EFFECT OF AMBIENT ATMOSPHERE ON SOLID STATE REACTION OF KAOLIN-SALT MIXTURES

M. Gábor, L. Pöppl, and E. Körös

Institute of Inorganic & Analytical Chemistry, L. Eötvös University
P.O. Box 123, H-1443 Budapest, Hungary

Abstract—The reaction of kaolin with NaCl was followed by dynamic thermal analysis and mass spectrometry under N_2, CO_2, and air atmospheres and in a 10^{-5}-torr vacuum. The weight loss was a function of the atmosphere used and, according to mass spectrometry, was due to the evolution of H_2O, HCl, and very small amounts of H_2. HCl was formed only after the release of 85% of the hydroxyl content of the kaolin. When the clay was pretreated with saturated salt solution, H_2O and HCl evolved in more or less the same temperature range, indicating that only some of the OH groups reacted with the chloride ion. High-temperature X-ray powder diffraction patterns showed that the sodium ion reacted with the non-crystalline metakaolin to give $NaAlSiO_4$. Chemical analysis showed that the reaction of kaolinite and sodium chloride started below 400°C. The rate of the reaction increased at higher water vapor concentration. From mass spectrometric data, the NaCl-treated kaolin appeared to adsorb CO_2. Desorption at several distinct temperatures suggests that CO_2 was adsorbed by different parts of the structure, i.e., holes and channels. X-ray powder diffraction and infrared absorption data indicate that the kaolinite structure persisted even after it had been heated with NaCl in a CO_2 atmosphere to as high as 800°C.

Key Words—Infrared spectroscopy, Gaseous atmosphere, Kaolin, Metakaolin, Salt, Thermal analysis.

INTRODUCTION

The atmosphere surrounding solids greatly influences the physical and chemical processes occurring at particle boundaries. Catalytic and adsorptive properties, color, and the shape, size, and distribution of pores of solids are all influenced by the nature of the surrounding gaseous atmosphere (Hedwall, 1966), and chemically inert gases may dissolve in solids and minerals (Freund *et al.*, 1983), causing topochemical effects on the heated substances.

The effect of ambient atmospheres on the thermal reactivity of clays has been investigated by only a few authors. By heating kaolin to 1000°C in N_2, air, CO, CO_2, and H_2O vapor, Sanford (1951) found that the reaction of the heated products with water vapor at 25°C depended on the type of atmosphere employed. Mackenzie (1968) showed that the presence of O_2 and CO_2 hindered the formation of crystalline phases from metakaolin at 1100°C, whereas water vapor and a 10^{-4}-torr vacuum promoted the process.

The reaction of metakaolin with alkali salts was studied at atmospheric pressure by Jagitsch (1958) who measured the diffusion of soda into metakaolin at 500°–700°C in a water-free system. The diffusion rate increased with temperature. Farmer (1966) demonstrated that the temperature of dehydroxylation of clays changed if they were pressed into discs with alkali halide. Yariv (1975) found that the layered structure of kaolinite was destroyed even at room temperature when the kaolinite was ground with KBr. Heller-Kallai (1975) showed during the solid state reaction of montmorillonite and KBr and KCl at 300°–520°C that excess cations were taken up by the clay with deprotonation

of structural hydroxyls. She later (1978) showed that during reactions of kaolinite with salts of alkali metals the clay became reactive after dehydroxylation. Alkali ions were apparently incorporated into the aluminosilicate structure without the formation of detectable metakaolinite.

The aim of the present investigation was to investigate the role of the non-reactive gas atmospheres on the reaction of kaolin with sodium chloride.

EXPERIMENTAL

Materials

The kaolin used in the investigation was from Georgia. The NaCl used was of analytical purity (Reanal). N_2 was high purity (99.99%); analytically pure CO_2 was obtained from dry ice. The composition of synthetic air was: 78.03% N_2, 20.90% O_2, 0.9333% Ar, 0.03% CO_2, and 2×10^{-3}–10^{-6}% noble gases.

