was formed, but the presence of $KHCO_3$ has been also proved. This stability of $KHCO_3$ may be caused by the reaction of intercalated CH_3COOK. During the decomposition of potassium acetate $KHCO_3$ could not be detected.

3/ Thermoanalytical and mass spectrometric data are summarized in Table 3. and Fig. 2. In the case of the mixture of kaolinite + NaCl the DTG curve indicated a 2nd peak at a temperature greater than the normal dehydroxylation peak. According to our earlier data (4) the mass spectra show that the first weight loss is due mainly to release of water, while the second one is due to the evolution of HCl as a result of high temperature hydrolysis of NaCl. When the salt is dispersed in the clay by treatment with saturated solution, the chloride ions may have been in closer contact with OH groups and the hydrolysis starts at a lower temperature. In the case of KCl the main features of TA-MS curves are similar but the temperature maximum of dehydroxylation increased, and the onset temperature and the range of the hydro-

TABLE 3

TG, DTG and MS data in He for kaolinite a mixture of kaolinite with alkali salts and kaolinite pretreated

Sample	Weight loss			DTG_{max}	MS $peak_{max}$	
	^{o}C	%		^{o}C	^{o}C	Reaction products
Kaolinite	250-650	13.35	13.65	490	490	H_2O; (H_2)
	650-900	0.30		-	-	-
Kaolinite + + 10 % NaCl	250-600	12.65	16.75	485	485	H_2O
	600-800	3.90		715	720	HCl
	800-900	-		-	-	-
Kaolinite sat. NaCl sol.	250-570	11.00		480	485	H_2O
	570-875	14.10	25.10	828	820	HCl
	875-950	-		-	-	-
Kaolinite + + 10 % KCl	200-535	11.67	15.37	498	498	H_2O
	535-746	3.70		-	625	HCl
	746-900	-		-	-	-
Kaolinite sat. KCl sol.	250-700	9.85	10.50	512	512	H_2O
					545	HCl
	700-800	0.65		-	-	-
CH_3COOK	390-520	28.42		450s	495	H_2O; Acetone; CO
				470s	497	CO_2
				493	505	H_2
	520-800	2.00		-	650	H_2
					800	CO
Kaolinite sat. CH_3COOK sol.	200-472	11.70		458	450	CO_2
					456	H_2O
	472-550	17.30	36.50	500	500	Acetone; CO_2, CO
					550	H_2
	550-855	6.60		800	800	CO
	855-950	0.90		-	-	CO_2

Heating rate: 6 ^{o}C/min, Flow rate: 55 cm^3/min lysis of salt decreased. This is connected to the lower heat of hydration of K^+ (see also the weight losses).

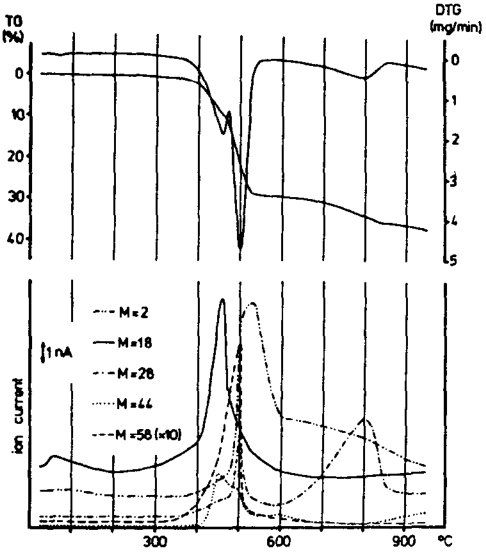

Fig. 2. TG, DTG and MS curves of kaolinite after pretreatment by saturated CH_3COOK solution.
M = mass number
The sensitivity of detector is tenfold at M = 58

The solid state reactions of intercalated samples at rising temperature are rather complex processes. For clarification we summarise the results of the decomposition of pure CH_3COOK in Table 3 The results will be published later in more detail (10). With rising temperature CH_3COOK melts, then decomposes above 390 °C in He gas. Th main gaseous reaction products are acetone, CO_2 and H_2O. The solid residue contains carbonate and carbon formed by cracking. At above 550 °C the formation of H_2 and a small amount of derivatives of acetone proves that acetate or its fragments are occluded in the obtained carbonate. The increasing amount of CO is due to the redox reaction of $K_2CO_3 + C \longrightarrow CO + K$. The decomposition of residual carbonate starts above 800 °C. The TA-MS data of intercalated kaolinite showed that the onset of dehydroxylation and the highest rate of water release takes place at a temperature 50 °C lower. This fact unambiguously proves that the thermal stability of the intercalated sample decreased. Along with water, CO_2 has been found. This may be the result of the decomposition of bicarbonate formed by intercalation. The nonintercalated acetate decomposes at the same temperature and in the same manner as discussed previously.

We also investigated the way in which the incorporated ions influence the crystalline phases formed above 1000°C. XRD spectra of the samples pretreated with KCl as well as of those intercalated and heated up to 1300 °C were taken (Table 1. Run 6 and 9). These revealed that the kaolinite did not transform to mullite or sillimanite in the case of KCl. The main crystal phase of the product has been identified as Al_2O_3. At the same temperature $KAlO_2$ has been formed from the partly intercalated kaolinite by the reaction of K_2CO_3 dissolved in silicate.

ACKNOWLEDGMENTS

The authors thank H.O. Becker (Munich) for valuable discussions and A. Bittó for the chemical analysis.

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