The chemical composition of the Georgia kaolin is: 43.8% SiO_2, 37.6% Al_2O_3, 13.8% H_2O, 2.6% TiO_2, 0.94% Fe_2O_3, 0.08% MgO, 0.017% CaO, 0.022% K_2O, 0.049% Na_2O, 0.22% P_2O_5, and 0.016% organic carbon. The specific surface area of the investigated sample was 17.9 m^2/g, as measured by the BET N_2-adsorption method.

X-ray powder diffraction (XRD) patterns showed that the kaolin sample was disordered along the *b* axis (kaolinite-M_d). Other clay minerals and quartz were not detected; the only crystalline impurity noted was a trace of anatase.

Methods

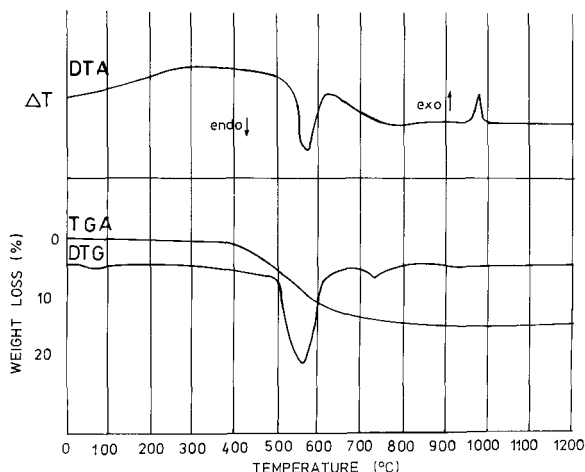The air-dried kaolin was ground in an agate mortar and sieved to produce a <45-μm size fraction. Aliquots

Figure 1. Thermogravimetric (TGA), differential thermogravimetric (DTG), and differential thermal analysis (DTA) curves for a mixture of kaolin + 10% NaCl in N_2.

Figure 2. Mass spectrometric curves of the gaseous reaction products for kaolin + 10% NaCl at 10^{-5} torr. M = mass number of the reaction products. The sensitivity of the detector is tenfold at M = 2, 36, and 44.

of the fine-grained sample were mixed in an agate mortar with NaCl. The salt content of the mixtures was 5 or 10%. Other aliquots of the samples were prepared according to Wada (1961). Here, kaolin was shaken with an aqueous salt solution for 2 hr. The sample was kept in a stoppered centrifuge tube for one week and shaken regularly. It was then centrifuged, excess liquid was removed, and the wet clay was stored in the centrifuge tubes for an additional week. The air-dried sample was examined without washing of the salt.

XRD studies were performed on a Philips powder diffractometer using CuKα radiation. High-temperature XRD patterns (to 1200°C) were obtained in a Nonius, Guinier-Lenné system, high-temperature chamber. Infrared spectra of samples contained in KBr discs were taken on a Zeiss UR-10 spectrometer between 400 and 4000 cm^{-1}.

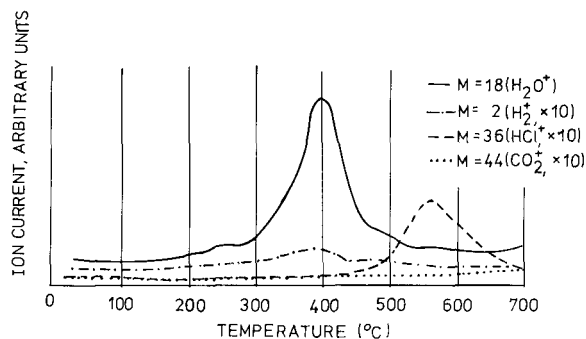Kaolin and the kaolin + NaCl mixtures were heated in a Mettler vacuum-thermoanalyzer, and thermo-

gravimetric (TGA), differential thermogravimetric (DTG), differential thermoanalytical (DTA), pressure (P), and temperature (T) curves were recorded simultaneously. DTA curves were obtained using Al_2O_3 as a reference material. The thermobalance was connected to a Balzers quadrupole mass spectrometer (MS), and gaseous reaction products were allowed to pass directly into the mass analyzer which was set for a scanning range of 1–100 mass units and which used a flow rate of 1 s/mass. The thermoanalytical investigations under different atmospheres were carried out using high-purity and carefully dried gases with constant flow rate. The gases were passed through fresh dried P_2O_5 and a molecular sieve. The synthetic air was passed over solid KOH to extract CO_2. The samples were placed in platinum crucibles in the thermoanalyzer and the whole chamber was evacuated to 10^{-2} torr. After evacuation it was filled with dried and purified gas.

Thermoanalyses with simultaneous mass spectrometric analyses was carried out at 10^{-5}-torr vacuum. The reaction of kaolin with sodium chloride was followed by both static and dynamic thermal techniques.

Table 1. High-temperature X-ray powder diffraction data for kaolin and mixtures of kaolin and 10% NaCl.

| Run	Sample	Temperature (°C)	Phases
1	Kaolin	20–530	Kaolinite + anatase
		530–1070	Anatase
		1070–1200	Anatase + mullite
2	Kaolin + NaCl	20–520	Kaolin + anatase + halite
		520–740	Anatase + halite
		800 (after iso-thermal heating)	Anatase
		870–1200	Nepheline
3	Kaolin + NaCl preheated in CO_2 at 800°C and cooled to 25°C	20–520	Kaolinite + anatase + nepheline + halite
		520–700	Anatase + nepheline + halite
		700–1050	Anatase + nepheline
		1050–1200	Anatase + nepheline + mullite
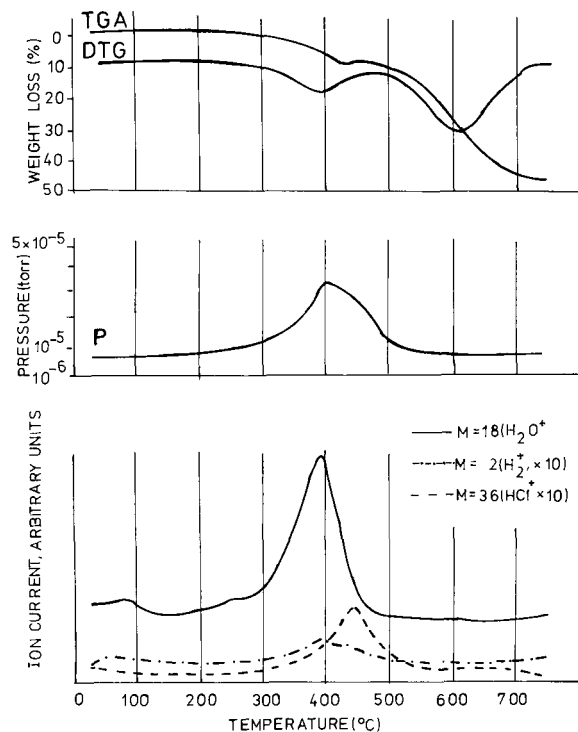
Figure 3. Thermogravimetric (TGA), differential thermogravimetric (DTG), and pressure (P) and mass spectrometric curves for kaolin at 10^{-5} torr after pretreatment with saturated NaCl solution. M = mass number of the reaction products. The sensitivity of the detector is tenfold at M = 2 and 36.

THERMAL AND MASS SPECTROMETRIC ANALYSES

Mixtures of kaolin and solid NaCl

Characteristic thermal analysis curves for a mixture of kaolin + 5% NaCl in N_2 are shown in Figure 1. The DTG curve of the mixture differs from that of kaolinite

alone by the existence of a second peak at a temperature greater than the normal dehydroxylation peak. The DTA curve shows that both reactions were endothermic.

The mass spectrometric analysis of the gaseous reaction products is shown in Figure 2. The temperature ranges of the simultaneous DTG and MS peaks in 10^{-5} torr are in good agreement with each other. According to the mass spectra, the first weight loss was due mainly to the release of water. A minor amount of hydrogen was formed during the dehydroxylation at 10^{-5} torr. Martens et al. (1976) attributed the formation of hydrogen to the following process: $2\,OH^- \to 2\,O^{2-} + H_2$; however, the clay contained 0.94% iron oxides which may have reacted with water vapor, resulting in the formation of hydrogen. The second weight loss was probably due to the evolution of HCl from the solid materials. CO_2 was identified in the evolved gas only after the collapse of the crystal structure of kaolinite.

From the TGA curves in the various atmospheres and in 10^{-5}-torr vacuum and the MS curves of kaolinite mixed with 5 or 10% solid salt, it appears that HCl formed only after the removal of 85% of the structural water. The dehydroxylation started on the surface with a reaction between adjacent hydroxyl groups (Gábor et al., 1977). Water vapor obviously escaped more rapidly from the surface layer than from the bulk of the material because the diffusion of water was undoubtedly slower farther from the surface. Consequently, the conditions for a reaction between the nascent water vapor and solid sodium chloride are fixed. High-temperature XRD patterns showed that after the collapse of the kaolinite structure, sodium ions reacted with the noncrystalline metakaolinite, and $NaAlSiO_4$ formed (Table 1, Run 2).

The amount of the HCl and Na^+ incorporated into the kaolinite was determined by chemical analysis. The results show that 5–10% of the solid sodium chloride was almost completely hydrolyzed. During isothermal

Table 2. Thermogravimetric data for kaolin and a mixture of kaolin + NaCl.[1]

Run	Atm.	Sample weight (mg)	Added NaCl (%)	Weight loss (%)				
				at 500°C	at 600°C	at 700°C	at 900°C	at 1200°C
1	N_2	24.79	—		12.10		13.31	13.31
2	N_2	24.75	5		11.92		15.15	15.15
3	N_2	22.66	10		13.23		16.08	16.68
4	air	25.79	—		10.97		11.09	11.09
5	air	26.09	5		10.58		13.84	13.97
6	CO_2	24.80	—		9.31		9.48	9.48
7	CO_2	18.45	5		7.10		12.52	12.52
8	CO_2	11.83	10		8.71		11.70	12.84
9	10^{-5} torr	8.38	—		13.64		13.91	13.96
10	10^{-5} torr	10.37	5	13.39		17.76		19.95
11[2]	N_2	102.15	~30		11.75		14.27	43.10
12[2]	10^{-5} torr	10.37	~30	12.25	27.58	46.34		

[1] Heating rate, 10°/min; at 10^{-5} torr, 2°/min; gas flow rate, 90 cm³/min; Pt crucible.
[2] Pretreated with saturated NaCl solution.
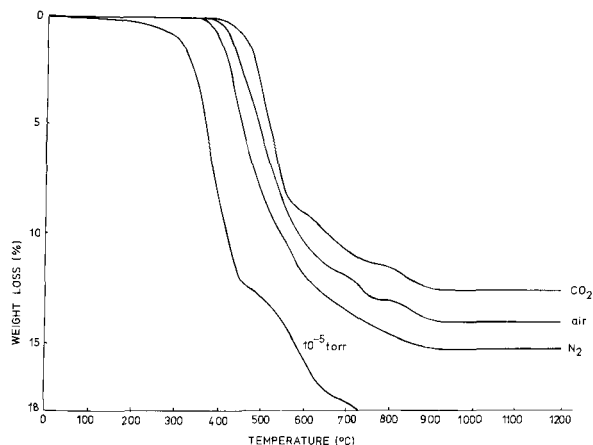
Figure 4. Weight loss of the mixture of kaolin and 5% NaCl in different atmospheres.

Table 3. Thermogravimetric and differential thermoanalytical (DTA) data for kaolin and 10% NaCl after isothermal heating at 400°C.[1]

Run	Atm.	Sample weight (mg)	Highest temp. (°C)	Weight loss (%)	DTA peak at 800°C[2]	Remarks
1	CO_2	10.07	1000	7.14		Without NaCl
2	CO_2	13.30	1000	2.71	+	
3	N_2	10.07	1000	10.33	−	
4	CO_2	1000	800	2.42	+	Samples were
5	CO_2	1000	800	0.90	+	cooled and their XRD, IR and DTA curves recorded

[1] Heating rate: 10°/min after isothermal heating; gas flow rate: 90 cm³/min; Pt crucible; isothermal pretreatment was in thermoanalyzer with a heating rate of 4°/min from 25° to 400°C; at 400°C for 120 min.

[2] NaCl m.p.

heating of the mixture at 400°C the amount of HCl formed was determined. The results show that the reaction of clay and sodium chloride started below 400°C. The rate of reaction increased at higher water vapor pressures (see Figure 2).

After the collapse of the octahedral structure, at 500°C volatile $FeCl_3$ formed by the reaction: $Fe_2O_3 + 6\ HCl = 2\ FeCl_3 + 3\ H_2O$. This reaction was also affected by the nature of the surrounding atmosphere. In nitrogen and air, part of the iron segregated as a solid iron oxide and did not react with HCl.

Pretreated kaolin with saturated NaCl solution

When the salt was dispersed in the clay by pretreatment with a saturated solution, water and HCl were released at 10^{-5}-torr vacuum at about the same temperature (Figure 3). Thus, the chloride ions may have

been in closer contact with hydroxyl groups and, therefore, "high temperature hydrolysis" may have occurred at lower temperature. The relatively small amount of HCl produced shows that only some of the hydroxyl groups reacted with chloride ions. The salt content of pretreated clay was rather high, ~30%; however, the higher salt content did not increase the weight loss in N_2 that accompanied the hydrolysis. Most of the salt evaporated, as evidenced by a significant weight loss without increasing the pressure (Figure 3, curve P; and DTG peak, Table 2, Runs 11 and 12).

Effect of the atmosphere

The influence of a non-reactive gas atmosphere on the solid state reaction was also investigated. The weight loss was higher in all experiments in the presence of NaCl, but differed in the different atmospheres under the same experimental parameters (Table 2, Figure 4). The weight loss in synthetic air (Run 5) was less than in N_2, and the second DTA peak (750°C) was exothermic, indicating an oxidation of HCl. Claws (1922) showed that a mixture of SiO_2 and NaCl heated in oxygen reacted as follows: $2\ NaCl + SiO_2 + \frac{1}{2}\ O_2 = Na_2SiO_3 + Cl_2$. In the presence of water vapor, HCl also formed and oxidized at about 600°C.

The present results show that the weight loss was smallest in an atmosphere of CO_2. A different endothermic peak appeared at about 800°C in the DTA curve obtained in CO_2. This peak was due to the melting of unreacted NaCl. These data suggest an interaction of CO_2 with a mixture of kaolin and NaCl. This interaction was investigated at the temperature of the beginning of the dehydroxylation, as well as in the temperature range of the faster dehydroxylation. Because dehydroxylated kaolin adsorbs evolved water vapor, it likely adsorbs non-reactive gases as well. Therefore, kaolin was heated with NaCl in the thermoanalyzer in a CO_2 atmosphere from 25° to 400°C at a heating
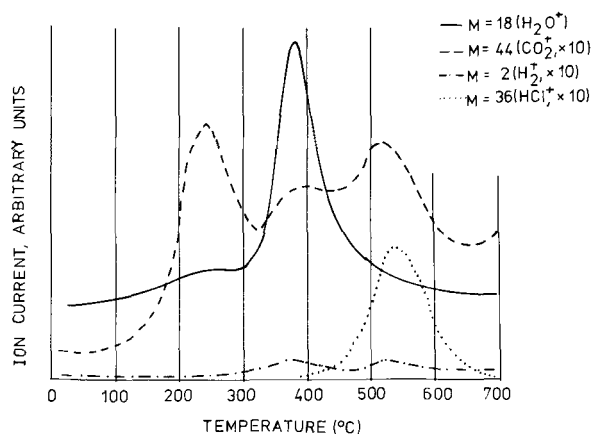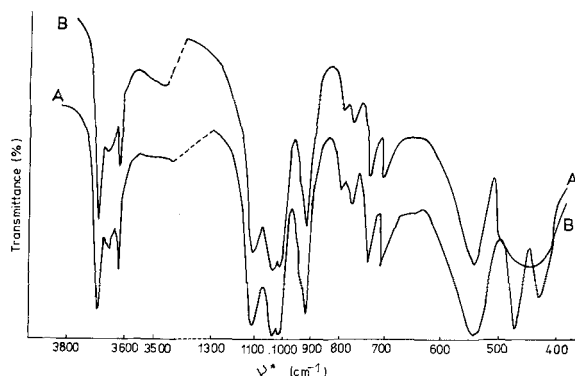

Figure 5. Mass spectrometric curves for the mixture of kaolin + 10% NaCl after pretreatment in CO_2 at 400°C and cooled to 25°C. M = mass number of the reaction products. The sensitivity of the detector is tenfold at M = 2, 36, and 44.

Figure 6. Infrared spectra of (*A*) kaolin and (*B*) mixture of kaolin + 10% NaCl after pretreatment in CO_2 at 850°C and cooled to 25°C.

rate of 4°/min and at 400°C for 120 min. The XRD pattern and IR spectra of the cooled samples were practically the same as those of kaolin samples heated without NaCl. The IR spectra indicated only a decrease in the concentration of hydroxyl groups. On the basis of mass spectra (Figure 5), the adsorption of CO_2 took place below 400°C in the presence of Na^+. Wilson and Galwey (1975) pointed out that the reactivity of the clays becomes significant in the temperature range immediately below that at which interaction between surface groups leads to dehydroxylation. Thermal desorption at 10^{-5} torr occurred between 150° and 550°C. That different interaction energies operated between the CO_2 molecules and various parts of the structure (i.e., holes and channels) is supported by desorption data obtained at different temperatures. The mass spectra of the preheated kaolin under the same conditions without NaCl show no desorption of CO_2.

Montmorillonite reacted similarly. The interaction of CO_2 with Na-montmorillonite was indicated by mass spectrometric analysis. No adsorption of CO_2 was noticed for a H-exchanged variety of the same clay.

The interaction of CO_2 and kaolin below 400°C also influenced the high-temperature hydrolysis of NaCl. TGA and DTA data after isothermal heating of mixtures of kaolin and NaCl (Table 3, Runs 2, 4, and 5) indicate that the weight loss of the samples heated in CO_2 was less than 3% below 1000°C. No metakaolin was detected in infrared and XRD patterns of cooled samples, and the kaolinite structure was unaltered even at 800°C (Table 1 and Figure 6).

In the presence of NaCl the interaction of kaolinite and CO_2 may have hindered collapse of the kaolinite structure even at this high temperature. During the isothermal heating at the temperature of the low-temperature dehydroxylation CO_2 gas apparently penetrated the holes and channels that formed during the first period of dehydroxylation and hindered the delocalization of proton required for the reaction of OH groups to form water. The rate of dehydroxylation was

therefore very low. Similar effects were observed by Nägerl and Freund (1970) during the dehydroxylation of $Mg(OH)_2$. The temperature of the dehydroxylation was higher when the surface was covered with KBr.

CONCLUSIONS

The effect of even a chemically "inactive" gas may be of great importance in both solid state reactions and clay mineral technology. Our further research work is aimed at elucidating the mechanism of the solid state reaction of kaolinite and sodium chloride and the role of carbon dioxide in more detail, as well as studying the high temperature hydrolysis of other alkali halogenides and different types of kaolinite.

ACKNOWLEDGMENTS

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